

National Review and Coordination Meeting
on
Nanoscience and
Nanotechnology
NS & NT 2007

21-23 February, 2007

Katriya Hotel & Towers
Hyderabad

Sponsored by

Nanoscience and Nanotechnology Initiative (NSTI)
Department of Science and Technology (DST)
Govt. of India

Organised by



International Advanced Research Centre for
Powder Metallurgy & New Materials (ARCI),
Hyderabad

National Review and Coordination Meeting
on
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Nanotechnology
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**NATIONAL REVIEW AND COORDINATION MEETING
ON
NANOSCIENCE AND NANOTECHNOLOGY
21-23 February, 2007**

Technical Programme

February 21, 2007 (Wednesday)

08:00 – 09:00 Registration
 09:00 – 09:30 Inaugural Function
 09:30 – 10:00 Award lecture: Prof. D. Chakravorty, IACS, Kolkata
 10:00 – 10:30 TEA

	Session I	Session II
10:30 – 13:00	5 presentations A1 (30 min each) Unit Centre	6 presentations A2 (20 min each) Synthesis & characterization
13:00 – 14:00	LUNCH	
14:00 – 16:30	5 presentations B1 (30 min each) Unit Centre	6 presentations B2 (20 min each) NanoBio
16:30 – 17:00	TEA	
17:00-18:30	3 presentations C1 (30 min each) Unit Centre	8 presentations C2 (10 min each) Students

February 22, 2007 (Thursday)

08:30 – 09:15 Plenary Lecture 1: Prof. A.K. Sood, IISc-Bangalore
 09:15 – 10:00 Plenary Lecture 2: Prof. D.D. Sarma, IACS, Kolkata
 10:00 – 10:30 TEA

	Session I	Session II
10:30 – 13:00	5 presentations D1 (30 min each) Major projects	7 presentations D2 (20 min each) Synthesis & characterization
13:00 – 14:00	LUNCH	
14:00 – 16:00	5 presentations E1 (20 min each) Nanofunctional materials	11 presentations E2 (10 min each) Students
16:00 – 19:00	Poster presentation (P1, P2)+ TEA	

February 23, 2007 (Friday)

08:30 – 09:15 Plenary Lecture 3: Prof. V. Ramgopal Rao, IIT-Bombay

09:15 – 09:45 TEA

	Session I	Session II
09:45– 12:00	6 presentations F1 (20 min each) Nanofunctional materials	13 presentations F2 (10 min each) Students
12:00 – 13:00	LUNCH	
13:00– 15:30	6 presentations G1 (20 min each) Thinfilms, nanocoatings, nanotribo, lithography	11 presentations G2 (10 min each) Students
15:30 – 16:00	TEA	
16:00 – 16:30	Awards for student presentation + Vote of thanks	

Total Number of Presentations

Award lecture	1
Plenary Lectures	3
Oral presentations for major NSTI Projects	18
Oral presentations for other NSTI Projects	38
Poster presentations for other NSTI Projects	44
Student presentations-Oral	43
Student presentations-Poster	33
TOTAL	180

Programme Details

ORAL PRESENTATIONS (NSTI PROJECTS)

DAY 1

Session-A1: Unit DST-I (5): February 21, 2007:10:30 – 13:00

p. 1-8

Sl No	PI/Co-PI	Project Title/Abstract Title
1	Prof. G.U. Kulkarni	Unit on Nano Science & Technology (UNANST-DST) at JNCASR, Bangalore
2	Prof. S. Chandrasekaran/ Prof. Venkateswaran	Unit on Nano Science & Technology (UNANST-DST) in Indian Institute of Science, Bangalore
3	Prof. A. Sharma	Unit on Nano Science & Technology (UNANST-DST) in Indian Institute of Technology- Kanpur
4	Prof. D. Chakravorty	Unit on Nano Science & Technology (UNANST-DST) at IACS Kolkata
5	Prof. A.K. Raychaudhuri	Unit on Nano Science & Technology (UNANST-DST) in S.N. Bose National Centre for Basic Sciences, Kolkata

Session-B1: Unit DST-II (5): February 21, 2007 14:00 – 16:30

p. 11-15

Sl No	PI/Co-PI	Project Title/Abstract Title
1	Dr. S. Sivaram	Unit on Nano Science & Technology (UNANST-DST) in National Chemical Laboratory, Pune
2	Prof. (Mrs.) S.K. Kulkarni	Unit on Nano Science & Technology (UNANST-DST) at Univ. Poona, Pune
3	Dr. Shantikumar V. Nair	Centre for Nano Technology (Implants, Tissue Engineering, Stem Cell Research) (Kochi)
4	Prof. T. Pradeep	Unit on Nano Science & Technology (UNANST - DST) in Indian Institute of Technology, Madras, Chennai
5	Prof. B.R. Mehta	Unit on Nano Science & Technology (UNANST-DST) at IIT Delhi

Session-C1: Unit DST-III (3): February 21, 2007: 17:00-18:30

p. 19-21

Sl No	PI/Co-PI	Project Title/Abstract Title
1	Prof. O.N. Srivastava	Unit on Nano Science & Technology (UNANST-DST) at BHU Varanasi
2	Prof. Balasubramanian Sundaram	Centre for Computational Materials Science at JNCASR, Bangalore
3	Prof. M.K. Sanyal	Unit on Nano Science & Technology (UNANST-DST) at Saha Institute of Nuclear Physics, Kolkata

ORAL PRESENTATIONS (NSTI PROJECTS)**Session-A2: Synthesis and characterization of nanomaterials (6):****p. 25-30****February 21, 2007: 10:30 – 13:00**

Sl No	Name	Project Title/Abstract Title
1	Prof. P.K. Bharadwaj	Modular synthesis of cryptand based nanostructures.
2	Prof. Sabyasachi Sarkar	Synthesis of water-soluble carbon nanotubes with tripodal ("Y" or "T" Types) tetrapodal, pentrapodal and other novel junctions
3	Dr. A. Gopalan	Investigation of the synthesis and characterization of functional/multi-component nanostructured (nanotube/nanorod/nanoribbon/nanocables) polyaniline based materials
4	Prof. Panchanan Pramanik	Synthesis of Nano-sized Metastable oxide solid solutions and studies of their properties.
5	Dr. G.T. Chandrappa	Nanostructured materials synthesized by hydrothermal and combustion/microwave routes and their application
6	Prof. Sabu Thomas	Nanomaterials: Synthesis, characterization and Applications

Session-B2: Nano Bio (6): February 21, 2007: 14:00– 16:30**p. 33-37**

Sl No	Name	Project Title/Abstract Title
1	Dr. S.V. Ramanan/Dr. B.M. Jaffar Ali	Single molecule and interfacial processes in nanobiology
2	Prof. H.B. Bohidar	Preparation & Characterization of bio-polymeric Nano-particles with potential for usage in laser Immuno-assay and drug delivery
3	Dr. G.V. Shivashankar	Development of nanofluidic channels and nanowires using biomolecular self-assembly
4	Dr. Lalit M. Bharadwaj	Study of molecular motors for targeted drug delivery and nanomolecular switching
5	Dr. Subho Mozumdar	Combinational DNA chips coupled with nanoparticle probe for scanometric detection.
6	Dr. K.N. Ganesh	DNA-Gold/Silver composite Nanoparticles: Design, Assembly and Fictionalization.

ORAL PRESENTATIONS (STUDENTS)**Session-C2: NanoBio (Students) (8): February 21, 2007: 17:00-18:30****p. 41-48**

Sl No	Name	Inst/Univ	Abstract
1	Jaya Jain	Agarkar Institute	A potent antibacterial formulation based on biostabilized silver nanopartilces
2	Viola B. Morris	RRL-Trivandrum	Synthesis of novel water soluble block copolymers in ionic liquid as potential gene delivery vector
3	J. Revathi	ARCI, Hyderabad	Synthesis of nano Ag for antibacterial applications
4	S. Prabhakaran	IIT, Mumbai	One-spot synthesis of amine-functionalized monodispersed magnetite nanoparticles for biorecognition

5	S. Shankara Narayanan	SNBNCBS, Kolkata	Aggregated CdS quantum dots: Host of biomolecular ligands
6	Abhilash Sasidharan	Amrita-IMS, Kochi	Impact of Zinc Oxide and Hydroxyapatite Nanoparticles on cytotoxicity and cellular adhesion on Microbes
7	D.R. Sobha Jaykumari	Univ Madras	Nanobiocomposite glucose biosensor based on nanohybrid of self assembled gold nanoparticles over single walled carbon nanotubes
8	C. Nagraj	Anna Univ., Chennai	Development of an instrument combining optical nanomanipulation with single cell electrophysiology to study cell membrane remodeling

ORAL PRESENTATIONS (NSTI PROJECTS)**DAY 2****Session-D1: Other major projects (5): February 22, 2007: 10:30 – 13:00****p. 55-62**

Sl No	PI/Co-PI	Project Title/Abstract Title
1	Prof. I. Manna	Synthesis and characterization of nanostructured materials for functional (magnetic, sensor, opto-electronic and chemical) and structural (hard coating and heterostructure) applications
2	Prof. S. Chandrasekaran/Prof. S. Sampath	IISc nanoscience and technology initiative
3	Prof. K. Chattopadhyay	Development of state-of-the-art analytical electron microscopy facility capable of high resolution imaging and analysis in the nanoscale as an Institute facility at the IISc (Bangalore)
4	Prof. J. Kumar	Semiconductor Nanostructures (Chennai)
5	Dr. Arun Chattopadhyay	Engineering nanoscale materials and their application in nanotechnology (Guwahati)

Session-E1: Nanofunctional materials (optical, magnetic, sensor applications):**(5) February 22, 2007: 14:00 – 16:00****p. 65-69**

Sl No	Name	Project Title
1	Dr. Harish Chander	Development of nanophosphors for industrial applications.
2	Prof. S.N. Kaul	Studies on nanomaterials and devices.
3	Prof. T.P. Radhakrishnan	Linear and nonlinear optical studies of metal/organic nanoparticles and ultrathin films
4	Prof. M. Abdul Khadar	Study of photoconductivity and photoluminescence of certain nanostructured materials
5	Prof. Arun M. Narsale/Prof. D.C. Kothari	Development of device-grade nanomaterials using ion beams.

ORAL PRESENTATIONS (NSTI PROJECTS)

Session-D2: Synthesis and characterization of nanomaterials (7):
February 22, 2007: 10:30 – 13:00

p. 73-79

Sl No	Name	Project Title
1	Prof. S. Ramasamy	Upgradation of existing UHV chamber preparation and investigation of the properties of nanostructured materials.
2	Prof. O.N. Srivastava	Nano Science and Technology: A Transdisciplinary approach.
3	Prof. S.K.Pabi	Development of nanocrystalline materials by different processing routes
4	Prof. K. Prasad Rao/Prof. B.S. Murty	Nanomaterials and nanotechnology-processes, characterization and applications.
5	Prof. Anil K. Bhowmick	Development and properties of polymer based nanocomposites.
6	Prof. A.K. Ganguli	Metal oxide core shell nanostructure for removal of toxins from water and atmosphere
7	Prof. Mukul Biswas	Some conducting polymer/binary polymer - Inorganic hybrid nanocomposite materials

ORAL PRESENTATIONS (STUDENTS)

Session-E2: Synthesis, characterization, phase transformation, properties, applications, etc (Students) (11): February 22, 2007: 14:00 – 16:00

p. 83-93

Sl No	Name	Inst/Univ	Abstract
1	G. Srinivasulu	IIT, Chennai	Barium titanate based multiferroelectric nanocomposite functional materials by high energy ball milling
2	R. Vengadesh Kumara Mangalam	JNCASR, Bangalore	Surface ferromagnetism and bulk ferroelectricity in nanostructured BaTiO ₃
3	Raksha Sharma	Delhi Univ., Delhi	Metal oxide/polyaniline nanocomposites: cluster size and composition dependent structural and magnetic properties
4	Shatabdi Porel	Hyderabad Univ.	In-situ synthesis of silver nanoparticles/gold nanoplates/palladium nanowires in polymer matrix and application in optical power limiting
5	Ashutosh C. Abhayankar	Hyderabad Univ.	Nanometer grain size as a new control parameter to study non-fermi liquid behaviour, quantum phase transitions and magnetically- mediated superconductivity in weak itinerant-electron ferromagnets
6	Rajeev R. Prabhu	University of Kerala	Study of optical phonon modes of CdS nanoparticles using Raman spectroscopy
7	S.K. Mandal	IIT, Kharagpur	Magnetic phases in transition metal doped ZnO and Ni based nanoparticles
8	P.R. Mishra	BHU, Varanasi	On the synthesis, characterization and photocatalytic application of nanostructured TiO ₂
9	A. Gomathi	JNCASR, Bangalore	Urea route to coat inorganic nanowires, C-fibres and nanotubes by boron nitride

10	N. Pinjala	IIT, Guwahati	Pattern formation by evaporation and its technological implications
11	Rahul Sharma	IIT, Roorkee	A study on the surface morphology of nano-sized electroless Ni-P coatings

ORAL PRESENTATIONS (NSTI PROJECTS)**DAY 3****Session-F1: Nanofunctional materials (optical, magnetic, sensor applications)(6): February 23, 2007: 09:45– 12:00****p. 101-105**

Sl No	Name	Project Title
1	Dr. Debajyoti Das	Development of nano-silicon structures as new quantum effect materials by ICP-CVD
2	Prof. Amitabha Patra	Synthesis and Luminiscence properties of doped nanostructures: Role of shape size and crystal phase
3	Dr. D.D. Sarma	Magnetic, optical and electronic properties of semiconducting nanoparticles doped with magnetic impurities.
4	Dr. K. George Thomas	Optical and electronic studies of photoactive molecules capped on metal nanoparticles and their molecularly bridged arrays on surfaces.
5	Dr. T. Prem Kumar	Carbon nano-tube based materials for electrochemical devices
6	Prof. D. Bahadur/Dr. S. Vitta	Synthesis of nanostructured magnetic materials for different applications.

Session-G1: Thin films, nanocoatings, nanotribology, lithography (6): February 23, 2007 13:00 – 15:30**p. 109-115**

Sl No	Name	Project Title
1	Prof. G.U. Kulkarni	Investigations of the properties and phenomena exhibited by Nanomaterials: nanofabrication, lithography and related aspects.
2	Dr. Arun Chattopadhyay	Nanolithography in color and design of microfluidic devices.
3	Dr. D. Ravinder	Development of Nano-wires and Nano-structural thin films of Boron for potential applications.
4	Prof. A.K. Pal	Nanocrystalline GaN Films: Preparation and Prospect for LED application
5	Dr. (Mrs) S.K. Mishra	Nanocomposite thin films of Si-C-N system for wear resistance and functional application by magnetron sputtering
6	Dr. Ramesh Chandra	Design and development of superhard graded nanocomposite coatings for industrial application and functional nanocomposite ceramic coatings: fabrication, characterization and application

ORAL PRESENTATIONS (STUDENTS)**Session-F2: Synthesis, characterization, Phase transformation, etc (Students) (13): February 23, 2007 : 09:45– 12:00****p. 119-131**

Sl No	Name	Inst/Univ	Abstract
1	M. Yougeshwari	Bharthiar Univ, Coimbatore	A novel approach to synthesize vertical ZnO nanorods on glass substrate by chemical method

2	B.S.B. Reddy	IIT, Kharagpur	Mechanosynthesis and mechanical–thermal synthesis of <i>in situ</i> aluminum based nanocomposites and their characterization
3	Sunny Josheph	MG. Univ., Kottayam	Soft chemical synthesis and characterization of calcium tungstate nanoparticles
4	Namdeo Lihitkar	Univ. Pune	Synthesis of titania nanoparticles using mesoporous molecular sieve MCM-41 as a template
5	K.K.R. Datta	JNCASR, Bangalore	Clay-Carbon composites
6	Sangeetha Kunjukunju	RRL, Trivanrum	Enzymatic depolymerization of chitosan to develop micro and nano particles
7	Rakesh Voggu	JNCASR, Bangalore	Use of fluoros chemistry in the solubilization and phase transfer of nanocrystals, nanorods and nanotubes
8	G. Nagaraju	Bangalore Univ.	Synthesis and characterization of silver molybdate nanorods/multipods
9	Uday Das	IACS, Kolkata	Synthesis of carbon nanotubes using Cu-Ag catalyst by spray pyrolysis technique
10	Deepti S. Sidhaye	NCL, Pune	Synthesis of nearly monodispersed Ni and Co nanoparticles in aqueous medium
11	S.K. Apte	CMET, Pune	Nanostructured packed gamma and alpha Fe ₂ O ₃
12	M. Venkata Kamalakar	SNBNCBS, Kolkata	Synthesis of metal nanotube arrays
13	Atikur Rahman	SINP, Kolkata	Wigner crystal formation in polymer nanowires

Session-G2: Surface, thinfilm, nanocoating, applications, etc (Students)(11): p. 135-145
February 23, 2007 : 13:00– 15:30

Sl No	Name	Inst/Univ	Abstract
1	T.S. Sreeprasad	IIT, Chennai	Preferential reactivity of surfaces of Au nanorods and their conversion to particles through other anisotropic structures
2	Kishore Kumar	IPR, Gandhinagar	Control of residual stress in Nano-structured PVD coatings
3	Rajasekhar Madugundo	DMRL, Hyderabad	Nanocomposite Nd _{4.5} Fe _{77-x} Mn _x B _{18.5} alloys for permanent magnet applications
4	S. Satish	VIT, Vellore	Laser surface modification of Ti-13Nb-13Zr using nano TiO ₂
5	S.R.C. Vivek Chand	JNCASR, Bangalore	Electrochemical supercapacitors based on carbon nanotubes and related materials
6	Abhijit Patra	Hyderabad Univ.	Tuning the size and optical properties in molecular nano/micro crystals
7	A.S. Bhattacharya	NML, Jamshedpur	Adhesion and mechanical investigation of nanostructures Si-C-N thin film deposited by RF magnetron sputtering at different substrate temperatures
8	Vikram Verma	IIT, Kanpur	Development of multilayer nanocoatings for data storage applications

9	Shamima Hussain	Jadavpur University, Kolkata	Effect of surface alloying on the surface plasmon properties of composite films of Ag-Cu nanocrystallites embedded in DLC matrix
10	Manoranjan Ghosh	SNBNCBS, Kolkata	Controlled growth of ZnO nano-dots to nano-rods and their optical properties
11	P. Gajendran	Madurai Kamraj Univ	Enhanced electrocatalytic reduction of oxygen on a poly (o-phenylenediamine) modified carbon nanotube electrode

POSTER PRESENTATIONS (NSTI PROJECT)
DAY 2
Session P1: February 22, 2007: 16:00-19:00
p. 149-192

Sl No	PI/Co-PI	Project Title
1	Prof. A.K. Sood	Carbon nanotube based sensors.
2	Prof. Kamanio Chattopadhyay	Phase transformation studies in nano-embedded materials
3	Dr. Swapan Kumar Pati	Electronic transport in molecular nano-systems.
4	Prof. M.S. Hegde	Nano M/CeO ₂ and M/TiO (M = Cu, Mn, Fe, Co, Ni, Pt, Pd etc.) for catalysis applications.
5	Prof. A.K. Raychaudhuri	Fabrication of pure metal and alloy films as interconnects for nanoelectronics and nano-electrodes by e-beam lithography and study of their stability towards electro, thermal and stress migration.
6	Dr. G.T. Chandrappa	Synthesis, characterization and applications of nanosized oxide materials.
7	Prof. A. Narayanasamy	Magnetic and electrical properties of nanostructured and nanocomposite magnetic materials.
8	Prof. Sriman Narayanan	Functionalised carbon nanotube sol-gel composite materials for chemical and biosensor fabrication and applications
9	Dr. K. Sreenivas	Nano Sized semi conducting oxide powders, films and catalysts by gas phase codensation for gas sensor applications.
10	Dr. S. Annapoorni	Oxide based nanomaterials and nanocomposites for magnetic memory and sensor applications.
11	Prof. A.K. Ganguli	Investigation of complex metal based nanosized using the reverse micellar, polymeric precursor and hydrothermal routes.
12	Prof. P.K. Bhatnagar	Development and characterization of CdSe, CdS and CdTe nanocrystalline embedded in borosilicate glass matrix
13	Prof. Satyendra Mishra	Studies on effect of mineral nanofillers on the mechanical and processing properties of polymers and their industrial applications.
14	Dr. Suprabha Nayar	Biomimetic route to hybrid nano-Composite scaffold for tissue engineering
15	Dr. K.L. Sahoo	Development and tailoring of properties of Al based amorphous alloys through evolution of nanophases.
16	Prof. Panchanan Pramanik	Synthesis of nano-sized titanium dioxide (TiO ₂) from naturally available ilmenite ores.
17	Prof. Subhadra Chaudhuri	Tailoring of room temperature Excitonic Luminescence in Mg _x Zn _{1-x} O/SiO ₂ nanocomposites and fabrication of electroluminescent devices.

18	Dr. Amitabha Patra	Upconverting nanophosphors for photonic applications.
19	Dr. Shyamal Kumar Saha	Preparation and characterization of metallic and semiconducting nanowire.
20	Dr. R. Ramaraj	Application of semiconductor and metal nanoparticles in photoelectrochemistry and catalysis.
21	Dr. Bharat Bhanudas Kale	Growth of nanoparticles of wide band gap semiconductors (CdS/CdSSe) in glass matrices for optical filters and study of physics of quantum confinement for photonic applications.
22	Prof. Anil Kumar	Synthesis & Photochemistry of composite metal semiconductor nanostructured materials
23	Dr. (Mrs.) Vijaya Agarwala	Synthesis and characterization of iron/nickel based nanomaterials using gas reduction and coating techniques.
24	Dr. R.C. Agarwala	Synthesis and characterization of Ni-P electroless composite coatings with nanosized particles.
25	Dr. Ramesh Chandra	Study of optical and mechanical properties of nanophase material
26	Dr. Tapas Kumar Kundu	Doped BaTiO ₃ nanoparticles
27	Prof. (Mrs.) S.K. Kulkarni	Optical and Morphological investigations of nanoparticles using scanning near field Optical Microscopy (SNOM).
28	Dr. C.K.S. Pillai/ Dr. Emillia Abraham	Investigation on the liquid crystalline phases of cation induced compacted and nanostructured DNA:implications for gene therapy
29	Dr. Sharath Ananthamurthy	Construction of an optical tweezer for nanometer scale rheology.
30	Prof. L.M. Manocha	Studies on development, microstructural analysis and physical properties of Aligned Carbon nanotubes and composites by CVD method
31	Dr. Vijay B. Shenoy	Nanostructuring of hard and soft films via pattern transfer.
32	Dr. Subhasis Ghosh	Fabrication and characterization of molecule-based nanostructures
33	Prof. Amalendu Chandra	Excess protons electrons and metal atoms in hydrogen bondedd nanoclusters: Studies of structural dynamical and electronic aspects through ab-initio molecular dynamics.
34	Dr. (Mrs.) Sheela Berchmans	Self-assembly of dendritic nanoreactors on electrode surfaces - The case of electrocatalysis.
35	Prof. T. Vasudevan	Synthesis and preparation of nanoparticle secondary cell materials of spinel structure and their compatibility to intercalation process
36	Dr. R. Saraswathi	Size-selective electrodeposition of metal, metal oxide and conducting polymer nanoparticles and their Nanocomposites for Technological applications.
37	Prof. Sambasivarao Kotha	Design of New and Novel Nanoconstruction Tools.
38	Dr. S.C. Watawe	Lithium nanoferrites by chemical method.
39	Dr. Gautam De	Metal nanocluster doped coloured coatings on glass and plastics using sol-gel technique
40	Dr. Tapas Kumar Kundu	Nanocrystalline spinel ferrites by solid state reaction route
41	Prof. A.K. Raychaudhuri	Fabrication of two AFMs
42	Dr. Sarit Kumar Das	Thermal and electrical conduction in nano-fluids
43	Dr. Gurmeet Singh	Investigation of the dissolution kinetics of some nanosized metal catalysts
44	Dr. K. Chandrasekhara Pillai	Efficient utilization of platinum nanoparticles enriched-substituted polyaniline network composite electrodes towards electrocatalytic

POSTER PRESENTATIONS (STUDENTS)

Session P2: Day 2: February 22, 2007: 16:00-19:00

p. 195-227

Sl No	Name	Inst/Univ	Abstract title
1	Mousumi Upadhyay Kahaly	JNCASR, Bangalore	Carbon doped boron nitride nanotube : A first principle study
2	Leela Srinivas Panchakarla	JNCASR, Bangalore	Solvothermal synthesis of nanorods of ZnO, N-doped ZnO and CdO
3	T. Vijaykumar	JNCASR, Bangalore	Nanolithography on modified Si surfaces using conducting AFM probe
4	Bhuvana	JNCASR, Bangalore	Nanoscale patterning of metals and inorganic materials by electron beam lithography
5	Sandeep Ghosh	IISc, Bangalore	Simple solvothermal synthesis of nanocrystals, nanorods and other nanostructures of nickel, ruthenium, rhodium and iridium
6	N. Sivakumar	Madras Univ	Studies on electrical and magnetic behaviour of nanostructured cobalt ferrite
7	Abhishek Verma	Delhi Univ	Size dispersion reduction in CdS _x Se _{1-x} quantum dots embedded in borosilicate glass matrix due to aging
8	Ajay Mishra	Hyderabad Univ	Tunable physical properties of nanoporous AuFe alloys by electrochemical charging
9	Rajesh Kodyath	Hyderabad Univ	Polyelectrolyte templating strategy for fabrication of Langmuir-Blodgett films capable of stable and enhanced optical second harmonic generation
10	G. Abdul Basheed	Hyderabad Univ	Determination of local spin structure and characteristic magnetic length in field-annealed VITROPERM by resonant gamma-rays and microwave absorption techniques
11	Rina Sahu	NML, Jamshedpur	Crystallization kinetics and mechanical properties of Al ₈₉ Ni ₆ La ₅ metallic glass
12	U. Sivaraman Sajeev	Amrita-IMS, Kochi	Preparation of nanofibres of PVA and poly caprolactone by electrospinning for biomedical applications
13	Ajay Kumar Shaw	SNBNCBS, Kolkata	Direct observation of protein residue relaxation dynamics in nanoenvironments
14	Rupa Sarkar	SNBNCBS, Kolkata	Size and shape-dependent electron- hole relaxation dynamics in CdS nanocrystals
15	Anindya Das	SNBNCBS, Kolkata	Large area growth of patterned two-dimensional array of gold nanoparticles
16	Roby Cherian	SNBNCBS, Kolkata	Bulk modulus enhancement in semiconductor nanocrystals
17	K.C. Barick	IIT, Mumbai	Spherical self assembled particles with Mn and Cr co-doped ZnO nanocrystals

18	Preetam Singh	IIT, Roorkee	In-situ high temperature XRD studies of ZnO nanopowder prepared via cost effective ultrasonic flame pyrolysis
19	Sonalika Vaidya	IIT, Delhi	Reverse Micellar route to the synthesis of oxalate/carbonate precursors of Ce and Zr and their decomposition to CeO ₂ and ZrO ₂ nanoparticles.
20	Nishima Wangoo	Punjab Univ., Chandigarh	Synthesis and characterization of quantum dots for bioapplications
21	E. Thirumal	Univ. Madras	Synthesis of amorphous Co and formation of nanocrystalline hcp Co by a novel annealing process
22	G. Siddaramana	Defence Lab, Jodhpur	Synthesis of rare earth doped nanophosphors through soft chemistry
23	M. Ethayaraja	IIT, Kanpur	On the modeling of nanostructure formation
24	Komathi Shanmuga Sundaram	Algappa Univ., Karaikudi	Fabrication of Fe(II)/Fe(III) loaded multi-walled carbon nanotube-poly(2,5 dimethoxyaniline) composite modified electrodes for electrocatalysis of ascorbic acid
25	Somnath Biswas	IIT, Kharagpur	A novel GMR material of Ag-coated CrO ₂ nanoparticles in form of thin fibrils derived through a polymer template
26	Rajkumar Singha	IIT, Kharagpur	Self assembled growth of Ge islands on Si(001) using molecular beam epitaxy
27	Debnath Raha	IACS, Kolkata	Control of nanocrystallization in silicon from (SiH ₄ +He+H ₂) plasma in RF-PECVD
28	Thressiamma George	MG Univ., Kottayam	Sol-gel synthesis and magnetic studies of nanophased CoFe ₂ O ₄ and CuFe ₂ O ₄
29	K.R. Bhayani	Agarkar Research Inst., Pune	Synthesis and characterization of albumin immobilized La _{0.7} Sr _{0.3} MnO ₃ nanoparticles for possible biomedical applications
30	Neha Tiwari	Univ. Pune	Seed mediated synthesis of gold nanorods and their optical properties
31	Subhranshu Sekhar Samal	NIT, Rourkela	Sonicated low volume fraction carbon nanotube reinforced epoxy nanocomposites and the role of dispersion on its mechanical properties
32	Gobinda Gopal Khan	Bengal Engg. Univ	Creation of nano-architectural pattern on electropolished aluminium surface
33	Kanchan M. Samant	Univ. Pune	Voltametric investigations on composite of carbon nanotubes-silver prepared by electrophoretic methods

SESSION A1

Research Activities at the DST Unit on Nanoscience at JNCASR

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The presentation will briefly cover the ongoing activities in the Unit. The main activity is related to synthesis and characterization of a variety of new nanomaterials- nanocrystals, inorganic nanorods, Nanocomposites and other structures, employing innovative procedures. Experimental data dealing with the size-depending properties of the nanomaterials will be presented. Some highlights of the potential device applications, such as carbon nanotubes based supercapacitors and oxide nanorods based gas sensors will also be demonstrated. Finally, our efforts nanoscale patterning of metals and inorganic materials employing electron beam lithography and AFM based techniques will be discussed.

Soft Lithography

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The project on soft lithography envisages the formation and use of soft matter for various applications. This includes biomolecules, organic thin films, polymers etc. In the area of polymeric materials, nanocomposites of metals and semiconductors in polymer matrices (example, PMMA) have been used to monitor the phase transformations in polymers. Bile acid -based organo- and hydro gels with nanoparticles have also been investigated. Liquid crystal-gold composites have been investigated for their electrical conductivity and dielectric behaviour. In the area of biomolecules based soft films, a DNA monolayer on a Langmuir film of metal arachidate has been formed to follow interactions of specific DNA-protein complexes. Well oriented, compact self assembled monolayers have been formed on metallic substrates and used to understand their interfacial properties with various solvents. The formation of droplets during pulsed laser deposition is of concern in the formation of thin films. The system containing $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ (LSCO) on LaAlO_3 (LAO) substrate has been studied using atomic force microscopy. The results pertaining to the above studies from different groups at the Indian Institute of Science will be presented and discussed.

Meso-scale Patterning: Understanding and Control of Self-Organized Phenomena in Thin Soft Films

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This talk is intended as an overview of: (A) the progress of the DST Unit on Nanosciences at IITK, and (B) our recent published work related to various surface instabilities and their control in thin (<100 nm) liquid and solid films. Our emphasis is on the novel techniques that not only have rich underlying science, but are also suitable for commercialization in large area, rapid and inexpensive patterning required for the bulk-nano applications such as the optical coatings, structured colors, super-hydrophobicity and smart adhesives. These ideas also have potential applications in engineering of self-organized meso-scale patterns in the soft materials for opto-electronics, MEMS, lab-on-a-chip devices and in nanoscale understanding of interfacial phenomena such as adhesion, debonding, wetting and friction at soft surfaces.

Fractals, nanodots, colloids and nanoscale arrays of Co₅₀Pt₅₀ magnetic alloys

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Magnetic nanoparticles have attracted considerable attention in recent years because of their technological applications in areas such as high density data storage, ferrofluid mechanics and biomedical/drug delivery systems. These applications are driven by the unique magnetic behavior of the individual magnetic nanoparticles. Since a large fraction of atoms in a nanoparticle is on the surface, a different physio-chemical environment of these atoms influences magnetic properties of magnetic nanoparticles in a nontrivial manner. The magnetic alloys of particular interest in nanoparticle form are the ordered and disordered phases of CoPt and FePt. Near the equiatomic composition, CoPt and FePt form a magnetically soft disordered face centered cubic (fcc) structure which can be transformed to an ordered face centered tetragonal (fct) structure on annealing at $T > 700$ °C and 550 °C respectively. The ordered phase has an order of magnitude higher anisotropy energy. We have successfully used vapor and liquid phase pulsed laser ablation techniques to synthesize nanoparticles of CoPt alloys. The magnetization dynamics of dried colloidal solution of surfactant-polymer coated nanoparticles has been examined in the framework of superparamagnetic blocking phenomenon based on log – normal size distribution. Our analysis reveals, in accordance with electron microscopy results, two size distributions which peak at 1.3 and 5.9 nm. The magnetic anisotropy energy of these particles is 0.9×10^6 Jm⁻³ and 0.1×10^6 Jm⁻³, respectively.

High coercively nanoscale structures of CoPt are grown on (001) SrTiO₃ with pulsed laser ablation in low pressure nitrogen ambient. At low growth rates the film morphology changes from a self-similar fractal to nanodots as the deposition temperature is raised from 700 to 800 °C. While the nanodots are L1₀ ordered phase with out-of-plane c-axis and coercivity $H_{c0} \approx 30$ kOe, the fractals have a non-zero inplane c-axis component of the L1₀ phase.

We have also prepared rectangular lattice of nanosize CoPt squares on NbN superconducting films using the technique of focused ion beam milling. Preliminary studies of electron transport in these systems reveal fascinating consequences of the antagonism between superconductivity and magnetism.

Synthesis and Characterization of Nanocomposites

**D. Chakravorty, A. Ghosh, S. Chowdhury, A.K. Nandi, S. Roy, P. Chowdhury,
A. Bhowmik, T.K. Mandal, A. Banerjee, D. Basak & S.K. Saha**

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Composites containing elements like Ti, Cr, Fe, Co, Sn etc inside a mesoporous silica framework were synthesized by hydrothermal technique. They exhibit interesting surface properties. Nanoporous inorganic and organic-inorganic hybrid materials were also prepared using different ionic surfactants. Detailed characterization of these materials was carried out. Nanostructured CuInS₂ thin films were fabricated by ion layer gas reaction method. The particles were found to have radii in the range 6 to 21 nm. Ga₂O₃-SiO₂ nanocomposites were prepared by a sol-gel method. Ga₂O₃ particles had diameters in the range 2 to 5 nm. ZnO nanocrystals with morphologies like nanorod arrays and flower-like assemblies were grown.

Surface confined living radical polymerization (SCLRP) technique was used to prepare core-shell particles comprising of metal (Au) or metal oxide (ZnO, TiO₂) core and polymer shells of controlled thickness. Colloidal metal nanoparticles-peptide conjugate were synthesized using newly designed tripeptides. Spongy gold nanocrystals with pronounced catalytic activity were made by modified-citrate reduction technique.

Poly (3-hexyl thiophene) (P3HT) – organically modified Montmorillonite (om-MMT) polymer nanocomposites were prepared and characterized. In situ Ag nanoparticles were produced by reduction of Ag⁺ with DMF in the presence of poly (Vinylidene fluoride) (PVF₂). Analysis of data by Avrami equation showed that two dimensional nucleation was operative with linear or diffusion controlled growth.

Silver molybdate glasses were used as templates to grow Ag₂MoO₄ nanoparticles, Ag₆Mo₁₀O₃₃ nanowires, Ag₂Mo₂O₇ nanorods and α -AgI nanocrystals. Silver nanowires of length 150 nm and diameter 30 nm were grown in Ag₂S doped tellurite glasses by electrodeposition technique. GaN nanowires of diameter 15 to 40 nm and lengths of a few microns were grown from the edges of platelets at a temperature of 1050°C. By annealing at 800°C dendrite-like GaN nanostructures were obtained. GaN nanorods of diameters in the range 40-100 nm were grown in ZnO/ quartz substrates. Nanometer-sized silicon powders were formed by 13.56 MHz radio-frequency capacitive glow discharge plasma of silane-argon gas mixture.

Unit for Nanosciences at the S.N.Bose National Centre for Basic Sciences

A.K.Raychaudhuri

Department of Materials Science, S.N.Bose National Centre for Basic Sciences

The focus of the centre are on the following problems areas: Synthesis of nanomaterials and their arrays, Investigations on Science (physical and chemical properties) of size reduction and confinement, Science of tools for nanosciences research like the physics of Scanning Probe Microscope, Computational materials science of nanoscale materials and science of confined biomolecules and biomolecular recognition. In addition to bulk and time averaged measurements the activities at the unit include both spatially resolved (Scanning Probe Microscope based) as well as temporally resolved measurements that include noise spectroscopy (low frequency) as well as ultra fast optical spectroscopy down to few tens of picosecond. In addition to the research activities the unit has programmes on advanced manpower training (including Ph.D) and it hosted the 2nd DST School on Nanosciences in 2005.

Some of the specific activities (experimental) where significant results have been obtained include: a) Synthesis of metal nanowires, nanotubes and complex functional structures using a novel electrodeposition technique and investigation of their transport properties from 3K - 700K to elucidate changes in transport properties on size reduction, b) Tuning of ground state properties of perovskite oxide nanomaterials (films, particles and wires) synthesized by chemical routes, c) Synthesis of ZnO nanocrystals, nanowires and films whose optical properties including band gap and Photoluminescence can be tuned by doping with Cd and Mg, d) Growth of ordered arrays of nanoparticles and wires using chemical and electric forces using a combination of nanoimprint lithography, optical lithography and e-beam lithography, e) Physics of dynamic force microscopy and force spectroscopy, f) Investigation of processes in biomolecules and confined biomolecules using picosecond spectroscopy to investigate effect of confinement on biomolecules, g) Understanding the energy transfer between biomolecule and quantum dots using ultra fast spectroscopy, h) Science of micelles and reverse micelles.

Significant new results have been obtained in theoretical activities in the following areas: a) Mechanical properties of nanomaterials, b) Formation of texture (including martensites) in nanomaterials during growth, c) Investigation of optical, electronic and magnetic properties of clusters, d) Mesoscopic transport in nanowires with multiple leads, e) Dynamics of colloidal crystals and f) Memory of magnetic nanoparticles.

Excited State Intramolecular Charge Transfer Reactions in Nano-sized Polar Solvent Pool

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Excited state intramolecular charge transfer (ICT) reactions in substituted benzonitril derivatives have been studied in polar solvent cage of nano dimension. The polar cages of different size have been generated by a combination of oil, polar solvent and a surfactant (anionic, cationic or neutral) in the reverse micelle phase. Confinement has been found to affect both the energetics and kinetics of ICT reactions. The rates of ICT reactions in these encapsulated environments are slowed down by a factor from five to even an order of magnitude compared to what has been found in the bulk solvent. Effects of electrolyte on these reactions in these encapsulated media have been investigated. Steady state and time dependent results indicate that the nature of surfactant used to generate nano-sized solvent cage may play an important role in determining both the rate and product of ICT reactions in these restricted media.

Fluorescent Quantum Dots: Potential Probe of Biomolecular Dynamics

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In recent years fluorescent quantum dots (QD) are used to structure and function of biological macromolecules. In order to use the quantum dots for a biomolecule, a vivid dynamical cauterization of the nanomaterial is essential. Recently, the dynamics of photoluminescence (PL) in CdS nanocrystals (NCs) with various sizes and shapes dispersed in water-in-oil microemulsions are studied with the picosecond resolved time correlated single photon counting (TCSPC), streak camera and nanosecond resolved gated photoluminescence (PL) spectroscopic techniques. We also study the effect of the shape of the NCs on their PL-anisotropy. In another study we have shown that 2-mercaptoethanol CDS quantum dot aggregate in aqueous medium have implications in the future application of the QD-nanoaggregate as host of small ligand molecules of biological interest. The results of our dynamical studies on fluorescent QDs will be discussed in the context of designing better, more effective physical and biological PL probes.

SESSION B1

Progress of the Unit on Nanoscience and Technology (DST- UNANST) Project at NCL

S. Sivaram

The NCL proposal under the NSTI initiative focuses on the synthesis of nanomaterials by novel methods utilizing the micro-organisms, foams as templates and their subsequent assembly using biological templates like DNA etc. A major objective of this project is also to study the applications of nanomaterials and nanomaterial-polymer composites as drug delivery systems and medical implants. In this presentation the progress achieved in the synthesis front as well as the assembly of nanoparticles will be presented. Special attention will be given to the synthesis of multicomponent oxides like BaTiO_3 using the fungus *Fusarium oxysporum* and the leaching of nanocrystalline SiO_2 from rice-husk using the same organism. The foam based method has been extended to the synthesis of alloy nanoparticles as well as multicomponent systems like CoFe_2O_4 and MgFe_2O_4 from the simple metallic systems. It has also been found that synthesis of Co and Ni nanoparticles in presence of an anionic surfactant sodium dodecyl sulphate (SDS) and oleic acid under specific concentration conditions lead to the formation of highly ordered assemblies of monodisperse spherical aggregates. These particles show large magnetocaloric effect in the vicinity of a low temperature magnetic transition in Co and $\text{Co}_{\text{core}}\text{Ag}_{\text{shell}}$ systems. It has been observed that surface modification of polyimide membranes by NH_3 plasma treatment and the subsequent layer-by-layer assembly of Au nanoparticles and amino acid lysine could lead to the gradual lowering of the surface contact angle which is regarded as an essential step for the utilization of polymer membranes for bio-implants and cell growth. Salient features of employing nanoparticles as drug delivery systems would be shown. Miscellaneous examples like shape transformations of monolayer capped Au NPs using halogen containing reagents, employing FMR spectral features to characterize magnetic-core-noble-metal-shell nanoparticles and some exciting results on the Physical manipulation of biological and chemical syntheses for nanoparticle shape and size control will be shown. Preliminary results about the synthesis of magnetic nanoparticles like Fe_3O_4 and $(\text{Fe}_3\text{O}_4)_{\text{core}}\text{Ag}_{\text{shell}}$ nanoparticles will be presented.

Nanoscience in the University of Pune

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DST Unit on Nanoscience (initially known as UNANST, Pune University) was established in University of Pune in March 2005. A large number of faculty members from various Departments such as Physics, Chemistry, Electronics, and Life Sciences (Microbiology, Zoology, Institute of Bio-information and Biotechnology), in the University working/interested in the field of Nanoscience have come together and decided to work in the inter-disciplinary areas of Nanoscience taking advantage of the existing expertise in the related field.

Through the brain storming sessions of faculty of the Unit, following research areas in Nanoscience have been identified as the areas in which faculty members have expertise. These are areas are as follows.

- i) Novel Quantum confined structures: Synthesis, Analysis, Applications and Theory
- ii) Magnetic and Ferroelectric Nanomaterials
- iii) Bio – Nanomaterials
- iv) Lithography for Nanodevices

A presentation will be made on the facilities available under the DST Unit on Nanoscience, some programs organized by the Unit, teaching on Nanoscience in University of Pune and some results obtained by different groups will be highlighted.

Setting up of a Centre for Nanotechnology at Amrita Institute of Medical Sciences (AIMS, Kochi) – Preliminary Results in Tissue Engineering

Dr. Shanti Nair

Head, Centre for Nanotechnology, AIMS

Co-PI: Dr. T. S. Ganesan, Head, Institute for Molecular Medicine, AIMS

Co-PI: Dr. K. V. Menon, Head, Department of Orthopedics, AIMS

Co-PI: Dr. Bipin Nair, Head, School of Biotechnology, Amrita Vishwa Vidyapeetham

Co-PI: Dr. Deepthy Menon, Assistant Professor, Nanomedicine, AIMS

Co-PI: Dr. Seema Nair, Research Scientist, Biotechnology and Toxicology, AIMS

Research Assistants: Dr. U. S. Sajeev, Mr. R. Krishnaprasad

Junior Research Fellows: Anitha V. C., Divya Rani VV, S. Abhilash, Sabitha M.

Technician support: Ranjith, Sajin P. Ravi

Progress and preparations in the setting up of a Centre for Nanotechnology with funding from DST is reviewed. A newly constructed state-of-the-art research floor of 30,000 square feet has been commissioned. 10,000 square feet is dedicated to the materials technology component while the remaining 20,000 square feet is dedicated to the Institute of Molecular Medicine. The tissue scaffold materials preparation and characterization and testing is housed in the 10,000 square feet section whereas the facilities for the cell & tissue culture work will reside with the Institute of Molecular Medicine. The materials processing section is divided into 5 laboratories of approximately 200 square feet, each dedicated to a specific part of tissue engineering of scaffolds which is discussed in the presentation. Preliminary results will be presented on preparation and characterization of biomimetic nanoparticles for use in scaffolds, cytotoxicity and cell-surface interactions of nanoparticles and nanocomposites on bacterial and human cells, creation of nanocomposites and synthetic extracellular matrices, mechanical behavior and high resolution microstructural characterizations. Three alternative synthetic routes for nanobiomaterials are explored, namely, chemical and biochemical, electrostatic and thermomechanical. Chemical routes are explored for the processing of biomimetic nano hydroxyapatite crystals for incorporation in polymer matrices and on surfaces and within nanofibers. Electrostatic methods are employed in the electrospinning of nanofibers of biodegradable polymers and blends of biodegradable polymers to control biodegradability and biocompatibility as well as mechanical properties. Finally, thermomechanical approaches are used to process nanocomposites of biopolymers and biopolymer blends containing nanohydroxyapatite crystals for implant applications. Specific experimental plans for future based on the preliminary results are discussed for input by the review committee.

Chemical interactions of noble metal nanostructures

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In this talk, I present a summary of our activities of the last one year. Our work is largely concerned with the chemical interactions of nanoparticles, nanorods and sub-nano particles in solution and in the form of thin films. Such chemical interactions result in novel chemistry and new physical phenomena. The chemical properties such as the degradation of pesticides on nanoparticles have been commercialized. The flow induced potential on nanoparticle surfaces has been extended to anisotropic nanostructures such as nanorods. Chemical interactions with carbon nanotubes lead to the distortion of the nanotube structure, which in turn results in visible emission from the nanotubes. Noble metal nanoparticles interact with proteins strongly and the chemistry of the proteins is preserved in some cases. Using nanoparticle chemistry, drugs have been delivered to cells. The chemistry of anisotropic nanostructures such as nanorods is similar to spherical particles in several cases, but there are also significant differences. Our studies on the dynamics of molecules at nanoparticle surfaces have been ongoing and a new model has been developed to understand the temperature dependent rotational dynamics at nanoparticle surfaces. We explored the chemistry to sub-nano dimensions with the recently discovered sub-nano clusters of gold.

Nanotechnological Route for Improving the Hydrogenation Properties of Palladium and Praseodymium Layers

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Hydrogen induced changes in the electronic and optical properties of Pd and rare earth metals make these materials highly suitable for sensor and switching applications. Our earlier work on Gd nanoparticles has shown that size and surface dependent properties results in large improvements in the device characteristics. The occurrence of structural transformations and large lattice expansion/contraction along with optical and electronic changes results in slow and incomplete change-over from the 'on' state to the 'off' state during hydrogen loading/deloading cycles. In this presentation, results of some recent investigations carried out in this direction will be discussed. In a study on the hydrogen sensing properties of Pd nanoparticles, it has been shown by controlling nanoparticle size, surface conditions and thickness, the opposing and entangled effects due to electronic and geometric changes can be controlled and thus separated. Due to the presence of interparticle gaps and complete conversion to PdH₂, the initial response is followed by a substantial decrease in resistance due to closure of conducting paths. This study thus sets the foundation for fabricating a novel gas sensor devices having pulse-like response. In a separate study, the size-dependent improvements in the structural, optical and electrical properties of Pr nanoparticle layers have been observed. A new methodology of improving the hydrogenation properties of solid state materials by using ion-induced nanotracks as two-way transport routes has been successfully implemented. A large enhancement in the hydrogen stoichiometry value (H/Pr) from 7.2% to 17.8% is observed with increase in the ion doze. The role of nanotracks in hydrogen removal during deloading is even more remarkable. It is observed that about 31% H can be removed during deloading in ion-irradiated samples (maximum possible is 33.3%, corresponding to PrH₃ to PrH₂ transformation) in comparison to only 12 % in case of un-irradiated layers. In addition, some important results on the synthesis and application of other nanostructured materials from our institute will also be presented.

SESSION C1

Synthesis, Growth, Characterization, Structure-Property Correlations and Product Development at DST:UNANST (BHU)

O. N. Srivastava (PI & Coordinator), R. S. Tiwari, Anchal Srivastava (Physics),

S. Lele, S. N. Ojha, R. K. Mandal (Metallurgy)

Shyam Sundar, Madhukar Rai, D. Dash (Medicine and Biochemistry)

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The early work in the BHU-DST-UNANST project freestanding monolithic uniform macroscopic hollow cylinders having radially aligned carbon nanotubes with diameters and lengths up to several centimeters were fabricated and used as filters to eliminate heavy hydrocarbons from petroleum and to filter bacterial contaminations from water.

In another work, structural, electrical and mechanical properties of multi-walled carbon tubes (MWNT) – polyethylene oxide (PEO) composites were investigated. Composites with different wt% (0 to 50 wt%) of MWNTs, were prepared and characterized. The conductivity measurements on the MWNT (~50 wt%)-PEO composite films showed an increase of eight orders ($\sim 7.5 \times 10^{-8}$ to 6.52 S cm^{-1}) of magnitude in conductivity to that of a PEO film.

Formation and microstructural characterization of coaxial carbon cylinders consisting of aligned CNT stacks were also investigated. Some other investigations involving CNT relates to admixing CNT to NaAlH_4 to increase the hydrogen desorption kinetics and admixing of CNT to MgB_2 superconductor to increase the critical current density. Efforts have also been made to synthesize gallium nitride nanocrystals on aligned carbon nanotubes.

The cuprous oxide (Cu_2O) nanostructures have been synthesized by anodic oxidation of copper through a simple electrolysis process employing plain water as an electrolyte. Two different types of Cu_2O nanostructures have been found. One type got delaminated from copper anode and collected from the bottom of the electrochemical cell and the other was located on the copper anode itself. The obtained nanostructures are nanothreads, nanorods and nanocubes. Similar growth of nanostructures of SnO_2 has also been obtained. For ZnO , vapour phase growth involving reaction of Zn vapour with oxygen has led to the formation of various nanostructures, e.g. nanotetrapores, nanorods, nanocombs etc. Correlation of nanostructural features with optical and field emission studies have been carried out. Other nanomaterials synthesized by us correspond to silicon carbide and titanium carbide nanostructured films.

Yet another variety of nanomaterials studied by us are the quasicrystalline materials: $((\text{Co}, \text{Ni})\text{Al}_2\text{O}_4)$. It is important to identify parameters that will be helpful in producing BMGs with thickness ~ 10 cms. Based on these we have identified and made and characterized the alloys of Al-La-Ni-Cu and Al-Ni-CU-Zr.

Research Activities at the Centre for Computational Materials Science, JNCASR

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The presentation will briefly cover the ongoing activities in CCMS. Phase transitions, structure, and dynamics of several metastable systems including supercooled liquids, gels will be discussed. Results on ab initio molecular dynamics simulations of nanoclusters of room temperature ionic liquids will be presented. First principles calculations on ferroelectricity in epitaxial thin films of BaTiO₃ and BaTiO₃/SrTiO₃ superlattices will be discussed. Quantum chemical calculations on stable metal clusters as well as on the origin of magnetism in geometrically frustrated lattices will be presented. Scaling relations for the dependence on size, material and structure of the elastic and vibrational properties of nanoclusters and periodic systems obtained using density functional theory will also be presented.

Facility for MOVPE growth of compound semiconductors and elucidation of their electronic structure by ARPES

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At Saha Institute of Nuclear Physics, we have initiated research and development activities on the compound semiconductor based nano-electronic device materials. This is a unique effort to develop and establish core technology for the futuristic devices based on epitaxial materials. Novel fabrication techniques that permit precise control of the structure, properties, size and position of nanoscale elements are the most important aspects of this activity. We shall focus on two-types of materials, namely Si-Ge and III-V systems. We have installed recently a Molecular Beam Epitaxy (MBE) facility for growing Si-Ge materials. A metal-organic vapor phase epitaxy (MOVPE) system will be installed soon for growing III-V materials. The focus of the MOVPE system will be the growth of InP nanowires, doping, nanowire heterostructures and exploit their potential application in futuristic quantum devices.

Study of the electronic structures of nanomaterials and nanostructures are also very important since they are responsible for the physical, chemical and other novel properties. Angle-resolved photoemission spectroscopy (ARPES) is the most direct momentum-resolved technique that is employed for the investigation of electronic structure of crystalline materials. The focus of our studies will be the low-dimensional semiconductor nanostructures grown by MOVPE-MBE systems at SINP. Low-dimensional nanomaterials show many interesting phenomena such as spin-charge separation, quantum-well states, surface states on the stepped terraces of the vicinal surfaces etc that can be explored using ARPES measurements.

Availability of various other characterization techniques in our laboratory will enable us to probe structure/composition-property relationship of these nanostructured materials. Department of Atomic Energy (DAE) has funded MBE and ARPES facility and the MOVPE facility is funded jointly by DAE and NSTI of Department of Science and Technology (DST). Salient features of this MBE-MOVPE-ARPES set-up will be discussed in our presentation.

SESSION A2

SYNTHESIS AND CHARACTERIZATION OF NANOMATERIALS

Porous Metal-Organic Open Framework Structures with Selective Metal Ions

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Synthesis of metal-organic open framework structures with void spaces are important due to their potential applications in diverse areas such as optoelectronics, supramolecular storage of molecules, catalysis, molecular magnetism and so on. Our present research activities involve the development of paradigms to have systems for gas absorption as well as optoelectronics. We have adopted the modular chemistry approach to synthesize a number of metal-organic open framework structures from relatively simple multidentate ligands. We have used alkaline earth, transition and inner-transition metal ions with ligands synthesized in the laboratory. Some of these systems show excellent gas absorption properties while few others exhibit interesting nonlinear optical activity.

Our approach has been both hydrothermal as well as room temperature synthesis. Some of the recent results will be discussed.

Biocompatibility of water soluble multiwall carbon nanotube on the growth of Escherichia-coli in relevance to its use in carrier systems for the delivery of therapeutic molecules

Sabyasachi Sarkar

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Since the discovery of carbon nano tube (CNT), there has been an awful lot of speculation about what it can deliver to the mankind. Proposed applications range from molecular electronics, biomedical uses such as drug delivery, through to the lofty goal of a space elevator. CNT-mediated drug delivery requires water soluble CNT possessing nano pores or channels for drug loading. Carbon soot was prepared by oil lamp or candle burning in air and it was purified under oxidative treatment with nitric acid to yield water soluble CNT. The presence of nanopores in water soluble CNT was verified by ^{13}C NMR in D_2O (0.01% H_2O) and by ESR measured in D_2O and D_2O - H_2O mixture. The unpaired spin present in these CNTs arising from sterically protected carbon radicals interact with proton of H_2O resulting super hyperfine interaction. Direct proof for the existence of the pore channels was made by quantum dot experiments using these CNTs as nano reactor. ZnS, ZnSe, CdS and CdSe were chemically synthesized inside these CNTs in aqueous medium. Using excitation at 371 nm all these impregnated CNTs show identical emission max., at 437 nm suggesting ZnS, ZnSe, CdS, and CdSe have identical size which is only possible once these are inside the CNT with identical pore size. Bio compatibility of this water soluble CNT must be a prerequisite to be considered prior to their biomedical uses. Escherichia coli, is a representative living material often used in laboratories We used E-coli strain DH5 α as a model organism to taste its compatibility with water soluble CNT. The growth of E-coli under water soluble CNT was studied by spread plate technique. In the first generation of E-coli there was not much effect and the cell division became impaired as observed by SEM and AFM images. At this stage, E-coli responded to 'SOS' and remained in aggregate not responding to cell division. In the next generation period (12 hours), the initial shock was apparently disappeared along with the start of cell division. The SEM images in the third generation displayed unique features where the CNTs were seen to be completely opened up with its rupturing in almost two halves. The heavily derivatized CNTs were thus found to be responsible for their hydrophilicity and these were found to be relatively reactive than the conventional underivatized CNTs. In the present experiment there are several enzymes present in E-coli which are capable to decarboxylate these CNTs resulting spontaneous opening of the CNT tube. Normally carbon powder is bio-friendly and has been in use internally in certain human ailments. The heavily carboxylated CNTs were shown to be compatible in the growth of Ecoli. E-coli were able to completely open up these CNTs after 36 hours suggesting good possibility of these CNTs to be used as drug carriers for the delivery of therapeutic molecule at a specified site.

Nanostructuring of poly (diaminonaphthalene) in the channels of mesoporous materials

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Self assembling approach has been conveniently used for nanostructuring of conducting polymers. The type of nanostructuring can also be tuned by judicious selection of the environment of the self assembly, structure of the monomer and mode of polymerization. Nanotubular polyaniline has been reported to be obtained through polymerization of aniline within the channels of mesoporous silica. In the present study, 2,5 – diaminonaphthalene was polymerized within the pores of mesoporous silica and the nanostructured poly (2,5 – diaminonaphthalene) PDAN formed in the pores was isolated from the pores. The morphology, structure and electronic properties for the nanostructured poly(diaminonaphthalene), PDAN-NS, are analyzed. PDAN-NS exhibits confining effect in the electronic properties as a result of nanostructuring within the pores of silica.

Soft Chemistry for Nano-Material Synthesis

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Co-ordination chemistry is a part of soft chemistry which was utilized by various branches of science and technology. The co-ordination phenomena generates extra stabilization of metal ions so that it can remain dissolved in solution even in presence of common precipitating agents.

We have utilized this concept for making

- 1) Nano-sized oxides
- 2) Metastable oxides in nano-size
- 3) Nano-porous (Mesoporous) materials
- 4) Nano-magnetic material for biological applications
- 5) Nano-rod of fluorescence materials

We have synthesized the multicomponent mixed oxides from the mixer of their co-ordination compounds. It has produced homogenous composition and phase formation occurs at relatively lower temperature. With small modification of the process , the sizes of the ultimate powders may reach nano-sizes. These process are successful for synthesis of nano-sized 1) Simple oxide 2) spinels 3) Chromites 4) Aluminates 5) Manganites 6) Titanates 7) Zirconates 8) Niobates 9) Tanatalates 10) alloys of ferroelectric materials, and many others through complexation routes. The complexing agents used are Triethanolamine, Diethanolamine, Oxalic acid, Tartaric acid, Citric acid, Ethylenediamine tetracetic acid (EDTA), Nitrilotriacetic acid (NTA).

The samples have been characterized by TEM, XRD and physical measurement. We have synthesized many meta stable oxide system like 1) $\text{Fe}_2\text{O}_3 : \text{Cr}_2\text{O}_3$ 2) $\text{ThO}_2 : \text{UO}_2$ 3) $\text{TiO}_2 : \text{MO}_2$ (M= Cr, Mn,Ce, Pr, Tb) 4) $\text{CrPO}_4 : \text{ABO}_4$ (A=Ni, Cu, Mn ,Zn and B= Mo, W). All these metastable phases have many unusual physical and chemical properties.

As the co-ordination compounds can retard the rate of formation of precipitation reaction, by controlling the reaction conditions it may generate gel, which may culminate into mesoporous materials in presence of templating agents, which are mostly surfactant.

Thus we have synthesized the mesoporous ZrSiO_3 , $\text{Zr}(\text{HPO}_4)_2$, $\text{Sn}(\text{OH})_4$, Nb_2O_5 , Ta_2O_5 , $\text{Zr}(\text{MoO}_4)_2$, $\text{Zr}(\text{WO}_3)_2$, $\text{TiO}(\text{HPO}_4)$ etc.

We have synthesized nano-sized magnetic materials for protein separation and cancer cell detection. In presence of complexing agent we have synthesized nano-rods of LnPO_4 and LnF_3 (where Ln = La, Y , Gd) doped with Eu^{3+} and Tb^{3+} having unique fluorescence properties. The concepts presented here are very versatile for nano material synthesis.

Synthesis, Characterization and Application of Nanosized Oxide Materials

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Part I: Hydrothermal method has been used for the preparation of ZnO, MoS₂ and CdSO₄ nanomaterials by varying the precursors' concentration, temperature and duration. Powder XRD patterns exhibit hexagonal phase of ZnO nanorods and hexagonal 2H-MoS₂ nanobundles. UV-visible spectrum of the ZnO nanorods shows blue shift compare to bulk ZnO due to the size effect. The samples showed strong photoluminescence. The morphology of the MoS₂ prepared using H₂S resembles with the morphology (bundles of nanofibers) of the products obtained using sodium sulphide. XPS results show S(2p) doublet peak (2p_{3/2} and 2p_{1/2}) at 161.25 and 162.94 eV respectively in which 2p_{1/2} and 2p_{3/2} orbital peaks coincide with each other. CdSO₄ nanotubes/wires possesses an intense UV emission at 372 nm compared to the bulk CdSO₄ (392 nm).

Part II: The porous nanocrystalline metal oxides; MgO, CaO and ZnO have been prepared through combustion process using metal nitrates as oxidizer and glycine as fuel. The powder XRD patterns confirm the crystallinity and phase purity of the powders. The average surface areas are found to be 107, 18.65 and 18.53 m²/g and pore diameters measured by N₂-desorption isotherms are 7.8, 6.1, and 5.2 nm for MgO, CaO and ZnO respectively. The SEM results reveal that the powders are weakly agglomerated into porous structure with poly crystallite nanoparticles. These metal oxides are employed as adsorbents for the removal of fluoride in ground water and, COD and colour from industrial effluents. From the results it was found that the combustion derived nanocrystalline MgO (as made) removes ~ 97% of fluoride, ~ 94 % of colour and ~ 91 % COD.

Perovskites such as LaMnO₃ and doped lanthanum manganites (La_{1-x}A_xMnO_{3+δ} where A=Ca, Sr and Ba; with $x = 0.0 \leq x \leq 0.5$ for Ca and $x = 0.0 \leq x \leq 0.3$ for Sr and Ba doping) have been prepared by low temperature combustion process (~300°C) using corresponding metal nitrates as oxidizers and oxalyl dihydrazide (ODH) as fuel. The Mn⁴⁺ content in as-formed samples is high (~34 %) and this favors cubic phase. In calcined (900 °C, 6 h) samples, Mn⁴⁺ content is reduced to ~ 28% and resulting into rhombohedral phase. A broad exothermic peak around 900°C in differential thermal analysis (DTA) curve and gradual weight loss from 650 °C in thermo gravimetric (TG) curve is correlated to the reduction of Mn⁴⁺ to Mn³⁺. The SEM micrographs show that the powders are voluminous and porous. The fluffy nature, voids can be attributed to large amount of gases evolved during combustion reaction. The samples exhibit a broad metal-insulator transition including LaMnO₃. The T_{M-I} values are shifting to lower temperature side on doping and these values are lower compared to the samples prepared by high temperature method (solid-state). It can be seen from MR measurements that the resistance decreases with increasing magnetic field and that of T_{M-I} shifts towards higher temperature.

Titanium Dioxide Filled Natural Rubber Composites

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Nanocomposites of natural rubber were prepared with TiO₂ filler by two-roll mixing method. The cure characteristics of the composites were studied using an Oscillating Disc rheometer (Monsanto R-100). The morphology of the composites was studied by scanning electron microscopy. The swelling studies of the composites were performed and the crosslink densities of the composites were determined. The effect of the TiO₂ filler on the mechanical properties of the natural rubber was also studied. It was observed that the tensile and tear strength increases with increase in filler content. The non-linear viscoelastic properties of the composites were studied using dynamic mechanical analyser in tension film mode. The effect of filler loading and temperature on the Payne effect has been investigated. Payne effect is assumed to arise from the elementary mechanism consisting of adsorption-desorption of macromolecular chains from the filler surface. The filler characteristics like particle size and specific surface area were found to be key parameters influencing Payne effect. It was observed that Payne effect is more pronounced at higher loading. Payne like behaviour was observed for unfilled compounds also. The amount and morphology of the fillers played a major role on the Payne effect. At low loading of TiO₂, there is not much variation in storage modulus, loss modulus and loss tangent compared to gum vulcanizates. But at higher loading, pronounced effect has been observed. This may be due to break down of filler networking due to higher strain amplitude at higher loading. The effect of temperature on the Payne effect was also studied. But surprisingly enhanced Payne- like behaviour has been observed for gum vulcanizates at room temperature where there are no filler-filler and no filler-polymer interactions, which are typically associated with filled vulcanizates. This is explained by the effect of chain disentanglements on straining.

SESSION B2

NANOBIO

Investigations of biomolecular interactions at nanoscales

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In this talk I will highlight the progress made towards this objective and present results of various experiments we have designed and implemented to capture biomolecular interactions at nanoscale.

1. Translocation of ssDNA across nanopores: A procedure has been developed to reconstitute hemolysin heptamer assembly as nanopores on PC/PE mixtures of lipid bilayer. Bilayer patch containing channels have been incorporated on micropipette tips and electrical characterization of single channel activity has been done.
2. Optomechanical control of polymer dynamics across nanopore: we have made ssDNA construct having biotin at one end which is ligated to streptavidin immobilized bead. Using this microbead-ssDNA system, we enabled transport across hemolysin channels and simultaneously controlled the process of DNA transport through optical manipulation of the bead.
3. Permeability of small molecules across nanopores: We have expressed and purified a hemichannel protein, connexin (Cx43), in a baculoviral system. We have used these hemichannels as model proteinaceous pore system, and incorporated them at the end of patch pipettes by the tip-dip method. The hemi-channel has 150 pS of conductance, as expected in 100mM CsCl saline. We have tracked the permeability of small molecules (R6G) across the channel and further quantified it by surface-enhanced Raman spectroscopy, SERS. This effort is the first time that the combination of patch and Raman techniques has been used. We are connexin bilayers. We have also studied dye translocation across whole connexin channels by a combination of patch and fluorescent techniques. The results show that short-lived molecules such as cAMP and IP3 should have receptors co-localized within 100 nm of the channel mouth.
4. Nanomechanics of cell membrane: change in membrane tension and cellular fluidity are good indicators of biological functions. To study spatio-temporal remodeling of mechanical properties of the cell, specifically at very small length and time scales, we have developed a methodology to determine cell membrane tension using optical tweezers. We have measured membrane tension on diverse cell systems, and under different physiological conditions to quantify the biochemical state. We will discuss the results of specific experiments relating depolarization on membrane tension of A7R5 smooth muscle cells and epithelial Hela cells with membrane tension measurement.
5. Rheology of biopolymers and cells : cell membranes and semiflexible biopolymers play a vital role in shaping cellular structure and rigidity. We demonstrate that using laser light scattering based particle-tracking methodology giving positional fluctuations of the trapped bead at high bandwidth; one can determine the microheological properties of the system. From power spectral analysis, we obtain shear and rigidity modulus of the polymer solution and cell membranes. We report the measurement for biopolymers such as dsDNA , ssDNA, polylysine and polyethyleneoxide solutions, and endothelial cells.

Kinetics of self-organization of polyampholyte nano-particles on substrates and in solutions

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An appropriate composition of a binary solvent, water-ethanol, provides the necessary thermodynamic environment for the polyampholyte (gelatin) molecules to form self-assembled nano-clusters having fractal dimension $d_f \approx 2.6$ in the bulk (3-D) and 1.7 on surfaces (2-D). The aggregation in the bulk of the solution appears to be an anomalous process and could be explained through Smoluchowski aggregation model. It gives a DLA (diffusion limited aggregation) type fractal dimension to the cluster, but shows extremely low polydispersity, which in fact is a signature of a slowly growing RCA (reaction controlled aggregation) process. We have proposed a RSA (random sequential adsorption) model for the self-organization of nano-structures on surfaces for this system. The temporal growth in hydrodynamic radii (R_h) of these structures in the bulk followed: $R_h(t) \sim t^z$ and the corresponding growth in scattered intensity $I(t)$ followed, $I(t) \sim t^z$ with $z=1/d_f$. Experimental results obtained from light scattering, rheology and atomic force microscopy experiments enable us to probe the kinetics of such growth processes. These nano-structures formed on surfaces followed a sequence of morphological time dependent changes, driven by selective but slow evaporation of ethanol, to yield several types of self-organized nano-assemblies.

Probing nanoscale chromatin architecture & function within single living cells

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In eukaryotes, the genome is differentially compacted by complexation with histones and other nuclear proteins into euchromatin and heterochromatin which are highly organized within the cell nucleus. Accessing genetic information requires decompaction of chromatin and this is regulated by molecular machines as well as epigenetic codes located on the histones. Spatio-temporal organization and controlled unfolding of local chromatin structure within the nucleus is essential for cellular development and function, and yet the physical bases of these processes are poorly understood. In this context, recent progress in single-cell biophysics combined with systems level approaches provide a new paradigm in understanding chromatin structure and function. Using such methods, my laboratory has, in the recent past explored the physical principles underlying dynamics of self-assembled structures, fluctuations and kinetic barriers in gene regulation. Using the above tools, we are now focusing on probing the coupling between nanoscale chromatin assembly and nuclear architecture in defining cellular transcription control and its memory. I will discuss some of our latest results on the functional organization of chromatin assembly and its role in transcription control within living cells.

In-Vitro Study of Actin Myosin Molecular Motors

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Molecular motors are well established nano-scale molecular machines present in living systems that are responsible for various dynamical processes from transporting single molecules over small distances to cell movement and growth. Actin-myosin is a muscular motor protein system that converts chemical energy into linear motion for nanoscale transport. In-vitro motility assay is an experimental technique, which can be used to utilize molecular motors for Nanodevice application.

Myosin was immobilized on different solid substrates like gold-coated glass slide, mica, silicon which involve both covalent binding using cross linkers like EDC, APTES, silanes and non-covalent binding employing Protein A, surface adsorption. Atomic force microscope was used to investigate topological characteristics of different surfaces.

The velocity of actin filaments sliding over myosin heads is calculated using tracking program developed in MATLAB. Velocity of actin filament on myosin tracks immobilized on gold coated glass surface is found to be $1.81\mu\text{m}/\text{sec}$ on mica surface is $2.99\mu\text{m}/\text{sec}$ and on glass slide cleaned with 0.1M KOH in ethanol is $3.65\mu\text{m}/\text{sec}$. In-vitro studies show that average velocity of the actin molecules was ranging from 1.0-1.5 $\mu\text{m}/\text{sec}$ at pH 8.0. Microchannels are fabricated on gold coated glass surface by ablating the surface using laser micro dissection system to control the position of the actin filaments

Nanorobotic application of the system has been demonstrated by transportation of carboxylated polystyrene microbeads attached to actin filament. Experiments are in progress to control directionality as well as the movement of actin filaments, by varying environmental conditions in terms of electrical and magnetic field, pH, temperature etc.

Nanosphere lithography : an efficient and reproducible method of generating array patterns in the Nanometer level

**Chandra Kumar Dixit, Ajeet Kumar, Amit Saxena, Abdullah Alqudami,
S.Annapoorni and Subho Mozumdar**

Array fabrication in the nano-domain is one of the major challenging tasks, as little mechanical control over the process is available. Various sophisticated instruments are commercially available ranging for chip designing in the micro-level, including micro-array spotters. However, there is still the need of another efficient system, which can replace these costly instruments and can work efficiently in the nano-domain. Here we have tried one of the traditional methods of array formation for the purpose of chip designing and fabrication.

Our group has successfully completed gold-based two-dimensional array formation using polystyrene as a basic matrix on a glass chip. Now the emphasis is on the development of a cheap nano-array for various diagnostic and research purposes. Our major concern is on the development of a protein and DNA chip. Primary work has been completed with unpredictably good results where we have immobilized HRP as a model protein molecule. We are now in the process of standardizing protocol for ds- and ss- DNA molecules.

In addition our group has been successful in preparing some very good quality metal nanoparticles which we have now used for catalyzing a large number of Organic Reactions. One such reaction is being further used for designing the nano-array patterns using a simple and user-friendly nanotechnology.

SESSION C2

A potent antibacterial formulation based on biostabilized silver nanoparticles

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In the present study we report that a novel patented concoction (comprising biostabilized 7-20 nm nanoparticles of Ag⁰, Ag₂O and Ag₂S in the ratio of 2:2:1) possesses excellent antibacterial activity against Gram-positive, Gram-negative and multi-drug resistant (MDR) bacterial strains. AFM and SEM imaging studies revealed that silver nanoparticles physically damaged the bacterial cell and ultimately led to cell death.

MIC obtained against standard and MDR showed that nearly 75% of the strains showed a MIC in the range of 3.12-6.25 µg/ml followed by 21 % strains showing a MIC value of 1.56 µg/ml and only 3.4% showing a very low value of 0.78 µg/ml. The nanoparticles preparation also showed 60-70% diminished cytotoxicity as compared to silver ions.

Results from time-kill study showed that silver nanoparticles tended to kill Gram negative bacteria effectively; achieving a 3 log₁₀ decrease in 5 to 9 h. On the other hand silver nanoparticles required 12 h of exposure to kill *Bacillus subtilis* and *Staphylococcus epidermidis*. Post nanosilver effect ranged ~ 1.3-11 h, with maximal effect against *P. aeruginosa* (11 h) and minimal effect against *Staphylococcus sp* (1.5 h).

Encouraged by these highly positive results, a silver nanoparticles-based formulation (S-gel) was prepared. It exhibited an anti-bacterial spectrum comparable to that of silver sulfadiazine (commercially used antibacterial agent), albeit at a 30-fold less silver concentration. The acute dermal LD₅₀ value of S-gel in Sprague Dawley rats was found to be greater than 2000 mg/kg body weight. After application at the dose of 2000 mg/kg body weight S-gel did not cause any mortality in the treated rats. Also it did not induce any signs of local or systemic toxicity during the observation period. S-gel did not induce any gross pathological abnormalities.

The above studies clearly indicate that biostabilized silver nanoparticles could provide a safer alternative to silver sulfadiazine, especially to prevent secondary bacterial infection in burn wounds, bed sores, etc. Currently appropriate human trials of S-gel are underway.

Synthesis of Novel Water-Soluble Block Copolymers in Ionic Liquid as Potential Gene Delivery Vector

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The basic concept underlying gene therapy is that human disease may be treated by the transfer of genetic material into specific cells of a patient in order to correct or supplement defective genes responsible for disease development. However, the practical application of gene for disease therapy has been hindered by the following major problems (i) poor transport into cells (ii) non-specific effects on cells (iii) rapid elimination from the body. In principle, two basic carrier systems, viral (adeno- and retrovirus) and non viral for DNA delivery are under development. The limitations of viral vectors, in particular their relatively small capacity for therapeutic DNA, safety concerns, difficulty in targeting to specific cell types have led to the evaluation and development of alternative vectors based on synthetic, non- viral systems. Cationic liposomes and polymers have been accepted as effective non- viral vectors for gene delivery with low immunogenicity unlike viral vectors. The development of self-assembling vectors for DNA delivery is based on synthetic block copolymers. The new convenient method for the synthesis of water-soluble block copolymeric carriers of polyethylene glycol (PEG) and copolymer of acidic amino acids such as aspartic acid and glutamic acids and a naturally occurring DNA binding cation spermine has been proposed as an effective gene delivery vector. It was prepared by the direct polycondensation in ionic liquid. The mixture of ionic liquid and triphenyl phosphite was used as both solvent and condensing agent. To prevent the formation of poly aspartic acid the amino group used was N-BOC protected. So after the polycondensation reaction the BOC group was deprotected using 50% (v/v) TFA/DCM mixture. The product was easily dispersed in water so the de protected group and the remaining unreacted solvents were removed washing with ethyl acetate. Since the spermine and amino acids contain free secondary and primary amino groups respectively, the product formed was a cationic polyamide. The cationic polyamides from aspartic acid and spermine(AS-SP) and glutamic acid and spermine(GL-SP) were characterized using IR, NMR and molecular weights were determined using MALDI-TOF. The peak at 1714 cm⁻¹ and 1659 cm⁻¹ shows the presence of primary amide group. And the peaks at 3417 cm⁻¹ and 3208 cm⁻¹ shows the presence of primary and secondary amines respectively. The cationic polyamides formed are hydrophobic and to make it hydrophilic it was coupled with PEG-2000 using ionic liquid as solvent. The use of PEG for this purpose is attractive since PEG polymers are hydrophilic, safe cheap and do not interact with plasma components. This block copolymer micelle was used to condense plasmid DNA and its physicochemical properties were studied using IR, AFM, and SEM.

Synthesis of nanosilver from aqueous solutions for anti-bacterial applications

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Metals including silver, copper and zinc are known for their antibacterial action. Nanosilver, due to its large surface area and high activity, is promising for antibacterial applications in drinking water dis-infection, wound dressing and so on. Although, various nonaqueous-based synthesis methods for preparation of colloidal silver by different capping agents have been reported, aqueous-based synthesis routes are very limited due to difficulty in obtaining the silver nanoparticles and stabilizing them. In the present work, we present the synthesis of pure silver nanopowders from aqueous precursors. Powders with size ranging from 30-80 nm have been prepared by changing the process conditions. These powders have been characterized by XRD, SEM, TEM, XPS, FTIR and UV-Visible photometry to know structure, morphology, bonding and surface chemistry. The nanosilver showed very good antibacterial activity against E. coli.

The antibacterial properties of these powders and nano silver coated ceramic filter candles will be discussed. Under collaboration with Byraju foundation 100 filter housings were successfully installed in 25 Health centers at various villages adopted by Byraju foundation. The antibacterial test of the filtered water was done by H₂S vial test method in the past six months and the antibacterial performance has been proven to be stable till date.

One-Pot Synthesis of Amine-Functionalized Monodisperse Magnetite Nanoparticles for Biorecognition

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Amine functionalized water soluble monodisperse magnetic iron oxide nanoparticles are excellent candidate for many importance application. The development of facile method to synthesis of functionalized (coupled with amino or carboxylic group) monodisperse magnetic nanoparticles and their water solubility is still challenging steps in biological and medical fields, such as magnetic resonance (MR) imaging contrast agents, targetable drug carries, hyperthermia inducing agents and magnetically controlled media for sensitive separation and detection of biomolecules. Specifically, in the detection of biomolecules, the size of the nanoparticles should be comparable to the size of biomacromoleules; in the capture of cell, the size of the nanoparticles should be 8 to 10 nm in diameter. This kind of magnetic nanoparticles might provide the highest possible selectivity and sensitivity.

Herein we report on the development of a facile one-pot method for the direct preparation of amine-functionalized water soluble monodisperse magnetite nanoparticles by using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ as a single iron source. The monodisperse magnetic nanoparticles are functionalized with amino group in the one-pot synthesis process, which make them water soluble and able to conjugate with biomolecules and cut short the complicated, time-consuming procedure for the functional modification of the surface for biological application. The amine group terminated magnetic nanoparticles make them convenient for the use in biological and biomedical applications. To the best of our knowledge, this is the first report on the direct synthesis amine functionalized monodisperse magnetite nanoparticles less than 10 nm in diameter. As synthesized amine-functionalized monodisperse magnetite nanoparticles are highly crystalline and water soluble. By controlling the reaction time and concentration of the amine terminated capping ligand, size can be tunable from 6 nm to 20 nm. The as-synthesized amine functionalized monodisperse magnetite nanomaterials were characterized by TEM, XRD, and FTIR measurements. Their magnetic properties were also studied by using a vibrating sample magnetometer (VSM) at room temperature. Work on coupling of various biomolecules such as nucleotides, protein and peptides to monodisperse magnetite nanoparticles is underway.

Aggregated CdS Quantum Dots: Host of Biomolecular Ligands

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In this contribution, we have studied structural and photophysical properties of aggregated CdS quantum dots (QDs) capped with 2-mercaptoethanol in aqueous medium. The hydrodynamic diameter of the nanostructures in aqueous solution was found to be ~160 nm using dynamic light scattering (DLS) technique, which is in close agreement with atomic force microscopy (AFM) studies (diameter ~150 nm). However, the UV-VIS absorption spectroscopy, powder X-ray diffraction (XRD) and transmission electron microscopy (TEM) studies confirm the average particle size (QD) in the nanoaggregate to be 4.0 ± 0.5 nm. The steady-state and time resolved photoluminescence studies on the QDs further confirm preservation of electronic band structure of the QDs in the nanoaggregate. In order to study the nature of the nanoaggregate we have used small fluorescent probes, which are widely used as biomolecular ligands (2,6-p-toluidinonaphthalene sulfonate (TNS) and Oxazine 1) and found the pores of the aggregate to be hydrophobic in nature. The significantly large spectral overlap of the host quantum dots (donor) with that of the guest fluorescent probe Oxazine 1 (acceptor) allows us to carry out Förster resonance energy transfer (FRET) studies in order to estimate average donor-acceptor distance in the nanostructure and found to be ~25 Å. The quantum dot aggregate and the characterization techniques reported here could have implications in the future application of the QD-nanoaggregate as host of small ligand molecules of biological interest.

Impact of Zinc Oxide and Hydroxyapatite Nanoparticles on cytotoxicity and cellular adhesion on Microbes

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The present investigation is focused on preliminary studies of biocidal effects of zinc oxide (ZnO) and hydroxyapatite nanoparticles on prokaryotic and eukaryotic microorganisms such as *Escherichia coli*, *Salmonella typhi*, *Pseudomonas aeruginosa*, *Klebsiella pneumonia*, *Staphylococcus aureus*, *Bacillus stearothermophilus*, *Enterococcus lecalis* and *Candida albicans*. Both nanoparticles are known to be biocompatible and are potential reinforcements for biomatrices. They also have potential value in regulating the biocompatibility and cellular adhesion of tissue engineering scaffolds. Towards this effect, bactericidal tests were performed on solid agar plates and liquid system with different concentrations and sizes of nanoparticles. Growth studies measured the influence of varying concentrations and sizes of the nanoparticles on microorganisms. Scanning Electron Microscopic analysis of bacteria thin sections were used to study biocidal action and cellular adhesion of these nanomaterials.

Nanobiocomposite glucose biosensor based on nanohybrid of self assembled gold nanoparticles over single walled carbon nanotubes

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Nanocomposites that utilize carbon nanotubes (CNTs) and polymers are of particular interest now a days. The presence of enclosed nanoparticles in carbon nanotubes (CNTs) is known to alter the CNT properties, making feasible several promising applications (catalysis, semiconductor devices, contrast agents in magneto resonance imaging, etc.). The use of gold nanoparticles and carbon nanotubes as building blocks to design new materials seems very appealing because of the possible electronic interactions between the two components and on the same time the potential organization of the nanoparticles in one-dimension. Attaching gold nanoparticles (GNP) to nanotube is of great interest for obtaining GNP/CNT hybrids. CNTs have been suspended in Nafion, which were used to modify the electrode for the development of an amperometric biosensor for glucose.

The direct electron transfer of enzymes with electrodes can be applied to the study of enzyme-catalyzed reactions in biological systems. However, the electroenzymatic activity of the entrapped enzyme strongly depends on the chemical and physical properties of the immobilization matrix. Enzyme-modified electrodes provide a basis for constructing biosensors, biomedical devices, and enzymatic bioreactors. The combination of nanometer materials and biomolecules is of interest in these fields, because nanoparticles can play an important role in immobilization of biomolecules due to their large specific surface area, excellent biocompatibility and good conductivity. The gold nanoparticles immobilized with carbon nanotubes can act as tiny redox centres and facilitate electron transfer. In our work, GOx was selected as a model enzyme because it has been well studied, and is inexpensive, stable and practically applicable.

Based on these investigations, as a first approach we take advantage of self-assembly of gold nanoparticles on carbon nanotubes by a simple method to obtain new nanohybrid materials. Glucose oxidase (GOx) was covalently attached to the SWNT/GNP hybrid to develop biosensor. SWNT/GNP/GOx nanohybrid was suspended in Nafion, a perfluorosulfonated polymer, to prepare nanobiocomposite. Such an operation eliminates the need for permselective membrane barrier or artificial electron mediators thus greatly simplifying the sensor design and fabrication. On the basis of cyclic voltammetry and electrochemical impedance investigations, we demonstrated that SWNT/GNP/GOx nanohybrid was successfully immobilized on the surface of GC electrode, and the electron transfer of the system was promoted by incorporation of the nanohybrid nanobiocomposite. The resulting electrode exhibited excellent electrocatalytic response towards the oxidation of glucose. The performance of the biosensor with respect to selectivity, linear range and sensitivity for the determination of glucose will be discussed.

Development of an instrument combining optical nanomanipulation with single cell electrophysiology to study cell membrane remodeling

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We have combined optical nanomanipulation technique with single cell electrical recording and ratiometric imaging of extra-cellular calcium release to investigate the role of calcium influx and membrane potential in the remodeling of cell membrane tension. Depolarization in smooth muscle cells induces an inward calcium influx, thereby increasing intracellular calcium leading to muscle contraction. It is expected that the cellular contraction should result in the remodeling of cell membrane tension. We have observed that depolarization induced by high extra-cellular KCl increased [Ca] as determined by Fura-2 imaging, in A7R5 smooth muscle cells. Epithelial HeLa cells used as control do not show [Ca] increase. Using the apparatus developed for simultaneous measurement of membrane tension and [Ca] release, we have attempted to decouple the role of depolarization and calcium leading to smooth muscle contraction. Implications of our results are further discussed.

PLENARY LECTURES

Tuning Nanotubes and Graphene

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Graphene-a two dimensional monolayer of carbon atoms is the most recent addition to the family of low-dimensional carbon, namely nanotubes and fullerene. Like in nanotube, Raman fingerprinting of Graphene is unique. Our talk will discuss our recent Raman experiments on Graphene and Single-walled carbon nanotubes. We will present measurements related to strong electron-phonon coupling in these low dimensional systems originating in Kohn-Anomaly.

How do nanocrystals grow: Understanding the bottom-up approach using time-resolved techniques

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It is now well understood that the bandgap, and consequently associated electronic and optical properties, of semiconducting nanoparticles can be tuned by varying the size due to quantum confinement effects. Colloidal methods constitute an important class of synthesis of such nanoparticles due to their high degree of flexibility, providing easy control over the average size. More than the average size, the entire size distribution function, controls the properties of such samples. This method of synthesis depends basically on controlling the reaction process leading to the formation of the semiconductor in a solution by controlling various factors like temperature and concentration. The primary difficulty of this method is the strong interplay between various factors in a way that is very little understood; however these very processes control the size along with the size distribution of the generated particles. Thus, the techniques of synthesis of high quality nanocrystals, indicated by the ability to grow a pre-defined size with a narrow size distribution, have remained largely in the realm of empiricism. Obviously there is a need to understand the mechanism of the growth process of the nanocrystals, though very little is known about it in such a complex reaction, often carried out in presence of a capping agent. We employ already established state-of-the-art techniques as well as a few novel approaches to study in real time the growth kinetics of a host of semiconducting materials to unravel a wide range of unexpected behaviours. We show that such studies help us to design routes to rational synthesis of high quality samples for possible device applications.

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Work based on:

1. R. Viswanatha and D. D. Sarma, Study of growth of capped ZnO nanocrystals: a route to rational synthesis, *Chem. - A European J.* 12, 180 (2006).
2. R. Viswanatha, H. Amenitsch and D. D. Sarma, *J. Am. Chem. Soc.* (accepted for publication in 2007).
3. R. Viswanatha et al., unpublished results.

SESSION D1

Magnetic phases in transition metal doped ZnO and Ni based nanoparticles

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We have investigated ground state magnetic properties and optical band gap of chemically synthesized Fe, Co, Mn doped ZnO Diluted magnetic semiconducting nanoparticles ($\sim 7 - 20$ nm). The strong irreversibility between zero field cooled (ZFC) and field cooled (FC) $M(T)$ curve is observed in the low temperature regime for Zn-Fe-O nanoparticles. The cusp like anomaly is observed in ZFC curve at freezing temperature (T_f) well below irreversibility temperature (T_m). The strong hysteretic $M(H)$ loop is observed at the temperature of 5 K with $H_c = 130$ Oe and $M_r = 1.94$ Bohr magneton / Fe^{+2} ion. The magnetic behaviour of Fe doped sample is very similar to a cluster glass phase where the clusters are strongly interacting and they undergo random dipolar inter cluster interactions, giving rise to strong competitive ferromagnetic and antiferromagnetic interactions, finally leading to freezing of those clusters. The ground state phase of Mn and Co ZnO DMS nanoparticles are observed to be antiferromagnetic like having non-saturating tendency of $M(H)$ even at a field of as high as 5 Tesla. The optical band gap of the DMS nanoparticles are estimated using recorded UV-Visible absorption spectra.

Further a comparative study of the structure and magnetic properties of ultrafine Ni nanoparticles prepared by the chemical reduction of $NiCl_2$ solution of four different concentrations has been carried out. The concentration of the $NiCl_2$ solution has a profound influence on the room temperature (300 K) magnetic state of the resulting Ni nanoparticles, even though all four samples show the same XRD pattern i.e., have the same crystal structure (tetragonal as proposed by us). It is found that samples obtained from lower concentration solutions (0.1M and 0.5M) show a linear response with magnetic field while those obtained from higher concentration ones (1M and 2M) are ferromagnetic at 300 K. This difference in magnetic behaviour has been explained on the basis of dipolar interactions between particles, which are strong in the higher molarity samples but comparatively weak in case of lower molarity ones. The proposition is further strengthened by the irreversibility in the field cooled (FC) and zero field cooled (ZFC) curves which, in the case of 1M and 2M samples, starts right from the measuring temperature of 390 K, clearly hinting at the blocked state of the particles and therefore to their ferromagnetic response at 300 K. An intriguing feature in the form of a sharp peak at 20 K is observed in the FC and ZFC curves of all samples, signaling some kind of transition. Appreciably high magnetization values are also seen in the $M-H$ plots at 5 K. We attribute this to the hitherto frustrated spins in the unit cell of tetragonal Ni, becoming frozen below 20 K and then getting aligned perfectly collinearly on application of magnetic field.

Synthesis, Characterization and Application of Nanometric metallic alloys

Indranil Manna

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Part I: Evolution of Amorphous/Nanocrystalline Microstructure in Al-based Ternary Alloys by Mechanical Alloying

In the proposed talk, the genesis of complete/partial solid-state amorphization of these alloys by high-energy planetary ball milling will be presented.

Dispersion of nano-intermetallic phases in amorphous matrix may be achieved either by continued milling or by subsequent controlled annealing. The identity and sequence of phase evolution have been monitored by x-ray diffraction, high-resolution transmission electron microscopy and differential scanning calorimetry. The microstructural evolution during mechanical alloying follows a complex and interdependent sequence of grain refinement, mutual dissolution (alloying), nanocrystallization and/or amorphization. The genesis of solid-state amorphization or nanocrystallization has been investigated by positron annihilation spectroscopy and nuclear magnetic resonance. Thermodynamic calculations based on modified-Miedema approach allow determination of appropriate composition range for complete/partial amorphization. Both kinetic and thermodynamic factors play a significant role in determining the final microstructure comprising nano-intermetallic and amorphous phases. Subsequently, we have evaluated mechanical property of the composites after compaction and sintering under special conditions of warm torsional compaction and found the mechanical properties quite encouraging. Thus, it appears that the present approach may be useful in developing high specific strength Al-based amorphous and nano-intermetallic dispersed amorphous matrix composites.

Part II: Nano-PARTICLE Dispersed Water/E-glycol Based Nanofluid for Advanced Heat Transfer Applications

We have made a systematic effort made to develop and characterize nanometric metallic ($\text{Al}_{70}\text{Cu}_{30}$ and $\text{Al}_{70}\text{Ag}_{30}$) and ceramic (Al_2O_3 , TiO_2 , ZrO_2) particles dispersed (in very low volume fraction) water and ethylene glycol based nanofluids and carry out suitable measurements of thermal properties of the nanofluid (conductivity and heat transfer coefficient). The as-received powders were characterized by XRD and TEM (phase analysis, grain size determination), DLS and BET (determination of particle size and distribution) and EDS (compositional analysis). Thermal conductivity of the base fluid and nanofluid was measured using an indigenously developed thermal comparator set up. The measurements, calibrated using standard heat transfer fluid, showed up to 200% increase in conductivity ratio. Heat transfer coefficient, measured through closed loop tube-in-tube heat exchange experiments for evaporator assembly, recorded 5-10 % increase with only 0.1-0.2 vol.% loading of nanoparticles.

Growth and characteristics of semiconductor nanostructures for optoelectronic devices

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We studied the growth of Ge islands on silicon and silicon dioxide matrix by r.f magnetron sputtering with variation of deposition time and temperature. Atomic force and transmission electron micrographs revealed the formation of Ge islands on Si and within SiO₂ matrix, respectively. Infrared and X-ray photoelectron spectroscopy were used to study the chemical bonding in the deposited films. Photoluminescence study has been performed at room temperature to detect the light emission from Ge nanocrystals due to quantum confinement. The optical properties of Er³⁺-doped glass containing Ge nanocrystals prepared by sol-gel technique have also been studied. Ge nanocrystals of size about 5-10 nm have been observed through TEM microscopy. The origin of several absorption peaks has been attributed to the transition from Er-⁴I_{15/2} ground state to different excited states. Room temperature photoluminescence spectra exhibit enhanced emission at 1.54 μm for Er-doped glass with Ge nanocrystals, the origin of which is attributed to energy transfer from Ge excitons to Er ions.

CdS nanowires have been grown successfully into porous alumina template by a simple chemical reaction process in a two-compartment cell. AFM, SEM and TEM micrographs revealed the growth and morphology of the nanowires. The diameter of the nanowires deposited into two different porous templates is measured to be 50-60 nm and 100-110 nm. Selected area electron and X-ray diffraction patterns show the growth of polycrystalline nanowire in hexagonal phase. UV-visible spectra revealed a clear blue shift in the absorption edge and resultant increase in band gap to 2.6-3.0 eV as compared to the bulk value of 2.53 eV. The resonance Raman scattering spectrum indicates the growth of stoichiometric CdS nanowires with good crystalline quality.

Soft Lithography and Nanopatterning

Convener: S Chandrasekaran

Unit on Nanoscience and Nanotechnology
Indian Institute of Science
Bangalore

The project on soft lithography envisages the formation and use of soft matter for various applications. This includes biomolecules, organic thin films, polymers etc. In the area of polymeric materials, nanocomposites of metals and semiconductors in polymer matrices (example, PMMA) have been used to monitor the phase transformations in polymers. Bile acid –based organo- and hydro gels with nanoparticles have also been investigated. Liquid crystal-gold composites have been investigated for their electrical conductivity and dielectric behaviour. The formation of droplets during pulsed laser deposition is of concern in the formation of thin films. The system containing $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ (LSCO) on LaAlO_3 (LAO) substrate has been studied. There is a tremendous interest in the last one-year to study a single, bilayer and n-layers of graphene, which can be prepared by mechanical exfoliation method. We have recently carried out Raman studies of these systems to understand the high frequency phonons. Results are being understood at present.

The results pertaining to the above studies from different groups at the Indian Institute of Science will be presented and discussed.

Three major equipments have been sanctioned in this phase of the project. (1) NSOM (Near field scanning microscope), (2) Kelvin probe microscope and (3) Langmuir Blodgett trough with Brewster angle microscope. The NSOM has been procured and installed already. Initial experiments have been performed on graphenes and polymeric materials. Kelvin probe microscope has been just procured and is in the process of getting installed. Brewster angle microscope with LB trough will be procured as soon as possible.

Nanoscience at IISc: 2002-2005

Convener: S Chandrasekaran

Institute Nanoscience Initiative
Indian Institute of Science
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The Nanoscience Program initiated by the DST has, in the first phase, sanctioned three major equipment to the Indian Institute of Science, Bangalore. These are (1) Optical Tweezers; (2) Scanning Probe Microscope; and (3) SEM with a writing facility. All the three equipment have been installed and are in good working condition.

We (A.K.Sood, Physics) have designed a dual optical trap setup around a microscope by coupling two split beams from a 1064 nm Nd:YVO₄ laser. We have performed experiments with samples like polystyrene beads, carbon nanotubes, ZnO nanorods and some biological samples like bacteria, RBC etc. The single wall carbon nanotubes when dispersed into very small bundles are very difficult to trap as the interaction of the SWNT bundles with the strongly localized electric field is very weak due to very small size and less dielectric contrast. Inorganic nanorods were also manipulated using point and line tweezers.

The SPM has been used by twenty different research groups across various departments. The students have been trained to use the equipment and are using independently.

Studies on self assembled monolayers (S. Sampath, Department of Inorganic and Physical Chemistry). Self assembled monolayers based on sulphur and selenium containing compounds have been assembled on gold and silver surfaces. SAMs based on silanes on alumina have also been studied. The interfacial solvent structures have been followed by AFM. The silane monolayers have been used to understand the thermal stability related to tribological properties. Bimetallic and alloy nanoparticles have been used to follow single electron charging events.

Imaging of biomolecules and biomolecular complexes by immobilizing them on Self-Assembled monolayers of fatty acid salts (Dipankar Chatterji, Molecular Biophysics Unit,). In this experiment, a novel way of immobilizing and imaging an enzyme using Langmuir Blodgett (LB) film as a substrate has been developed. The NiA LB films are characterized using contact angle measurements, surface pressure-area isotherms and Atomic Force Microscope (AFM). The immobilized RNAP molecules are imaged using Intermittant Contact AFM.

Our (P S Anil Kumar, Physics) motivation for optimizing the e-beam lithography technique is to make Magnetic Random Access memory (MRAM) devices. These MRAM devices are the next generation memory storage technology which has a potential to replace the existing memory elements as it is having added advantages.

Electron Microscopy of Nanostructures: Facility buildup and applications**K. Chattopadhyay**Institute Nanoscience Initiative
Indian Institute of Science, Bangalore 560012

This presentation will detail the progress achieved in setting up a state-of-the-art facility for electron microscopy at the Indian Institute of Science. This will include the difficulties we have faced and successes we have achieved in this venture with generous support from Department of Science and Technology. The experiences gained in running a common multi-user facility as well as its current status will be elaborated. We shall also present a bouquet of various results obtained using this facility. Finally, we shall present results obtained on a specific problem of characterization of two-phase nanoparticles using this microscope.

Growth and Characterization of Gallium Nitride and its alloys

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Theoretical investigations have been carried out on the nucleation of ternary compounds ($\text{In}_x\text{Ga}_{1-x}\text{N}$ and $\text{Al}_{1-x}\text{Ga}_x\text{N}$) on GaN substrates using classical heterogeneous nucleation theory. The amount of stress induced supercooling / superheating due to lattice mismatch between the ternary alloy and GaN substrates has been calculated numerically. The lattice mismatch between the $\text{In}_x\text{Ga}_{1-x}\text{N}$ ternary alloy and GaN has been calculated numerically and incorporated into the expression for stress induced supercooling for various values of interaction parameters. Chloride – VPE system has been established for the growth of GaN and high quality layers have been grown under optimized condition. GaN MIS structures Ti/BaTiO₃/GaN have been fabricated and excellent results have been obtained. Ti/GaN, Pd/GaN Schottky diodes have also been fabricated and extensive investigations have been carried out.

GaN nano-wires have been grown on (0001) sapphire substrates. 5 N purity metal gallium and GaN powder and Boron trioxide were made to react by passing ammonia gas and nano structures of GaN have been obtained. Experiments have been carried out at different growth temperatures and also by varying the proximity conditions of the substrate. GaN samples were characterized by X-ray diffraction technique, which shows wurtzite structure of GaN. SEM image show the nanostructures and the dimensions of the nanowires are around 60 – 80 nm. Raman studies show vibrational modes at 432 and 644 cm^{-1} and they are attributed to Manganese incorporation in the GaN nanostructures. These results have been observed for the first time and reported. EPR measurements show the ferromagnetic properties of the Mn doped GaN nanowires.

40 MeV Li^{3+} ions irradiations were carried out at room temperature and low temperature on 3 μm thick n-GaN epilayers grown by Metal Organic Chemical Vapour Deposition technique on sapphire substrates. XRD results of Irradiated samples reveal Gallium oxide formation, which is due to GaN/ Al_2O_3 interface mixing upon ion irradiation. AFM images of GaN show uniform nano tracks formation on the GaN surfaces. The nano tracks dimension is around 80 nm. PL measurements show blue shift after irradiation at low temperature.

Gallium nitride epitaxial layers have been grown on Sapphire substrate using vapour phase epitaxy, pulsed laser deposition and metalorganic vapour phase epitaxy (MOCVD). The grown layers were characterized by photoluminescence, X-ray rocking curves, Raman spectroscopy and Time resolved Photoluminescence. The electrical characteristics of the GaN were measured using I-V and C-V on Schottky contacts. The GaN samples were also irradiated using high-energy ion beam (Sn^+). The structural characteristics of the pristine and irradiated samples were analysed in detail. Metaloxide Semiconductor High Electron Mobility Transistors (MOSHEMTs) using AlGaIn/GaN were fabricated and studied in cooperation with Nagoya Institute of Technology, Japan.

Engineering Structures with Nanoscale Materials

Arun Chattopadhyay

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The Centre for Nanotechnology at IIT Guwahati emphasizes on both the theoretical and experimental aspects of nanoscale science and technology. There are several research programmes that are currently running with the aim of generating newer nanoscale materials; development of alternate forms of lithography for integrating these materials and works toward fabrication of devices for potential applications. Some of the ongoing works are exemplified below.

Based on the recent development in our laboratories, we are currently pursuing the generation of polymer-metal nanoparticle composites for potential use as pH and temperature sensors. The sensor designs are based on the photoluminescence and colloidal properties (such as aggregation and optical extinction) of the composites. We have also incorporated both catalytic and sensor properties in order to have multifunctional components in a single device structure. Further, efforts are being placed on generating polymer-metal nanoparticle composite where the electroluminescent and photoluminescent properties of the polymer could be changed by incorporation of metal nanoparticles.

We have recently developed a scheme combining top-down and bottom-up approaches in generating patterned CdS quantum dots (Qdots) in polymer film. We have also developed a method in systematic organization of colloidal nanoparticles and molecular materials into two-dimensional arrays of functional materials. Interestingly, we observed that chemical reactions could be carried out on the surface in order to generate systematic patterns with Qdots.

The Centre for Nanotechnology is pursuing extensive works on nanobiotechnology with a multidisciplinary approach. For example, it has been recently discovered that Au NPs can be generated by reduction of HAuCl₄ using pure enzyme as the reducing agent. These Au NP incorporated enzymes have higher biocatalytic properties than pure enzymes. In addition, currently research works are being pursued on the potential of combination of traditional gene therapy and nanomaterials to have superior medical benefit. Further, we are working on understanding the mechanism of bacteriostatic and bactericidal properties of Ag NPs.

Finally, we have recently developed electrochemical actuators consisting of dendritic assembly of nanoscale metallic structures. These dendritic fibrous structures, grown in aqueous solution, can be actuated by an external electric field or magnetic field. Systematic development of nanoscale machines with external control is the ultimate aim in this respect.

SESSION E1

**NANOFUNCTIONAL MATERIALS
(OPTICAL, MAGNETIC, SENSOR APPLICATIONS ETC.)**

Time Resolved Spectroscopic Studies on Some Nanophosphors

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Time resolved spectroscopy is an important tool for studying energy and charge transfer processes, coupling of electronic and vibrational degrees of freedom, vibrational and conformational relaxation, isomerisation, etc. It employs very short pulses of high-energy radiation like UV, laser etc, which can be spectrally tuned as per the electronic transitions of the material to be studied.

ZnS, ZnO and (Zn,Mg)O nanophosphors have been investigated with respect to time resolved photoluminescence decay. The decay of undoped and doped ZnS nano phosphors have been studied both in powder as well as thin film form. Photoluminescence (PL) of ZnS nanophosphors typically exhibit a purple/blue emission peak termed as self activated (SA) luminescence and emission at different wavelengths arising due to impurities. PL decay of both SA and impurity related emission of ZnS nanophosphors indicate slower decay for the impurity related luminescence compared to SA luminescence. The lifetimes obtained from decay curves range from ns to ms level and also suggest the radiative recombination path involving donor acceptor pair recombination or internal electronic transitions of the impurity atom.

Steady state and time resolved photoluminescence (PL) spectroscopic characteristics of thin films of ZnMgO nanophosphors are investigated next. A series of ZnMgO nanophosphor thin films with varied Zn: Mg ratios were prepared by chemical bath deposition in solution. Photoluminescence (PL) excitation and emission spectra exhibit variations with changing Mg ratio with maximum PL output produced by a sample with 100:25 as Zn: Mg ratio. Time resolved PL decay measurements at peak emission wavelength were done. Luminescence lifetime of the order of few nanoseconds and as short a lifetime as 10^{-10} sec was observed for ZnO and ZnMgO (100:10) nanophosphors. With increasing Mg ratio, PL decay shifts into microsecond range. Times resolved PL of ZnMgO nanophosphors in the composition range 100:10 to 100:30 could be fitted into biexponentials and have two decay times on the order of 7 μ s and 20 – 70 μ s.

ZnO and ZnMgO alloys up to 50% Mg were prepared and studied as powder by solid state mixing and sintering at high temperature in reducing atmosphere. X ray diffraction showed hexagonal ZnO structure with small signature of MgO, which increased with increasing Mg content. Particle size estimated from Scherrer formula was in the range of 40 nm. Photoluminescence (PL) studies showed excitation peak around 290 nm (4.3 eV) and 350 nm (3.5 eV). Pure ZnO nanophosphor showed emission peak around 508 nm, which blue shifted with increasing Mg content. Time resolved decay of PL indicated decay time in the microsecond time scale. Optical absorption spectra showed bandgap about 5.6 eV for ZnMgO nanophosphor with 50% Mg content.

Study on Nanomaterials

S. N. Kaul, C. Bansal, C. S. Sunandana, M. G. Krishna, K. C. James Raju, A. C. Abhyankar, G. A. Basheed, A. K. Mishra and D. Bharathi Mohan

School of Physics, University of Hyderabad, Hyderabad – 500 046

A detailed comparative study of polycrystalline (p-) and nanocrystalline (n-) Ni_3Al revealed that (i) long-range ferromagnetic order in p- Ni_3Al disappears in the nanocrystalline at a particle size ≈ 50 nm and a strongly exchange-enhanced paramagnetic susceptibility is seen. (ii) In the nanocrystalline state, the density of states at the Fermi level and the effective magnetic moment per Ni atom in the paramagnetic state reduce by nearly 20%, and (iii) non-Fermi liquid behaviour in n- Ni_3Al at low temperatures gives way to d-wave superconductivity (induced by antiferromagnetic spin fluctuations) at $T < 3.9$ K.

Annealing melt-spun amorphous ribbons of nominal composition $\text{Fe}_{73}\text{Cu}_1\text{Nb}_3\text{Si}_{16}\text{B}_7$, in a magnetic field (H), develop uniaxial magnetic anisotropy with easy axis along H and exhibit several novel attributes. The samples are nanocomposites consisting of ferromagnetic nanocrystalline grains embedded in a ferromagnetic amorphous matrix and possess a magnetic permeability as large as 150,000. Magnon-magnon interactions are important in the thermal renormalization of the spin wave stiffness, the origin of 'in-plane' anisotropy field and the characteristic magnetic length.

Electronically tunable properties of nanoporous Au-Fe alloys were investigated. The conductivity, magnetization, and strain were observed to change reversibly with addition and removal of charge. Nanocluster assembled Cu and Ag films were also synthesized by inert gas condensation and their temperature dependent dc resistivity behavior was studied in the range 23K-293K. The cluster size dependence of resistivity was analyzed in the framework of the Bloch-Grüneisen model. The results show a temperature independent residual resistivity contribution and a temperature dependent contribution with a substantial change in Debye temperature with cluster size

Ultrathin Ag films (<10 nm thick) produced by either thermal evaporation or RF sputtering are quasi-continuous and reveal plasmonic resonances (both bulk and surface) and upon brief iodization one sees a gradual decay of plasmons and a progressive evolution of excitonic features characteristic of wurtzite AgI nanospheres/rods/plates. Metal Induced Lateral Crystallization (MILC) of amorphous Si (a-Si) films has been investigated and will be reported at this meeting.

The effect of grain size and film thickness on the microwave dielectric properties of nanostructured oxide thin films such as sputtered TiO_2 , ZrO_2 and BST has been studied. The X-band microwave (8-12 GHz) dielectric properties of these films were determined using the extended cavity perturbation technique. A correlation between the observed variations and the processing parameters will be presented.

Linear and Nonlinear Optical Studies of Metal/Organic Nanoparticles and Ultrathin Films

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(Co-investigators : D. Narayana Rao, School of Physics, University of Hyderabad & E. D. Jemmis, Inorganic and Physical Chemistry Unit, Indian Institute of Science)

We have developed a simple and environmentally benign methodology for the fabrication of metal nanoparticle- embedded polymer films; particle generation is carried out in situ without additional reducing agents and leads to free-standing as well as supported films. The fabrication protocol facilitates direct imaging of the nanoparticle-embedded film by electron and scanning probe microscopies, without the need for microtoming. The size and shape of metal nanoparticles can be fine-tuned by controlling the concentration and thermal annealing parameters. The metal nanoparticle-embedded polymer films exhibit efficient optical limiting at nanosecond and femtosecond time scales. Potential antimicrobial and catalytic activities are under investigation.

Polyelectrolyte templating is shown to be an effective strategy to stabilise nonlinear optical chromophore based Langmuir-Blodgett (LB) films against molecular aggregation under laser irradiation and thus prevent the degradation of the second harmonic generation (SHG) capability of these films. The methodology is of general utility in addressing the inherent structural instability of LB films. Polyelectrolyte templating is also found to have profound impact on the formation and stability of multilayer LB films. Optimal choice of the template leads to stable multilayer ultrathin films of a hemicyanine based amphiphile showing enhanced SHG response.

Fabrication of molecular nano/micro crystals and their size-dependent photophysical attributes is another area we have explored. Detailed investigations on a zwitterionic molecule led to the correlation of the observed effects with molecular assembly patterns revealed through crystallographic investigations on single crystals and computational modeling. We have proposed a new paradigm to visualise the size-dependent optical properties of molecular nanocrystals based on the concept that the range of intermolecular interactions of varying strength accumulate in a step-wise manner, as the rigidity of the crystals increases with size. The interesting phenomenon of a molecule showing strong blue fluorescence in the solution, nano/microcrystal and bulk solid states has been investigated recently.

Study of Photoconductivity and Photoluminescence of Certain Nanostructured Materials

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Nanoparticles of CdS, ZnO, PbS, CaWO₄ and PbMoO₄ of different grain sizes and ZnS of one grain size are synthesized through chemical precipitation technique. The nanoparticles of CdS are subjected to heat treatment at low temperature (150°C) for different time duration to study the effect of heat treatment on the properties of the sample. Also, nanostructured CdS films are prepared by chemical bath deposition (CBD) technique. Attempts are being made to prepare nanostructured films of ZnS through CBD technique and films of ZnO by RF magnetron sputtering. X-ray diffraction is used to study the crystal structure of the samples and to determine the average grain size employing Scherrer's formula after correction for the strain broadening using Hall-Williamson's analysis. HRTEM analysis of the samples is carried out to determine the particle size/grain size. Lattice contraction experienced by different planes of the nanoparticles is estimated using the XRD peak positions as well as from the HRTEM micrographs. The absorption spectra of the nanoparticles as well as film samples are recorded and analyzed. The absorption edges of the samples CdS, ZnS, ZnO and PbS are found to be blue shifted compared to the absorption edge of the corresponding bulk crystals indicating quantum confinement effect. The nanoparticles of ZnO of the smallest size of ~ 8 nm also show blue shift of the absorption edge even though this size is much more than the exciton diameter for ZnO. The grain sizes of the nanoparticle samples are calculated using Brus formula based on effective mass approximation and are compared with the sizes obtained from XRD and HRTEM analyses. The absorption spectra of nanoparticles of PbMoO₄ and CaWO₄ are also analyzed. Raman spectra of the nanoparticle samples of CdS, ZnS, ZnO, and PbMoO₄ are recorded and interpreted. FTIR spectra of nanoparticles of some of the samples are recorded and the effect of the nanosize of the particles on the spectra are studied. The FTIR spectra of the samples are also analyzed based on theory of average dielectric constant. Photoluminescence spectra of nanostructured samples of different grain sizes are recorded and studied systematically. Microhardness of pellets of nanoparticles of PbMoO₄ and CaWO₄ of different grain sizes is measured using Vicker's indentation method. The effects of heat treatment of the nanoparticles of CdS at low temperature for different time intervals on their crystal structure, UV-Vis, photoluminescence and Raman spectra are systematically investigated. X-ray diffraction studies show that the CdS nanoparticles undergo partial phase transformation from cubic to hexagonal when the heat-treatment is extended to 16 hours. Detailed study of the photoconductivity of the nanostructured samples is in progress. Nanoparticles of the diluted magnetic semiconductor (DMS) Cd_{1-x}Mn_xS of different composition from x = 0 to x = 0.3 are synthesized. These particles are subjected to low temperature heat treatment for different time intervals. The structure of the particles is analyzed and the UV-Vis, photoluminescence and Raman spectra of the samples are studied systematically.

Ion beam synthesis of Nanostructures

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We have used innovative combinations of low energy and SWIFT heavy ions to create defects which act as nucleation sites for the formation of nano-particles in controllable manner in different kinds of glasses. We have used a technique in which, using single ion beam treatment parameter it is possible to gain control over the size of copper nanoparticles in fused silica and BK7 glasses. Further, we have followed the same method to form Si-nc in SiO₂. In these samples, the absorption edge shifts towards higher energies and size of the silicon nanoclusters decreases with an increase in ion beam fluence used for pre-mixing irradiation. In another work, Swift heavy ions were used to study the effects of electronic energy loss on Cu cluster formation in fused silica after post irradiation annealing. Irradiation fluences exceeding $4 \times 10^{13} \text{ cm}^{-2}$ and annealing temperatures above 1100 K are more effective in forming larger nanoclusters. In another study, we observed the variation in the absorption bandgap ranging from 1.0 to 1.6 eV in Germanium thin films deposited on pre-irradiated fused silica substrates. Cathodoluminescence measurements were performed on swift-heavy-ion irradiated and annealed Au/SiO₂/p-Si structures. 5 nm Au was deposited on 500 nm SiO₂ thermally grown on [100] oriented p-type Si wafers. It was concluded that swift-heavy-ion irradiations create E' centres in SiO₂ and annealing transforms E' centres into NOVs. As NOVs are thought to be precursors to the formation of Si-nanoclusters (Si-nc), the present study leads to the knowledge of a possible synthesis route to form Si-nc. In another study Soda-lime glass (main constituents: 72 mol % SiO₂ and 13.8 mol % Na₂O) was subjected to an ion-exchange procedure for different time interval at 330°C in a mixed AgNO₃ (2 wt%)/NaNO₃ melt. In the ion exchange substrates, Ag nano-particles were formed. Sequential implantation of oxygen and silver ions (after annealing) were used to form silver oxide nano-particles. It was shown that silver clusters in silver oxide nano-particles cause red photo luminescence at 608 nm.

SESSION D2

SYNTHESIS AND CHARACTERIZATION OF NANOMATERIALS

Deposition of Nanopowders by RF/DC Sputtering and Inert Gas Condensation Technique

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The RF/DC sputtering unit with three targets facility for sequential and co-sputtering has been installed successfully with existing ultra high vacuum chamber. This allows the preparation of nanocrystalline materials, RF/DC sputtering, in scale-up quantity. At present we are able to get around 2 gram in a single run. Cu nano particles were deposited through sputtering with a dc power of 850 W of nano-Cu (11 nm) per hour. We can go up to 1200 W safely. The design aspect of the three target sputtering gun will be discussed. Also the nanocrystalline materials SnO₂, PbF₂, ITO, ZnO doped ZnSe were prepared by inert gas condensation technique (joule heating) and characterized. ¹¹⁹Sn solid-state NMR results of nanocrystalline SnO₂ show that the IGCT prepared samples have good crystallinity and phase purity compared to the samples prepared by chemical method. Current versus voltage characteristics (I–V) of nanocrystalline SnO₂ materials have been investigated in air at room temperature. SnO₂ exhibited nonlinear I–V characteristics of the current-controlled negative resistance (CCNR) type, and that the threshold field (break down) voltage is higher for the samples prepared by the IGCT method than for those prepared by the chemical method due to the formation of a tin oxide layer over the crystalline tin. Nanocrystalline relaxor ferroelectric PMN-PT without pyrochlore phase was synthesized. It was found to have very high dielectric constant near the phase transition temperature. For the nanocrystalline ZnO doped ZnSe, the grain size dependent photoluminescence emission and microstructures were investigated.

Nanoscience and Technology : A Transdisciplinary Approach

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Early work under the above project started exploration of formation of nano-quasicrystalline materials. The first each system looked into corresponded to $Al_{70}Ni_{15}CO_{15}$ decagonal phase through high energy ball milling. The pre-alloyed $Al_{70}CO_{15}Ni_{15}$ were subjected to pull milling performed at a speed of 400rpm for 5, 10, 20 and 40 h under hexane medium with a ball : Charge ratio 20:1. The nano-phase constituents were confirmed by X-ray diffraction and transmission electron microscopy techniques. The stability of the nano-D phase in the milled powder was also investigated under various annealing treatments. After 10 h milling, the evolution of the nano-decagonal phase was observed. This nano-phase was found to be stable up to 40 h of milling. The milled powder after 40 h of milling confirms the existence of a nano-decagonal phase. The particle size of the milled powder was ~ 10-15 nm. An isothermal heat treatment of the milled sample at 500°C for 10 h still shows the existence of the nano-decagonal phase, although a coarsening of the nano-domain has been observed.

Another R & D effort under this project deals with investigations on the formation of carbon nanotubes without iron inclusions and in aligned configurations through ferrocene - ethylene pyrolysis.

The above said objectives have been achieved through optimization of growth parameters e.g. heating rate of ferrocene, pyrolysis temperature, flow rates of Ar and C_2H_4 . The optimum results relating to synthesis of CNTs without Fe inclusions correspond to : 1100°C pyrolysis temperature, heating rate of ferrocene-80°C/min and flow rate of Ar of ~ 500 sccm. The CNTs without Fe inclusions in high yield has been obtained by the pyrolysis of ferrocene at 1000°C under flow of the carrier gas Ar (~ 300 sccm) and flow of C_2H_4 (~100 sccm). Yet another requirement for CNTs synthesis is that of growth in aligned configuration. The optimum result relating to synthesis of aligned CNTs bundle has been obtained at 1000°C pyrolysis of ~ 100 sccm. These CNTs have been found to have outer diameter between ~ 20 to 60 nm and lengths between ~ 15 to 20µm. In addition to the above described CNTs, helical CNTs have also been synthesized by vapor phase pyrolysis of ferrocene at 1000°C under a flow of Ar of ~ 300-250 sccm and C_2H_4 of ~ 100 sccm. The growth of helical CNT is considered to be due to the non-uniformity of the carbon extrusion speed from the catalyst (Fe). Another area of study corresponds to grants of nitrogen bearing bamboo, carbon nanotubes. The details of nitrogen bonding with carbon in CNT will be described and discussed.

Development of Nanocrystalline Materials by Different Processing Routes

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Mechanical alloying (MA) of 11 alloys of Al-Ni-Ti system selected through Miedema's model showed that the negative enthalpies of mixing and amorphization were not reliable index for predicting the amorphization by MA in this system. Complete amorphization by MA could be achieved for the first time in a ternary Al-rich (i.e. > 80 at. % Al) Al-ETM-LTM alloys. Compaction and sintering of nanostructured $Al_{88}Ni_6Ti_6$ under controlled atmosphere with or without pressure resulted in up to 92% density and 8 GPa nanoindentation hardness.

For better stability of Al-based nanocomposite at elevated temperatures, it was attempted to generate matrix and second phase of similar lattice (fcc structure). For this nanostructured (~15 nm) $L1_2-Al_3(Ti,Zr)$ intermetallic phase of composition $Al_{75}Ti_{25-x}Zr_x$ ($x = 0-25$) was first successfully synthesized directly by MA. Nanocomposites with different volume fraction of $L1_2-Al_3(Ti,Zr)$ intermetallic of $Al_{75}Ti_{15}Zr_{10}$ composition in Al-base were produced by MA, and subsequent hot-pressing gave a density of 97% and hardness of 8.6 GPa which is higher compared to RSP product of these alloys.

Pore-free bulk Al based metal matrix nanocomposites reinforced with 2 wt.% Al_2O_3 particles of ~10 nm size, produced through casting route by other researchers, were characterized. A large increase in as-cast hardness, i.e. Hv 90 compared to Hv 20-50 of commercial Al, was observed. TEM revealed the nano-sized non-agglomerated but nonuniform dispersion of reinforcements. Cold and hot working made the particle dispersion more uniform. Cold working rapidly increased the hardness of nanocomposite to Hv 120, and the Al_2O_3 particles remained undeformed in the matrix with high dislocations density.

A dramatic decrease in the sintering temperature of elemental W from the conventional temperature of $\geq 2500^\circ C$ to the modest $1700-1790^\circ C$ was obtained by making the W powder nanostructured through high energy mechanical milling (MM) prior to sintering. The mechanical properties, viz., hardness and elastic modulus these sintered W specimens were somewhat superior to those reported for the conventionally sintered W.

Nanocrystalline Ni-Al catalysts were prepared by MA for decomposition of H_2O_2 . Pronounced catalytic activity of nano-sized metastable NiAl phase of $Ni_{30}Al_{70}$ composition demonstrated that the MM / MA can induce and markedly enhance the catalytic activity. Surface enrichment of total Ni content compared to in bulk composition was observed by XPS in all compositions of NiAl phase; but surface Ni-present only as alloyed-Ni (i.e. Ni bonded to Al) was primarily responsible for the catalytic activity. Ni-vacancies, and not the antisite defects in NiAl phase seem to promote this catalysis. For nanostructured ternary disordered NiAl (Cr) phase the catalytic activity could not be correlated to alloyed-Ni content on the surface, and here the Cr^{+3} content may have a dominant role.

Atomic Force Microcopy studies on Nanocrystalline and Glassy alloys

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The present talk would concentrate on the work carried out on the atomic force microscope (AFM) facility established from the grants of the Nano science and Technology Initiative of DST at the Indian Institute of Technology Madras. The paper will highlight the work done on Cu based nanocomposites, magnetic nanocomposites and Cu based bulk metallic glasses in order to understand the microstructural features in these advanced materials. The attempts to synthesise high strength Cu based conductors has led to the development of Cu-W and Cu-Ta nanocomposites, which have been thoroughly characterized by AFM in addition to XRD and TEM. The excellent resistance of these nanocomposites for grain coarsening on annealing at high temperatures is clearly demonstrated by the AFM studies. Imaging of the magnetic domains in the NdFeB hard magnets through magnetic force microscopy (MFM) has clearly demonstrated the potential of this tool in imaging the magnetic domains in these materials. AFM studies on crystalline and bulk glassy samples of $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ alloy has been carried out to study the material pile-up and sink-in regions around the indentation during micro indentation technique. These studies were carried out in order to understand the deformation behavior in these materials. The results indicate that the glassy alloy has shown plasticity with little strain hardening. The crystallized counter part, in contrast, does not show any significant pile up. The results are compared with the nanoindentation studies performed on these samples. The deformation behavior of both crystalline and glassy samples is discussed based on these results.

Structure-Property Relationship of Specialty Elastomer – Clay Nanocomposites

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In this study, unmodified (MMT) and modified (CL) montmorillonite nanoclays having a 2:1 tetrahedral–octahedral layer structure (TOT), high aspect ratio and high cation-exchange capacity have been chosen to prepare fluoroelastomer [terpolymer of vinylidene fluoride, hexafluoropropylene, tetrafluoro ethylene (F)] and block copolymeric [poly (styrene-ethylene-co-butylene-*b*-styrene (SEBS), having 30% styrene content] nanocomposites. Their structures have been elucidated by techniques including Atomic Force Microscopy and correlated with the x-ray diffraction, mechanical and dynamic mechanical properties.

In the first part of present study, topographic and phase imaging in tapping mode AFM was performed to investigate the size of clay-platelets, the polymer-filler interface, and spatial distribution of the nanoclays (unmodified and modified clays) in the fluoroelastomer. The phase images of the unmodified clay filled (F-MMT4) and modified clay filled (F-CL4) nanocomposites revealed that the width of clay particles was lower in the case of the unmodified clay filled system (10 ± 3 nm) than that of modified system (15 ± 2 nm).

Interestingly, the polymer was able to exfoliate both the unmodified and modified clays as evident from X-ray diffraction studies. But the particle size is much lower in the case of F-MMT4 and distribution is also better in this particular sample as also observed using the TEM and AFM. The results of AFM characterization are also in good accord with mechanical and dynamic mechanical properties. The storage modulus of F-MMT4 is also much higher than F-CL4 and F in both glassy and rubbery regions. The results have also been explained with the help of thermodynamics and wetting behavior of the clays.

In the second part of study, the AFM images exhibited a well-ordered phase separated morphology consisting of domains corresponding to hard component and darker domains corresponding to softer rubbery ethylene-co-butylene (PEB) lamella for triblock copolymer poly [styrene-*b*-(ethylene-co-butylene)-*b*-styrene (SEBS). On incorporation of 4 wt% MMT clay into SEBS, agglomerated structure is obtained in SEBS-MMT4. The best exfoliation was demonstrated by SEBS-CL4 system. The clay particles in the matrix were analysed from almost zero pull-off and snap-in force in the force-distance curves of SEBS based nanocomposite in single point and force-volume modes by AFM. Mechanical and dynamic mechanical thermal properties are best with SEBS-CL4 nanocomposites, with the values being much better compared to the neat SEBS system. The higher polymer-filler interaction is a result of exfoliation / intercalation in this nanocomposite. These values are much higher than those of SEBS-MMT4 composite.

Core Shell nanostructures synthesized using the reverse micellar route

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Core shell nanostructures have a wide area of application such as in medicine, catalysis, coatings etc. These materials have created interest to the scientific community because the presence of a shell can alter the properties of core. The shell can also enhance the stability and dispersibility of the core. We have synthesized various core shell nanostructures viz. Ag@TiO₂, CdS@TiO₂, NiS@TiO₂ and Nickeloxalate@TiO₂ using the reverse micellar route. This method has found to be a versatile route for the synthesis of a large variety of oxide nanoparticles which are homogeneous and monodisperse. Several dielectric, optical and magnetic nanoparticles have been synthesized by this method. Ag@TiO₂ core shell nanostructures have potential applications in the photocatalytic processes associated with TiO₂. The core-shell nanostructures have been characterized using powder x-ray diffraction, dynamic light scattering and transmission electron microscopy. TEM images for Ag@TiO₂ show that the core size is 25nm with 10 nm shells. Electron diffraction clearly shows that the core is mainly cubic silver and the surrounding shell is of TiO₂. UV/Visible spectroscopic studies indicate shift in the absorption band with respect to pure silver nanoparticles. Effect of temperature on the structure of these particles will be discussed. The structure and optical properties of other core-shell nanostructures like CdS@TiO₂ and CdS@SiO₂ will also be discussed.

Some conducting Polymer / Binary polymer-Inorganic Hybrid nanocomposite materials

Prof. Mukul Biswas

Speciality polymers comprising polyN-vinylcarbazole(PNVC), Polyaniline(PANI), polypyrrole(PPY), polythiophene (PTP) are well-known materials for high temperature stability outstanding conductivity and novel optoelectronic properties. However, Nanocomposites of such speciality polymers with MMT clay, synthetic zeolites as encapsulates or intercalates will be expected to provide a better opportunity for their properties to be utilized in the form of cost-wise cheap and useful advanced materials. In this background, suitable procedures were developed for the polymerization of thiophene (TP), furan (F), aniline (ANI), and pyrrole (PY) by MMT-clay. The composites were fully characterized in regard to thermal stability, morphology (SEM, TEM), conductivity and crystallinity. Suitable mechanisms of the polymerization of the various monomers un-aided by oxidant were proposed.

In addition to MMT clay, work was also initiated to prepare composites using zeolites as co-component with several polymers. Conducting composites of PNVC, PPY, PANI with 13X zeolite were prepared and characterized in regard to various useful bulk properties.

An interesting class of nano composites was developed which involved composite formation between the speciality polymers and carbon allotropes. In this respect, acetylene black, carbon nanotubes (MWCNT) and buckminsterfullerene (BMF) were used as one of the components in composite formation with the above mentioned speciality polymers. A notable feature of these carbon allotropes is that AB, BMF or MWCNT are capable of directly initiating the bulk polymerization on NVC monomer and thereby form a nanocomposite thereof.

Extensive work was performed to characterize these various composites in regard to structure (FTIR, UV-visible, Emission) and relevant bulk properties (Thermal stability, DTG, DTA studies), morphological properties (SEM, TEM, XRD) and conductivity characteristics. Outstanding conductivity values were realized with the carbon allotrope based composites of PNVC (dark conductivity ~ 10 - 12 S/cm) with values increasing with the weight ratio of MWCNT and PNVC in the composite. Highly conducting composites of PNVC-FO resin (more thermally stable than PNVC) with AB were prepared and characterized. These studies are being extended to preparation of AB based Nanocomposites of polystyrene (PS), polyacrylamide (PAA), poly2-vinylpyrrolidone and several other polymer systems.

In another interesting extension of the work procedures were developed to modify an already formed nonconducting composites say PNVC/PF/PTP-metal oxide/MMT clay by loading of a second polymer component. Work in such systems was initiated and binary polymer composites like PPY-(PF-MMT), PANI-(PF-MMT), PPY-(polymethylmethacrylate (PMMA)-SiO₂), PANI-(PMMA-SiO₂), PPY-(PNVC-13X) and PANI-(PNVC-13X) were prepared.

SESSION E2

**SYNTHESIS, CHARACTERIZATION, PROPERTIES,
APPLICATIONS OF NANOMATERIALS**

Barium Titanate Based Multiferroic Nanocomposite Functional Materials by High Energy Ball Milling

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Effective conversion between magnetic and electric signals is extremely desirable for a large number of device applications. Multiferroics, which are simultaneously ferroelectric and ferromagnetic, can exhibit coupling effects between ferromagnetic and ferroelectric properties. For instance, spontaneous electric polarization can be modulated by an applied magnetic field, and the spontaneous magnetization can be changed by an applied electric field. In composite multiferroics, the magnitude of such effects is strongly dependent on the efficacy of the elastic coupling between magnetostrictive and piezoelectric components, and in some intrinsic multiferroic materials systems, the exact nature of the magnetoelectric (ME) coupling is not well understood. In order to elucidate and quantify the nature of the ME coupling, it is important to measure the ME coefficient, α_{ME} , which can be defined as the ratio of the induced electric field E caused by the applied magnetic field H , dE / dH .

The present study is focused on nanostructured $BaTiO_3 + Fe_3O_4$ ($NiFe_2O_4$) multiferroics, which were prepared by high energy ball milling. $BaTiO_3$ (99%) and Fe_3O_4 ($NiFe_2O_4$) were used as the starting materials for preparation of nanostructured multiferroics. Milling has been carried out in Fritsch P-5 planetary ball mill up to 20h with 10:1 ball to powder weight ratio at 300 rpm. XRD has been carried out on milled powders for structural analysis and TEM, AFM and SEM techniques are used for microstructural characterization. Compaction and sintering studies were performed and densities measured on green and sintered pellets were 85% and 97-99%, respectively. Conventional and microwave sintering results were compared. The influence of microwave sintering in reducing the sintering temperature from 1200°C to 1050°C and time from 2h to 10min has been demonstrated. Dielectric properties were measured with HIOKI 3535 LCR HITESTER in the frequency range of 100kHz to 120MHz. D_{33} measurements have been made by a wide range (10 to 2000pC/N) d_{33} meter. Magnetization behaviour has been studied using vibrating sample magnetometer (VSM). ME effect has also been measured to estimate the magnetoelectric effect between the ferromagnetic and ferroelectric phases. The results have been compared with the multiferroic composites prepared by conventional techniques. The paper discusses the improved properties of nanocomposite multiferroics.

Surface ferromagnetism and bulk ferroelectricity in nano-structured BaTiO₃

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Recently, it has been reported that the non-magnetic oxide nanoparticles such as CeO₂ and Al₂O₃ show room temperature ferromagnetism. The origin of ferromagnetism was suggested to be due to defects on the surface of the nanoparticles. From the application point of view, there is an urge to synthesis materials that can show both ferromagnetism and ferroelectricity. In this regard, we synthesized nanostructures of BaTiO₃, a well-known ferroelectric material, to study its magnetic properties. Nanostructures such as assembly of nanoparticles in a rod-like fashion and unassembled nanoparticles were synthesized. The synthesized BaTiO₃ nanostructures crystallized in the polar tetragonal symmetry (space group P4mm) and exhibited a room temperature ferroelectric hysteresis and ferromagnetic hysteresis. Assembled nanoparticles showed enhanced ferroelectricity and higher magnetic moment compared to those that of unassembled nanoparticles. The enhanced ferroelectricity can be attributed to the assembly and higher magnetic moment to the smaller particle size of the individual nanoparticles in the assembly. The ferroelectricity arising from the second order Jahn-Teller distortion and the ferromagnetism may be from defects on the surface of nanoparticles.

Metal oxide/polyaniline nanocomposites: Cluster size and composition dependent structural and magnetic properties

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The properties of magnetic nano particle system are known to be dominated by the size of individual nanoparticle, cluster size of these particles and the magnetic interparticle interactions. The role of magnetic interparticle interactions can be best probed in particles dispersed in matrix where the volume concentration can be systematically varied.

Nanocomposites of iron oxide, nickel ferrite/conducting polymer in the form of powder and self standing sheets with varying compositions have been studied to understand the above variations. Single crystalline phase viz $\gamma\text{-Fe}_2\text{O}_3$ and NiFe_2O_4 were observed through X-ray diffraction (XRD). The presence of conducting polymer was confirmed through Fourier transform infrared spectroscopy. The amount of polymer present in the composite, the transition temperature of iron oxide and thermal stability of polymer was determined through Thermo gravimetric and differential thermal analysis. The degradation temperature of polymer was higher for self-standing sheets as compared to powders. The transition temperature of iron oxide (ferromagnetic to paramagnetic phase) was found to decrease in its composite form. The particle size was estimated to be 10-20 nm from the XRD and Transmission Electron Micrographs. The cluster size was found to reduce with increasing polymer concentration and chains of particles were observed for a particular concentration. Fibrous structures were observed for polymer films whereas clusters were observed for composite films as seen from scanning electron microscopy. The room temperature magnetic hysteresis measurements show reduction in saturation magnetization with increasing polymer concentrations. The low value of coercivity ~ 160 Oe was observed for low polymer composites. On increasing polymer concentration the coercivity and remanence becomes negligible indicating superparamagnetic phase. Susceptibility measurements show a reduction in blocking temperature with increasing polymer concentration. Beyond a certain composition, system shows paramagnetic behaviour. This is also confirmed through Zero field cooled-Field cooled measurements

***In situ* Synthesis of Silver Nanoparticles/Gold nanoplates/Palladium nanowires in Polymer Matrix and Application in Optical Power Limiting.**

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Advances in nanoscience and technology are closely linked to the development of new methods for the synthesis and assembly of nanoparticles. We have developed a simple and environment-friendly *in situ* process for generating metal nanoparticles inside polymer films. Factors including potential device applications and health hazard issues make it advantageous to fabricate and assemble nanoparticles inside matrices such as polymers. The polymer we have used, poly(vinyl alcohol) (PV A), acts as the reducing agent, stabilizer for the nanoparticles and the matrix for homogeneous distribution and immobilization; it is also environmentally and biologically benign. The method provides a convenient route to free-standing films of the nanoparticle-embedded polymer by using a sacrificial layer of polystyrene (PS). The process also allows efficient control of particle size, size distribution and shape by adjusting the composition of the films and parameters related to the thermal treatment. The small sizes and narrow size distribution in the case of silver nanoparticles, the shape control in the case of gold nanoplates and crystal-to-crystal transformation to obtain palladium nanowires achieved under optimal conditions of synthesis will be discussed. The method we have developed opens up a wide range of possibilities for the fabrication of free-standing metal or semiconductor nanoparticle-embedded polymer films.

Metal nanoparticles are known to be promising materials for the development of optical limiters. An ideal optical limiter exhibits appreciable linear transmission below a threshold input fluence of laser light and a clamped transmission above it. Such devices are of great relevance in the context of the protection of optical components and human eye from laser-induced damages. We have used a frequency doubled Nd:Y AG laser (532 nm, 6 ns, 10Hz) and a Ti:Sapphire laser (800 nm, ~ 100 fs, 1 kHz) as the excitation sources for the nonlinear optical studies, using Z-scan experiments. Typical optical limiting behavior, for the case of Ag-PV A, Au-PV A and Pd-PV A films are presented in Fig. 2; it is notable that the thin Ag-PV A films exhibit characteristics comparable to that of colloidal silver with path length of the order of 1 - 2 mm. Our fabrication methodology allows us to produce thin free-standing films of the metal nanoparticle-polymer composites. Results on polymer films with Ag, Au and Pd nanostructures will be presented.

Nanometre grain size as a new control parameter to study non-Fermi liquid behaviour, quantum phase transitions and magnetically-mediated superconductivity in weak itinerant-electron ferromagnets

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A detailed comparative study of magnetization, electrical and galvanomagnetic transport in polycrystalline (p-) and nanocrystalline (n-) Ni_3Al has revealed the following new and novel physical phenomena. (i) Long-range ferromagnetic order prevalent in p- Ni_3Al for $T \leq T_C = 54$ K ceases to exist in the nanocrystalline state when the average particle size falls below 50 nm. (ii) n- Ni_3Al exhibits a strongly exchange-enhanced paramagnetic susceptibility due to predominantly antiferromagnetic (ferromagnetic) spin fluctuations below (above) $T \cong 30$ K. (iii) In the nanocrystalline state, the density of states at the Fermi level and the effective magnetic moment per Ni atom in the paramagnetic state reduce by nearly 20%. (iv) The residual resistivity, $\rho(T=1.7\text{K})$, is nearly six times larger than that in p- Ni_3Al while the temperature coefficient of resistivity over the entire temperature range of 1.7 K to 300 K is roughly three times smaller in n- Ni_3Al . (v) Contrasted with Fermi liquid behaviour of electrical resistivity, $\rho(T)$, in atomically-ordered p- Ni_3Al , $\rho(T)$ in n- Ni_3Al exhibits a non-Fermi liquid behaviour in the temperature range $4\text{K} \leq T \leq 22\text{K}$. (v) Antiferromagnetic spin-fluctuation-mediated superconductivity at $T < 3.9$ K manifests itself as a sudden increase in positive magnetoresistance for temperatures below 4 K. These observations strongly suggest that nanometer grain size can be used as yet another control parameter (as against the conventional control parameters such as external pressure or magnetic field) to study non-Fermi Liquid behaviour, quantum phase transitions and magnetically-mediated superconductivity in weak itinerant-electron ferromagnets.

Study of Optical Phonon modes of CdS nanoparticles using Raman spectroscopy

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The reduction in the grain size to nanometer range can bring about radical changes in almost all of the properties of semiconductors. CdS nanoparticles have attracted considerable scientific interest because they exhibit strongly size-dependent optical and electrical properties. In the case of nanostructured materials, confinement of optical phonons can produce noticeable changes in their vibrational spectra compared to those of bulk crystals.

In this paper we report the study of optical phonon modes of nanoparticles of CdS using Raman spectroscopy. Nanoparticle sample for the present study was synthesized through chemical precipitation technique. The CdS nanoparticles were then subjected to heat treatment at low temperature (150°C) for extended time intervals. The crystal structure and grain size of the samples were determined using X-ray diffraction. The Raman spectra of the as-prepared and heat treated samples were recorded using conventional Raman, FT-Raman and micro-Raman techniques. The spectrum of as prepared sample exhibited an intense, broad peak at 301 cm⁻¹ corresponding to the LO phonon mode. Higher order phonon modes were also observed in the spectra. A noticeable asymmetry in the Raman line shape indicated the effect of phonon confinement. Other features in the spectra are discussed in detail.

Magnetic phases in transition metal doped ZnO and Ni based nanoparticles

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We have investigated ground state magnetic properties and optical band gap of chemically synthesized Fe, Co, Mn doped ZnO Diluted magnetic semiconducting nanoparticles (~ 7 - 20 nm). The strong irreversibility between zero field cooled (ZFC) and field cooled (FC) $M(T)$ curve is observed in the low temperature regime for Zn-Fe-O nanoparticles. The cusp like anomaly is observed in ZFC curve at freezing temperature (T_f) well below irreversibility temperature (T_m). The strong hysteretic $M(H)$ loop is observed at the temperature of 5 K with $H_c = 130$ Oe and $M_r = 1.94$ Bohr magneton /Fe⁺² ion. The magnetic behaviour of Fe doped sample is very similar to a cluster glass phase where the clusters are strongly interacting and they undergo random dipolar inter cluster interactions, giving rise to strong competitive ferromagnetic and antiferromagnetic interactions, finally leading to freezing of those clusters. The ground state phase of Mn and Co ZnO DMS nanoparticles are observed to be antiferromagnetic like having non-saturating tendency of $M(H)$ even at a field of as high as 5 Tesla. The optical band gap of the DMS nanoparticles are estimated using recorded UV-Visible absorption spectra.

Further a comparative study of the structure and magnetic properties of ultrafine Ni nanoparticles prepared by the chemical reduction of NiCl₂ solution of four different concentrations has been carried out. The concentration of the NiCl₂ solution has a profound influence on the room temperature (300 K) magnetic state of the resulting Ni nanoparticles, even though all four samples show the same XRD pattern i.e., have the same crystal structure (tetragonal as proposed by us). It is found that samples obtained from lower concentration solutions (0.1M and 0.5M) show a linear response with magnetic field while those obtained from higher concentration ones (1M and 2M) are ferromagnetic at 300 K. This difference in magnetic behaviour has been explained on the basis of dipolar interactions between particles, which are strong in the higher molarity samples but comparatively weak in case of lower molarity ones. The proposition is further strengthened by the irreversibility in the field cooled (FC) and zero field cooled (ZFC) curves which, in the case of 1M and 2M samples, starts right from the measuring temperature of 390 K, clearly hinting at the blocked state of the particles and therefore to their ferromagnetic response at 300 K. An intriguing feature in the form of a sharp peak at 20 K is observed in the FC and ZFC curves of all samples, signaling some kind of transition. Appreciably high magnetization values are also seen in the M-H plots at 5 K. We attribute this to the hitherto frustrated spins in the unit cell of tetragonal Ni, becoming frozen below 20 K and then getting aligned perfectly collinearly on application of magnetic field.

On the Synthesis, Characterization and Photocatalytic Applications of nanostructured TiO₂

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Nanocrystalline semiconductive materials are attracting much attention due to their potential applications in solar energy conversion, nonlinear optics, and heterogeneous photocatalysis. In the present investigations, we have synthesized ultrafine nano-structured TiO₂ photocatalysts, which have been used in the photocatalytic degradation of phenol (one of the most common water pollutants). These catalysts have been prepared through sol-gel technique using titanium tetra-isopropoxide as a raw material for the synthesis. Characterization techniques such as XRD, SEM and TEM have been employed for structural /microstructural investigations. XRD results show that the as synthesized TiO₂ particles, which exhibit a single anatase, phase TiO₂. SEM and TEM investigations revealed that the average sizes of the TiO₂ particles are ~5-10 nm. The optical properties of the samples were investigated through UV-visible and fluorescence techniques. It has been observed that absorption edge corresponds to ~410 nm (Band gap ~3.02 eV). The emission peak in the fluorescence spectrum at ~418 nm corresponds to the band gap energy ~2.97 eV. A photocatalytic reactor has been fabricated, which consists of a quartz tube with a fused silica oxygen inlet for oxygen purging during the illumination and an outlet. Concentration of phenol (initial concentration ~100 ppm) with illumination time was monitored by measuring the absorbance of pure and illuminated phenol through UV-visible spectrophotometer. Significant decrease (~35%) in the phenol concentration was recorded in the water subjected to photochemical dissociation. The improved surface area is an important factor for the aforesaid decrease in phenol concentration. Feasible/plausible mechanism for the same has been put forward.

Urea route to coat inorganic nanowires, carbon fibers and nanotubes by boron nitride

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Boron nitride (BN) in particular has received much attention because it is insulating, does not interact with molten metals and have higher oxidation resistance than carbon. Such excellent properties promote the broad applications of BN, which include high-temperature insulators, self-lubricating and heat dissipating coatings, passivation layers, diffusion masks and wear-resistant coatings. Thus BN coating should be valuable. A simple route involving urea as the nitrogen source has been employed to carry out boron nitride coating on carbon fibers, multi-walled carbon nanotubes and inorganic nanowires. The process involves heating the carbon fibers and nanotubes or inorganic nanowires in a mixture of H_3BO_3 and urea, followed by a heat treatment at $1000^\circ C$ in a N_2 atmosphere. We have been able to characterize the BN coating by transmission electron microscopy as well as x-ray photoelectron spectroscopy. The urea decomposition route affords a simple method to coat boron nitride on one-dimensional nanostructures.

Pattern Formation by Evaporation and Its Technological Implications

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Well-ordered patterns in nature are ubiquitous and have been a source of fascination for ages. Their manifestation has allowed for a deeper understanding of many natural phenomena in non-equilibrium systems, and the ability of complex systems to form patterns has been extensively exploited in science and technology. We report here both experimentally and with numerical simulation the formation of ring deposits and uniform discs by controlling the evaporation from the droplet free surface. We have observed that the formation of rings requires not only pinned contact line but also it is also significantly influenced by the solute transport due to evaporation from the free surface. The manipulation of the droplet free surface that is available for evaporation should allow one to experimentally control the deposition and assembly of colloids and other materials. Numerical simulations were performed by solving the solute conservation equations in cylindrical coordinates as a two-dimensional axisymmetric moving boundary value problem. The results indicate that evaporation from the free surface causes the particles to accumulate near the free surface, which eventually flow towards the contact line by moving along the surface under the influence of capillary force, leading finally to deposition along the contact line. This work demonstrates that in the evaporation induced pattern formation the role of evaporation from the free surface is important in addition to the evaporation from the contact line. Further, ordered colloidal particle arrays serve as a platform for developing nanoscale devices whose functionalities are enabled by the physical (i.e., optical, electrical, and magnetic) properties of the individual particles and their arrangement. For example, there has been increasing interest in one -" dimensional (1D) and two dimensional (2D) nanoparticles arrays because they provide a model system to study transport phenomena between nanoparticles in addition to their potential technological applications, such as chemical sensors and lithography masks. Here we also report a facile, high throughput, evaporation induced lithography – free approach to create multi dimensional arrays of nanoparticles, single molecules and microparticles employing the restricted evaporation of colloidal suspensions. The mechanism of formation of these arrays has been discussed based on liquid capillary bridges and numerical simulations have been performed.

A study on the surface morphology of nanosized electroless ni-p coatings

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Nanocoatings are defined to have either the thickness of the coating or the second phase particles that are dispersed into the matrix in the nanosize range. Electroless, EL (without using electricity) is one of the classical coating technology in that deposition is purely systematic chemical process i.e. sensitization, activation, nucleation and growth of nanosized alloy globules first vertically then horizontally during the reduction process onto the catalytic surface of the substrate. In this investigation, Atomic Force Microscopy (AFM) and Field Emission Scanning Electron Microscope (FESEM) tools have been used to study the surface morphology of EL Ni-P deposition on various substrates like glass, Si-wafer, Al sheet with same experimental condition like pH of 9 and temperature at 90°C and bath composition.

AFM, FESEM studies ascribe the systematic nucleation and growth of Ni-P globules to produce coating. First the Ni atoms nucleate on the nucleation sites of Pd ions (less than 1 nm) developed onto the surface of substrate under study during activation process. P atom easily goes into the Ni lattice to form Ni-P alloy nano sized (1-2 nm) globules then further growth takes place in all possible direction autocatalytic that increase the globular size from few nm to ten to hundred nm size results into the coating layer uniformly within 10 to 60 sec.

With the help of AFM tool, surface parameters of EL Ni-P coatings like average grain (particles) size, number of globules (grains), and surface roughness due to the globules have been measured in different scanned area of 5000 x 5000, 2500 x 2500, 1000 x 1000, 500 x 500, 200 x 200, 100 x 100, and 20 x 20 square nm with the increasing deposition time from 10, 20, 30 and 60 sec.

Elemental distribution analysis in terms of both quantitative and qualitative has been carried out using FESEM-EDS on various globules ranging in nm size to know the atomic level distribution of Ni and P.

PLENARY LECTURE

Development of a bio-nano system for a cardiac diagnostics**Ramgopal Rao**

Indian Institute of Technology, Mumbai

In this talk the current status of an ongoing effort in the Electrical Engineering Department at IIT Bombay on the development of an integrated system to provide point-of-care diagnostic support for cardiovascular diseases will be presented. The system under development monitors the molecular markers to detect cardiac attacks, especially incipient cardiac attacks that go undetected before major/fatal attacks occur. The system comprises of “infarcSens” or “iSens”, which is a cantilever and molecular FET based affinity biosensor array for sensing myocardial infarction and subsequent cardiac status prognosis, using a suite of molecular markers. The sensing electronics and the associated data management software, for tracking the markers with time required for creating an epidemiological database, is also currently being developed. The multidisciplinary team from the departments of Electrical, Bioengineering, Chemistry, Material Science and Mechanical Engineering is currently working on this project, which is supported under the NPSM programme by the Govt of India.

SESSION F1

NANOFUNCTIONAL MATERIALS
(OPTICAL, MAGNETIC, SENSOR ETC., APPLICATIONS)

Nanocrystalline silicon films prepared using helium dilution to silane in RF-PECVD

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Nanocrystalline silicon (nc-Si:H) thin film has attracted demanding applications as a component layer in many devices because of its adequate association of a number of useful opto-electronic properties e.g., high electrical conductivity, excellent optical transparency and simultaneous efficient dopability. It is being used as window layer and also at the tunnel junction in multijunction solar cells, as carrier injection layer in thin film transistors. It has promising utilization in high speed switching devices by virtue of its high carrier mobility. Luminescent properties demonstrated by quantum confined nano-Si structures has opened up potential opportunities for applying them in silicon optoelectronics.

The most common and convenient process for preparing nanocrystalline silicon (nc-Si) thin films from radiofrequency silane plasma is to create a highly hydrogen diluted ensemble of SiH_n precursors. However, high hydrogen dilution significantly reduces the ultimate yield of the material. In addition, atomic hydrogen induced nanocrystallization involves stringent parametric conditions e.g., high electrical power, high substrate temperature which might appear incompatible to certain stages during multilayered device fabrication.

In quest of an alternative, people have already tried with various inert gas plasma e.g., with He, Ar, etc., and have identified their analogous role as that of H_2 , in the formation of Si:H network. Moreover, higher deposition rate at lower RF-power in case of He-dilution has been attributed to the enhancement of secondary electron emission co-efficient induced by He ions. However, the network structure remains mostly amorphous at moderate deposition temperature.

On de-excitation of metastable and ionic He, electronic energy is transferred to the growing surface as well as to the reacting precursors and thereby enhances their mobility. Again, since atomic weight of He is much lower, metastable or ionic He bombardment at the growing surface is not much harmful as the bombardment of ionic precursors; rather the energy transfer due to ionic bombardment will enhance the effective temperature at the growth-zone. Utilizing these beneficial aspects of structural relaxation aided by He-plasma at an optimized parametric condition, compact and ordered network leading to silicon nanostructures has been obtained at relatively low temperature with relatively high growth rate.

Synthesis and Luminescence Properties of Doped Nanostructures: Role of Shape, Size and Crystal phase

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We will demonstrate simple solution based method for preparing different doped nano-materials with distinct and well-defined morphologies, including spherical, hexagonal, tetrapod and rod, by controlling the reaction conditions and understanding their optical properties with changing shape, size and crystal structure. The mechanism related to morphology control of LaPO_4 : Eu nanorods/ nanoparticles are proposed and discussed. We describe the “oriented attachment” growth mechanism for nanorod-to-nanoparticles transformation with increasing the temperature of heating. Our results also suggest that the diameter of the nanorod may be a critical determinant factor in governing the resultant shape of the product nanomaterials. The role of surface coating, doping and heating on the modification of crystal structure of ZrO_2 , local structure of Zr and Eu and their effect on the photoluminescence properties of Eu_2O_3 doped and coated ZrO_2 nanocrystals will be discussed. X-ray absorption fine structure measurements were carried out to understand the local environment surrounding Zr and Eu ions in Eu doped and coated ZrO_2 nanocrystals. It is found that the local structure play most important role on the modifications of luminescence properties observed in Eu-doped and coated ZrO_2 nanocrystals.

Magnetic, optical and electronic properties of semiconducting nanoparticles doped with magnetic impurities

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Under this project proposal, we carried out a large number of syntheses attempting to dope various transition metal ions in several semiconducting nanocrystals, followed by investigating electronic, optical and magnetic properties of such doped as well as undoped samples. Our attempts primarily involved ZnS, CdS and ZnO nanocrystals hosts and most substantially Mn as the dopant, though we also explored other dopants such as Fe, Co, Ni, and Cu. While much of the results are still being analysed and will be reported later in the literature, the published articles are cited in refs. 1-15 below, that reported a part of our investigations of electronic, optical and magnetic properties of doped and undoped semiconducting nanocrystals. Our attempts at synthesising the highest quality nanocrystals required an in-depth understanding of the growth mechanism of such nanocrystals in the bottom-up approach. Such studies, arising as an extension of the proposed research, led to several interesting and often surprising results. Once again, most of these are yet to be reported in published literature, a limited number of reports have already appeared in the published form and cited below as refs. 16-18. During this period, we also published a limited number of review articles on the subject matter of this proposal; these are cited as refs. 19-23.

In this presentation, I shall review only a part of our investigations, emphasising the results on electronic, optical and magnetic properties of doped semiconducting nanocrystals we have obtained under this project, highlighting some of the so far unpublished results.

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Optical Properties of Hybrid Nanomaterials

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The presentation will highlight our recent efforts to understand the interfacial properties of hybrid nanomaterials and their utilization as sensors for the selective detection of biologically important molecules and ions. We have also assembled photoresponsive rigid rod molecules (for e.g., phenyleneethynylenes) on two-dimensional surfaces and investigated their current-voltage characteristics and these aspects will be discussed.

(i) Optical of hybrid nanomaterials: Several chromophore functionalized metal nanoparticles were synthesized by functionalizing pyrene and ruthenium trisbipyridine ($\text{Ru}(\text{bpy})_3^{2+}$) chromophores on to the surface of gold nanoparticles with a view to investigating the ground as well as excited state interactions between the metal surface and the chromophoric systems. We have probed the local environment close to the surface of Au nanoparticle using pyrene alkyl thiols of varying lengths and found that the surface is polar in nature.

(ii) Phosphorescent nanomaterials: Chelating groups such as 2,2'-bipyridine were anchored around Au nanoparticle and its complexation with $\text{Eu}^{\text{III}}/\text{Tb}^{\text{III}}$ ions yielded red emitting Au-BT: Eu^{III} and green emitting Au-BT: Tb^{III} phosphorescent nanomaterials (nanophosphors). An attractive feature of the present systems is their ability to hold a large number of luminescent lanthanide complexes around Au nanoparticles without affecting the long-lived line-like emission properties. We have used these phosphorescent nanohybrid systems as high affinity sensors for the selective detection of cations through isomorphous substitution of lanthanide ions.

(iii) Hierarchical intergration of Au nanorods: Interaction of various bifunctional molecules with Au nanorods was investigated using absorption studies and transmission electron microscopy. Based on these studies a novel approach of covalently linking Au nanorods to nanochains using various bifunctional molecules was reported. The new band observed in the near-infrared region results from the selective coupling of the longitudinal surface plasmon oscillations of Au nanorods in 1D-nanochains.

(iv) Nanomaterials as biosensors: We report a unique procedure for the selective detection of micromolar concentrations of cysteine and glutathione ($\gamma\text{-Glu-Cys-Gly}$) in the presence of other α -amino acids, by exploiting the anisotropic surface binding properties of Au nanorods. An elegant colorimetric methodology have been developed for the detection of lead ions from aqueous medium in the presence of other interfering metal ions just by mixing various bifunctional molecules and Au(III) ions without the aid of any specialized equipment.

(v) Scanning tunneling spectroscopy of molecular/nanoparticle assemblies: We have also investigated the self-organization of substituted phenyleneethynylenes on two dimensional surfaces using Scanning Tunneling Microscopy (STM). The two dimensional packing of these molecules differ with functionality and we have succeeded in determining the current-voltage characteristics of these self-organized molecules using Scanning Tunneling Spectroscopy (STS).

Carbon nanostructures as High-Capacity Lithium-Insertion Anodes

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Oxidatively opened multi-walled carbon nanotubes were filled with salts of lithium-alloying metals such as tin and bismuth by capillary action. The salts were reduced to the corresponding metals to yield metal-filled carbon nanotubes. ICP-AES analysis of the reduced samples indicated that the metal loadings were about 5 wt.%. The first-cycle insertion and deinsertion capacities at a 0.1 C rate for the tin-filled nanotubes (CNT:Sn = 1:1) were 2474 and 889 mAh.g⁻¹., respectively. The corresponding values for the bismuth-filled nanotubes (CNT:Bi = 1:1) were 1203 and 481 mAh.g⁻¹. The reversible capacities of the tin-filled and bismuth-filled nanotubes (CNT:metal = 1:1) at 0.1 C rate were remarkably high, being 844 mAh.g⁻¹ (40th cycle) and 402 mAh.g⁻¹, (100th cycle), respectively. The capacities generally peaked at a CNT:metal ratio of 1:1. For mixed loadings of tin and bismuth, the highest reversible capacities were obtained at a CNT:Sn+Bi ratio of 1:1, being 708 mAh.g⁻¹ at 0.1 C rate. The high-rate cyclability (0.3 C) of the materials was also impressive, sustaining more than 150 cycles. The capacities of the metal-filled nanotubes far exceeded the cumulative values that may be expected from the constituents, suggestive a synergistic effect. Although the initial irreversible capacities were high (as much as 64.1%), the capacity loss decreased with cycling, being just 4% (40th cycle) and 3% (100th cycle) at 0.1 C rate for the tin-filled and bismuth-filled nanotubes, respectively. A general feature of the cycling profiles is that the capacities of the materials increase with cycle number. The coulombic efficiency also increases with cycle number. This study is a demonstration of metal-filled carbon nanotubes as a novel class of anode materials for lithium-ion batteries. However, a major drawback is the high initial irreversible capacities, which precludes their immediate application.

In another study, kish graphites were investigated as lithium-insertion anodes. Kish graphites, recognized by their flakiness, silken touch and fineness, is a by-product in the steel-making industry. Traditionally, it is produced by precipitating carbon from a supersaturated solution of carbon in steel. In a variation of this process, we have demonstrated the production of kish graphites with non-biodegradable plastic wastes as precursors. This is a filth-to-wealth process in which an environmentally hazardous material is converted into a technologically useful product. In our study, we used ABS (acrylonitrile-butadiene-styrene terpolymer), an e-waste, as a precursor. The plastic material was simultaneously carbonized and the resulting carbon dissolved in a melt of cast iron at 1600°C. Upon cooling, the excess carbon in the melt precipitated as graphite. The graphitic product gave specific lithium insertion capacities exceeding 400 mAh.g⁻¹ over several cycles. The 'excess' capacity, far exceeding the theoretical value of 372 mAh.g⁻¹ obtainable with perfectly graphitic carbons, is ascribed to nanocarbon structures in the kish graphite.

SESSION G1

THIN FILMS, NANOCOATINGS, NANOTRIBOLOGY, LITHOGRAPHY

Investigations of the properties and phenomena exhibited by Nanomaterials: nanofabrication, lithography and related aspects.

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An overview of the activities pertaining to the Project will be presented. Synthesis of new nanomaterials such as inorganic nanorods and nanowires has been achieved. New methods of synthesis for metal and semiconductor nanocrystals at liquid-liquid interface have been developed. Detailed studies have been carried out on the optical and electrical properties of metal and semiconductor nanocrystals- on individual nanocrystals as well as on mesoscale lattices of nanocrystals. We have employed extensively scanning probe methods- STM and AFM in characterizing the nanostructures. Besides carrying out routine topography measurements, the probe microscopes have been used for I-V characteristics as well. While spectroscopy with STM is common, the method of conducting AFM (CAFM) required some innovation and effort. C-AFM has advantages over other probe microscopic techniques in that it is a direct contact measurement with nanometer resolution. Some of the research highlights are the realization of a molecular switch (a conducting molecule held between two metal nanocrystals as electrodes), tunable coulomb blockade in Pd-thiolates, rectifying action in a nanocrystal-organic bilayer etc. Besides, many results have been obtained in the laboratory using dip-pen nanolithography based on AFM. Indigenously developed colloidal inks were used in creating nanometric patterns on different substrates. Our studies have shown that the method is not only useful in making nanoconduits but also in patterning functional nanomaterials.

Engineering Structures with Nanoscale Materials

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The Centre for Nanotechnology at IIT Guwahati emphasizes on both the theoretical and experimental aspects of nanoscale science and technology. There are several research programmes that are currently running with the aim of generating newer nanoscale materials; development of alternate forms of lithography for integrating these materials and works toward fabrication of devices for potential applications. Some of the ongoing works are exemplified below.

Based on the recent development in our laboratories, we are currently pursuing the generation of polymer-metal nanoparticle composites for potential use as pH and temperature sensors. The sensor designs are based on the photoluminescence and colloidal properties (such as aggregation and optical extinction) of the composites. We have also incorporated both catalytic and sensor properties in order to have multifunctional components in a single device structure. Further, efforts are being placed on generating polymer-metal nanoparticle composite where the electroluminescent and photoluminescent properties of the polymer could be changed by incorporation of metal nanoparticles.

We have recently developed a scheme combining top-down and bottom-up approaches in generating patterned CdS quantum dots (Qdots) in polymer film. We have also developed a method in systematic organization of colloidal nanoparticles and molecular materials into two-dimensional arrays of functional materials. Interestingly, we observed that chemical reactions can be carried out on the surface in order to generate systematic patterns with Qdots.

The Centre for Nanotechnology is pursuing extensive works on nanobiotechnology with a multidisciplinary approach. For example, it has been recently discovered that Au NPs can be generated by reduction of HAuCl_4 using pure enzyme as the reducing agent. These Au NP incorporated enzymes have higher biocatalytic properties than pure enzymes. In addition, currently research works are being pursued on the potential of combination of traditional gene therapy and nanomaterials to have superior medical benefit. Further, we are working on understanding the mechanism of bacteriostatic and bactericidal properties of Ag NPs.

Finally, we have recently developed electrochemical actuators consisting of dendritic assembly of nanoscale metallic structures. These dendritic fibrous structures, grown in aqueous solution, can be actuated by an external electric field or magnetic field. Systematic development of nanoscale machines with external control is the ultimate aim in this respect.

Preparation and characterization of Boron – Nano wires by Pulsed Laser deposition

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Boron Nano- wires were deposited from a target of boron on sapphire using XeCl excimer laser operating at 308 nm and frequency of 30 Hz. The crystallographic characterization of the nano-wires were performed using X- ray diffraction (XRD). Microstructure, surface morphology and grain size were obtained from SEM and TEM.

Electrical properties of nano-wires such as electrical conductivity and thermoelectric power were studied in temperature 300 - 350 K by four terminal and two terminal method. The Seebeck Coefficient is negative for the nano-wire and showing that these nano wires behave as n – type semiconductor. On the basis of these results an explanation for the conduction mechanism in boron nano-wires is suggested.

Nanocrystalline GaN films : Preparation and Prospect for LED Application

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In an effort to realize a p-n junction composed of nanocrystalline p-GaN and n-GaN, we have developed a multistage sputtering unit comprising of four targets. The multi-target jig holds 1% Be-doped GaN, 1% Si-doped GaN, undoped GaN and Al targets. The targets could be sputtered sequentially to deposit different layers one after the other as required. The system could be pumped to $\sim 10^{-7}$ torr by using turbo-molecular pumping work station. The temperature of the substrate during the deposition could be adjusted suitable by a cold finger.

Nanocrystalline undoped n-GaN and p-GaN in the thin film form were deposited onto fused silica substrates by high pressure sputtering of GaN, Si (1 At %) and Be (1 At %) doped GaN targets, respectively. The band gap values were always found to be higher than that of the bulk. The blue shift in band gap could be attributed to the quantum confinement effect. The photoluminescence peak positions indicated that no significant energy shift in the peak positions was noticed with reduction in crystallite size but the intensity of the peak decreased for films with the reduction in crystallite size. The optical absorption in these films could be explained by the combined effects of phonon and inhomogeneity along with optical loss due to light scattering at the nanocrystallites.

Schottky diode structures for both the p- and n- type nanocrystalline GaN (Au/p-GaN/Al and Al/n-GaN/Au) were fabricated out of the above films. Corresponding current-voltage and capacitance-voltage characteristics of the schottky diodes were recorded and analyzed in the light of the existing theories. I-V and C-V characteristics of the above Schottky diodes were measured at different temperatures and analyzed by using the existing theories. Efforts are being made to realize a p-n homojunction by using p-GaN and n-GaN layers.

Nano composite thin films of SiCN systems for wear and functional applications

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Nano-composite ternary Si-C-N materials have recently drawn interest due to its potential novel properties compared to those of crystalline Si_3N_4 and SiC mixture. These materials can possess properties such as high hardness, wide band gap characteristics, a wide transparency window, promising field emission characteristics, high temperature oxidation resistance, chemical inertness and promising wetting behaviour. Size decides the hardness of the film. Nano-composite coatings are potential materials for wear resistance, high temperature, optoelectronic applications where not only hardness but the combinations of properties such as toughness along with high hardness under different loading conditions etc are required. Beside the effect of different microstructure evolution, understanding of mechanical and adhesion behaviour for such nano-composite thin film is still under investigation. Although various deposition techniques like PECVD (Plasma enhanced chemical vapour deposition), Pulsed laser deposition (PLD), Ion Beam sputtering deposition (IBSD), Magnetron Sputtering etc. have been used to prepare nanocrystalline Si-C-N compounds as low temperature depositions, better adherence and easy scaling up is possible. Moreover it is comparatively much cleaner process.

In the project a systematic investigation on the deposition of Si-C-N films under varying deposition conditions such as pressure, substrate temperature, nitrogen content by RF and DC sputtering has been carried out on Si, glass and steel substrate. Significant role of the different deposition parameter on hardness and structure and the content in the film were observed. With the increase of nitrogen partial pressure in a limit, the films became smoother and fine particle growth. The hardness varied between 4400 Hv to 473 Hv depended on deposition condition. It was found that amount of phases of $\beta\text{-C}_3\text{N}_4$, Si_3N_4 , graphite in the film and the effective particle. The AFM studies also suggested that the increased hardness was due to reduction in particle size and localized formation of C_3N_4 and Si_3N_4 phase in the films. The x-ray photoelectron spectroscopy analyses showed the formation of C-N and Si-N bonds for the harder film. The increased nitrogen concentration in the sputtering gas mixture to 99% resulted in large particle growth and graphitic phase formation, which exhibited a low hardness value of 4.7 GPa. The high C content and low Si content in the deposited films facilitated the graphitic phase. The C_3N_4 phase was found to get stabilized in the presence of Si_3N_4 . Nanoindentation studies showed hardness and modulus values of 21 GPa and 230 GPa respectively. TEM & AFM studies revealed amorphous nature of SiCN film when deposited at lower temperatures (up to 100°C) but at higher temperature (500°C) films showed crystalline grains in amorphous matrix. $\beta\text{-C}_3\text{N}_4$ phase formation was confirmed. An appreciable critical load between 2-24 Newtons was required to detach the films from the substrate which was very much dependent on substrate temperature.

A Study on Characterisation of Mechanically stable Nanocrystalline TiN films on Glass Substrate

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Nanocrystalline TiN films have been identified as a potential material for tribological application, because of their interesting properties like very high hardness, wear resistance, and adhesion. It possesses enhanced mechanical and physical properties as compared to its bulk form. The improved strength and hardness of the nanocrystalline film is due to the Hall-Petch effect. It is well known that TiN films exhibit very good adhesion on crystalline substrates but on amorphous substrates like glass, it is not mechanically stable and peel off with time due to the differential thermal expansion and nitrogen pressure. Therefore, it is very essential to find out the process conditions at which the TiN film is mechanically stable on glass with the minimum thermal stress. Therefore, the present work has been focused to deposit the TiN film on glass substrate by DC magnetron sputtering at different processing conditions such as substrate temperature (RT to 500°C) and sputtering pressure, and establish the required process parameters to obtain the mechanically stable film. The TiN films with different thickness values ranging from 0.1 to 1µm were deposited using the optimum process conditions. The phases in the films were identified by XRD and their microstructures were characterized by using AFM, FESEM and TEM. The mechanism of formation of nano TiN crystals in the thin films has been substantiated in the present work.

Nanotechnological Route for Improving the Hydrogenation Properties of Palladium and Praseodymium Layers

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Hydrogen induced changes in the electronic and optical properties of Pd and rare earth metals make these materials highly suitable for sensor and switching applications. Our earlier work on Gd nanoparticles has shown that size and surface dependent properties results in large improvements in the device characteristics. The occurrence of structural transformations and large lattice expansion/contraction along with optical and electronic changes results in slow and incomplete change-over from the 'on' state to the 'off' state during hydrogen loading/deloading cycles. In this presentation, results of some recent investigations carried out in this direction will be discussed. In a study on the hydrogen sensing properties of Pd nanoparticles, it has been shown by controlling nanoparticle size, surface conditions and thickness, the opposing and entangled effects due to electronic and geometric changes can be controlled and thus separated. Due to the presence of interparticle gaps and complete conversion to PdH₂, the initial response is followed by a substantial decrease in resistance due to closure of conducting paths. This study thus sets the foundation for fabricating a novel gas sensor devices having pulse-like response. In a separate study, the size-dependent improvements in the structural, optical and electrical properties of Pr nanoparticle layers have been observed. A new methodology of improving the hydrogenation properties of solid state materials by using ion-induced nanotracks as two-way transport routes has been successfully implemented. A large enhancement in the hydrogen stoichiometry value (H/Pr) from 7.2% to 17.8% is observed with increase in the ion doze. The role of nanotracks in hydrogen removal during deloading is even more remarkable. It is observed that about 31% H can be removed during deloading in ion-irradiated samples (maximum possible is 33.3%, corresponding to PrH₃ to PrH₂ transformation) in comparison to only 12 % in case of un-irradiated layers. In addition, some important results on the synthesis and application of other nanostructured materials from our institute will also be presented.

SESSION F2

**SYNTHESIS, CHARACTERIZATION, PHASE TRANSFORMATION
OF NANOMATERIALS**

A novel approach to synthesis vertical ZnO nanorods on glass substrate by simple chemical method

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ZnO is an II-VI wide bandgap (3.37eV) semiconductor compound with excellent chemical, thermal and electrical properties. Semiconductor nanorods have attracted much interest due to their physical properties and potential for diverse electronic and photonic application. At present various chemical, electrochemical and physical deposition techniques have been employed to create oriented array of ZnO NRs. Here a novel aqueous solution method has been developed for growing well-aligned crystalline ZnO nanorods (NRs) on a glass substrate. At first we used a new and simple (SILAR) method to grow ZnO as seed layer and subsequently a simple chemical growth method was used to grow vertical ZnO NRs. One-dimensional NR array of ZnO were obtained by solution growth process using zinc acetate and hexamethylenetetramine as aqueous solution at different pH levels. The seed layer was found to considerably influence the orientation, crystallinity and morphology of ZnO nanorods. We confirmed this by growing ZnO NRs on unannealed and annealed seed layers. X-ray diffraction (XRD) analysis confirmed the ZnO nanorods exhibit hexagonal wurtzite structure with well orientation along C-axis. Scanning Electron microscope (SEM) confirmed the diameter of the film is 62 nm (grown at pH 6) and 72 nm (grown at pH 7). From the SEM analysis we found that the diameter of ZnO NRs mainly depend on the concentration of reactants, reaction temperature and solution pH etc. The Raman spectrum confirmed two main peaks of ZnO at 437cm⁻¹ and 581cm⁻¹ due to E₂ and E₁ phonon vibrations. We believe that our novel approach can be further investigated with different doping for different applications.

Mechanosynthesis and Mechanical Thermal Synthesis of In-situ Aluminium Based Nanocomposites and Their Characterization

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The aim of the present work is to produce in-situ aluminum based nanocomposites by mechanical activation and mechanical-thermal activation of chemical reaction between aluminum and metal oxides like NiO, CuO, ZnO, TiO₂ and rare earth oxides (REO). The general equation representing an oxide-metal displacement reaction involving aluminum as reductant is $3/y M_xO_y + Al \rightarrow Al_2O_3 + 3x/y M$.

A) Mechanical-Thermal synthesis of Aluminum based nanocomposites:

1. Al+ MnO₂+ CuO system of work:

Powder mixture (Al-6wt%MnO₂-6wt%CuO) is subjected to a high-energy ball milling with tungsten balls and vial. The crystallite size and lattice strain in the powder particles can be determined using the x-ray peak broadening techniques. Transmission electron microscopy (TEM) has been used for a direct measurement of the size distribution of particles in sample. Milled sample is also investigated by a differential thermal analyser (DTA) in the temperature range of 50–1000°C, with a heating rate of 10 °C min⁻¹ in argon atmosphere. The microstructures of the sintered samples have been observed in SEM. During mechanical milling there are no additional peaks. The shifting of Al peaks to lower angles as well as broadening are observed. The absence of additional peaks indicates that no new crystalline phase has formed. Some of the CuO and MnO₂ peaks are hardly discernible in the patterns due to their low concentrations. The peak broadening indicates the crystallite size refinement and/or the introduction of lattice strains. Each of the DTA traces shows an endothermic peak which is caused by the Al melting and an exothermic peak which is caused by the reduction reaction. The high energy ball milling increases the sintering rate of the composite powder due to an increased diffusion rate. Mechanical milling process not only improves the distribution and homogeneity of the disperse phase in the matrix compared to unmilling process, but also increases the properties in terms of morphology, matrix crystallite size and fine size distribution of reinforcement compared to the unmilled but sintered composites.

2. Al+ ZnO+ CuO system of work:

Different approaches have been investigated to synthesize Al(Zn)-4Cu/Al₂O₃ composites by displacement reactions involving Al, ZnO and CuO. The reactions have been performed either by mechanosynthesis, exothermic dispersion or a combined mechanical and thermal activation process. Differential thermal analysis, x-ray diffraction and scanning electron microscopy have been used to study the various reaction mechanisms and transformations. High-energy ball milling of the powder modifies the reactivity of the system. A milling treatment not only reduces the reaction temperature, but also can induce a different reaction path. It is reported here that an appropriate mechanical-thermal treatment may lead to the synthesis of an Al(Zn)-4Cu/Al₂O₃ composite. The hardness and wear resistance of the in situ composites increase with the milling time.

Soft chemical synthesis and characterization of calcium tungstate nanoparticles

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It is well known that the studies of ABO_4 type crystals are of interest due to their luminescent, scintillator and laser host applications. Calcium tungstate is a commercially important material with scheelite structure, attracted scientists due to their interesting structural and luminescence properties. For the synthesis of $CaWO_4$ crystals different groups employ numerous methods over the years and most of them require high temperature heating. At high temperatures there is a tendency for the WO_3 group to evaporate, resulting inhomogeneous composition of tungstates. Phosphors prepared by wet chemical method have higher uniformity in particle size distribution with good crystallinity and exhibit higher photoluminescent intensity than those prepared by solid-state reaction. The metal tungstates exhibit the blue luminescent spectra, which is based on the radiative transition within the tetrahedral (WO_4^{2-}) group.

In this investigation $CaWO_4$ nanoparticles are successfully synthesized by controlled precipitation in aqueous and polyvinyl alcohol (PVA) medium at room temperature. Structural characterizations are carried out by XRD and SEM. The TGA and DTA curves of the as prepared sample showed that the crystallization is held at room temperature itself. The average particle size calculated for the $CaWO_4$ nanoparticles are 25 and 22 nm respectively in aqueous and PVA medium. The scanning electron microscopic studies showed that the surface morphologies of the $CaWO_4$ nanoparticles in aqueous medium resemble tennis balls and resemble dumbbells in PVA medium. Investigations on the room temperature luminescent properties of the synthesized $CaWO_4$ nanocrystals show strong emissions around 400 nm with light of excitation wavelength 240 nm.

Synthesis of titania nanoparticles using mesoporous molecular sieve MCM-41 as a template

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Nano crystalline titanium oxide (TiO₂) is one of the most useful oxide because of its widespread applications in photo catalysis, solar energy conversion, sensors, mesoporous membranes and in optoelectronics. The control of particle size and monodispersity of TiO₂ nanoparticles is a difficult task by using usual chemical method. The inorganic template such as MCM-41 of uniform pore size (2-10 nm) can be utilized to overcome this difficulty and one can obtain nanoparticles of uniform size. We have demonstrated here the incorporation of titanium in ethanol medium inside the uniform pores of MCM-41(Si-MCM-41) by incipient impregnation wetness method. The calcinations of the TiO₂/MCM-41 sample leads to the agglomeration of TiO₂ nanoparticles. The size of as synthesized TiO₂ nanoparticles are found in the range of 3-4 nm confirmed from transmission electron spectroscopy. The other characterizations of these composites is done by using UV-Vis, X-ray Diffraction, FT-IR, X-ray photoelectron spectroscopy, and Photo luminance Spectroscopy techniques.

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Clay-Carbon Composites

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Functionalized clay-carbon nanocomposites were synthesized by treating exfoliated clay with glucose under hydrothermal conditions. The extent of exfoliation was studied using X-ray diffraction and Transmission Electron Microscope. Metal nanoparticle embedded clay-carbon nanocomposites were also prepared by utilizing the functionalized carbon nanostructures interspersed with clay nanosheets. Generation of metal nanoparticle pillared porous structures by the removal of carbon nanostructures from the composites is under investigation.

Enzymatic depolymerization of chitosan to develop micro and nano particles

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Chitosan has received much attention as a functional non-toxic biopolymer for diverse applications, especially in the biomedical, pharmaceutical, agricultural, food and cosmetic industries. The application of this native polysaccharide is limited by its high molecular weight resulting in its low solubility in acid-free aqueous media. The low molecular weight chitosan, the product of depolymerization, shows innumerable applications in various fields, possess a number of interesting biological activities, such as antibacterial, antifungal and anti tumour properties as well as immuno enhancing effects and also been focused for the gene therapy. In contrast to chemical hydrolysis, enzymatic hydrolysis of chitosan has several benefits, and produce more readily soluble, unmodified, oligomers with a uniform degree of polymerization (DP) under milder reaction conditions. Hence the down stream processing will be minimal. It has been reported that, the proteases hydrolyse chitosan similar to chitosanase, which catalyzes the endohydrolysis of B-1, 4-linkages between D-glucosamine (GlcN-GlcN) residues randomly. The deacetylation and depolymerization of chitosan was achieved by using two types of industrially available cost effective proteases, one is subtilisin, a bacterial serine was observed in the initial one hour for both the enzymes as the reducing sugar content was increased. The chito oligomers having an average molecular weight of 51 KDa, was obtained under the optimized conditions. The degree of deacetylation of chitosan was increased to 96 % from the original 80 %, which is mainly due to the breakage of NH-CO bond in the N-acetyl glucosamine by the action of the proteolytic enzyme. The affinity of the immobilized enzyme towards the substrate increased as the K_m value decreased to 7.93×10^{-5} from 3.37×10^{-4} Moles/ml whereas and the catalytic efficiency ratio (k_{cat}/K_m) decreased to 94.1 from 158.

The subtilisin was immobilized onto high silica fabric by covalent linkage by amino silane-glutaraldehyde coupling and used in a batch as well as in a packed bed reactor. The activity of immobilized subtilisin obtained was 0.0483 IU /g of the silica cloth carrier. The immobilized enzyme retained 97% of its original activity after 10 cycles of use, showing a high reusability and stability. Continuous production of deacetylated chitosan oligomers were carried out in a packed bed reactor (size, 12 X 26 cm; weight 20.91gm; total enzyme loading 83.01 mg protein, total enzyme activity, 0.947 IU). 2% (w/v) chitosan was pumped in a continuous up-flow mode at 50:1:2 °C at different flow rates (2.28 ml min⁻¹, 0.98 ml min⁻¹ and 0.28 ml min⁻¹). The low molecular weight chitosan was used to make micro and nano particles, by carefully adding 70% methanol and 0.1 % tri poly phosphate (TPP) and an anionic surfactant under vigorous stirring condition. The microparticles were recovered by centrifugation and the nano particles were obtained after lyophilizing the solution in the presence of sucrose, which acts as a stabilizer. The chitosan particles can be used to condense DNA, immobilize enzyme, drugs, pesticides, hormones, anti bodies, nutraceuticals which can

Use of Fluorous Chemistry in the Solubilization and Phase Transfer of Nanocrystals, Nanorods, and Nanotubes

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Fluorous chemistry, involving the use of a fluorous label for the functionalization of a substrate and a fluorous solvent for extraction of the functionalized substrate, is shown to be effective in solubilizing gold and CdSe nanoparticles in a fluorous medium, through phase transfer from an aqueous or a hydrocarbon medium. While these nanoparticles were functionalized with a fluorous thiol, single-walled carbon nanotubes and ZnO nanorods could be solubilized in a fluorous medium by reacting them with a fluorous amine. Fluorous chemistry enables the solubilization of the nanostructures in the most non polar liquid medium possible.

Synthesis and characterization of silver molybdate nanorods/multipods

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Synthesis of low dimensional metal molybdates and tungstates have attracted a lot of interests due to their strong applications in various fields such as photoluminescence, microwave applications, optical fibers, humidity sensor and catalyst. Most previous approaches for preparation of these families of molybdates and tungstates need high temperature reaction conditions. Silver molybdates of the type $Ag_2Mo_4O_{13}$, $Ag_2Mo_2O_7$, and Ag_2MoO_4 were traditionally synthesized by the reaction of MoO_3 with Ag_2O . Because of high electrical conductivity, these materials found important applications in conducting glass. Hydrothermal method comes popular for environmental reason, low cost and energy saving. In this paper, we report the synthesis of silver molybdate nanorods/multipods by a simple hydrothermal approach. The effects of concentration of the precursors, reaction time and temperature on the morphology of the products were discussed. Silver molybdate nanorods/multipods were synthesized using ammonium molybdate and silver nitrate solutions taken in Teflon lined stainless steel autoclaves, sealed and maintained at 180 °C for several hours. The autoclaves were cooled and the resulted solid was retrieved from the solution by centrifugation, washed with distilled water followed by ethanol and finally dried in air. The obtained products are characterized by powder XRD, FTIR, UV-visible and SEM micrographs. Photoluminescence property of the silver molybdate nanorods has been carried out at room temperature. PXRD pattern of the sample shows a mixture of anorthic $Ag_6Mo_{10}O_{33}$ (JCPDS No. 72-1689) with lattice constants $a=7.59$, $b=8.31$, $c=11.42$ Å, $\alpha =82.6$, $\beta =102.9$, $\gamma =106.48$ and anorthic $Ag_2Mo_2O_7$ (JCPDS No. 75-1505) $a=6.095$, $b=7.501$, $c=7.681$ Å $\alpha =110.4$, $\beta =93.3$, $\gamma =13.58$. UV-visible spectrum of silver molybdate nanorods exhibits a strong absorption around 415 nm. SEM images of the sample show that the silver molybdate nanorods of about 70-580 nm thickness and several micrometers in length are identified. Room temperature photoluminescence spectrum of the sample possesses green emission at 560 nm and an intense yellow emission at 648 nm.

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Synthesis of Carbon Nanotubes using Cu-Ag Catalyst by Spray Pyrolysis Technique

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Carbon nanotube (CNT) becomes an important material on nanoscale science and technology. It has outstanding electronic (conducting or semiconducting depending on tube chirality), thermal and mechanical (~1000 GPa Young's modulus) properties. On the otherhand, CNT has a large surface area that provides plenty of sites for its good adsorption. The Cu-Ag catalyst exhibits good antibacterial properties. Hence synthesis of carbon nanotubes using Cu-Ag catalyst will perform both the antibacterial activity as well as high absorptivity.

In this research work, carbon nanotubes (CNT) are synthesised by a simple spray pyrolysis technique using turpentine oil as a source of carbon. In spray pyrolysis techniques vaporization and pyrolysis of carbon source occur simultaneously. Ar is used as the carrier gas to generate the turpentine mist in the nebuliser. The CNT growth is catalysed by a mixture of Cu and Ag nanoparticles. The effect of variation of Cu and Ag weight ratio, on the synthesis and properties of carbon nanoparticle is studied in details. All CNT are synthesised at 700°C. The CNT is analysed by Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), Raman and X-ray diffraction.

The SEM micrograph of the CNT, synthesised using mixture of Ag and Cu catalysts shows well aligned nanotubes (ANT) of ~ 60 nm outer diameter. The EDX spectra of a tube show presence of carbon along with Cu and Ag. The TEM morphology also confirmed the presence of CNT in the powder sample. The HRTEM analysis of that sample shows multiwalled solid fibre, whereas the CNT synthesized using only pure Ag catalyst are multiwalled carbon nanotubes with inner diameter of 25 nm. The presence of Ag catalyst inside the tube is also observed from the HRTEM. The Transmission Electron Diffraction (TED) pattern shows presence of <002> plane of carbon along with some unidentified planes. It is also observed that pure Cu nanoparticle is not effective for carbon nanotube synthesis. The X-ray diffraction patterns (XRD) of the catalyst as well as the CNT using the catalysts is measured. The XRD pattern of CNT show graphite peaks of carbon at $2\theta = 26.66^\circ$ (<002>) as the most dominating peak.

In conclusion, in this work, antibacterial activity of Cu-Ag catalyst has been studied. CNT has been synthesised using Cu-Ag catalyst, which can be used as antibacterial material along with high absorptivity. The work is till in progress.

Synthesis of nearly monodisperse nickel and cobalt nanoparticles in aqueous medium

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Currently, extensive research is being carried out in the field of nanoscience due to the fact that nanoparticles display properties strikingly different from their bulk counterparts. In this context, synthesis of metal nanoparticles especially those showing magnetic behaviour is further gaining importance as they have numerous applications in diverse areas like catalysis, magnetic data storage, medical diagnosis etc. Nickel and cobalt nanoparticles are being prepared by different groups using a variety of techniques like decomposition of organometallic compounds at high temperature, reverse micelle method etc. In our group, we have synthesized nearly monodisperse Ni and Co nanoparticles in aqueous medium. For this, we have followed a simple wet chemical route at an ambient temperature. Metal salts have been reduced in the presence of a surfactant and a cosurfactant to result in the corresponding nanoparticles. The selection of surfactant and co-surfactant concentration is crucial here as the fidelity of the reaction depends on it. In our experiment, sodium dodecyl sulfate and oleic acid with different concentrations have been employed for this purpose. The nanoparticles thus prepared have been characterized using techniques like Transmission Electron Microscopy, High Resolution TEM, Fourier Transform Infra Red Spectroscopy, Thermogravimetric Analysis, magnetic measurements etc. The TEM images depicted the monodispersity and uniformity of the nanoparticles synthesized at optimum concentration of the surfactant and co-surfactant. From the magnetic measurements, it was inferred that the cobalt and nickel nanoparticles prepared show superparamagnetic nature at room temperature. The HRTEM, FTIR and TGA measurements were used to understand the pathways through which the synthesis of these nanoparticles takes place. The observations made by using various concentration ratios of SDS and oleic acid and these measurements point towards the fact that the formation of micelles and their aggregation induced by metal ion addition plays a vital role in the synthesis and stability of these nearly monodisperse nanoparticles.

Nanostructured naked γ and α -Fe₂O₃

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Fe₂O₃ is an important raw material for production of hard and soft ferrite. The effect of nanosize Fe₂O₃ is well known in the synthesis of ferrites. The nanosize Fe₂O₃ is also useful for the burning catalyst in the propellant. Considering the vast applications of nanosize Fe₂O₃ in ferrite and space/ defense, the nanosize γ -Fe₂O₃ was prepared using combustion method. In this study, ferric nitrate was used as a precursor along with gelling agents. The effect of temperature on the formation of γ -Fe₂O₃ has been studied. The structural characterization of the product was performed using XRD. SEM and TEM study showed a unique naked structure morphology with particle size in the range of 45-50nm.

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Synthesis of metal nanotube arrays

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Arrays of nanowires are prepared using nanoporous membranes. Arrays of metallic (metal and alloy) nanowires are usually prepared by the process of electrochemical deposition in these porous membranes. In last decade a lot of work has been done in this field regarding the growth of metallic nanowires. However there have been very few reports of making metal nanotube arrays. Metal nanotube arrays are highly promising from the point of technology. We present a simple unique and new way of preparing metal nanotube arrays by controlled electrochemical deposition in nanoporous membranes. Copper nanotube arrays have been prepared by this method are characterized by SEM, TEM and XRD techniques. The experimental results agree with the simulation results of tube formation mechanism. The computer simulation results also predict some more interesting tubular structures like helical, spiral etc.

Wigner crystal formation in polymer nanowires

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The search for theoretically predicted Wigner crystal (WC) in one-dimensional (1D) wires of structurally disordered materials exhibiting properties of charge-density-waves (CDW) have remained unsuccessful. Based on the results of a low temperature conductivity study we report here formation of such 1D Wigner crystal (1DWC) in polypyrrole nanowires having low electron densities. The current-voltage characteristics of all the nanowires show a 'gap' that decreases rapidly as the temperature is increased confirming the existence of long-range electron-electron interaction in the nanowires. The measured current show power-law dependence on voltage and temperature as expected in 1DWC. A switching transition to highly conducting state has been observed above a threshold voltage, which can be tuned by changing the diameters of the nanowires and the temperature. Frequency dependence of the threshold voltage is consistent with the CDW characteristics. Current biased measurements shows negative differential resistance (NDR) above the threshold as expected for the sliding state of the CDW. An increase in noise has been observed in the sliding state also the noise power shows maxima as a function of applied bias, which confirms the sliding motion of the WC.

SESSION G2

SURFACE, THIN FILM, NANOCOATING APPLICATIONS ETC.

Preferential reactivity of the surfaces of gold nanorods and their conversion to particles through other anisotropic structures

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We report the shape transformation of gold nanorods to spherical nanoparticles, assisted by cupric ions. The reaction proceeds through a series of transient structures. In the presence of a larger concentration of cetyltrimethylammonium bromide (CTAB), selective etching of the tips of the nanorods occurs to a greater extent, although the rod body also undergoes etching. The subsequent transformation is driven by the surface reconstruction of nanorods so as to generate more stable surfaces. As the stability of various planes depends on the protecting agent used, the reactivity is modified by controlling its presence at the surface. We show that the body of the rods is more susceptible for reaction at reduced CTAB concentrations. The process of reaction leads to several anisotropic transient structures which were imaged using high resolution TEM. The transformation occurs due to the hydroxyl radicals produced by Cu^{2+} in presence of ascorbic acid. Several control experiments were conducted and a mechanism has been proposed. The cupric ion induced shape transformations can be extended to other ions and knowing the mechanism allows the control of the process to stabilize various anisotropic structures.

Control of Residual Stress in Nano – structured PVD coatings

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Sputter deposition using planar magnetron is utilised to fabricate variety of coatings. Most of the functional properties of these coatings (for eg. Hardness) are enhanced if the crystallite size is reduced. However these coatings tend to develop a high amount of residual stress which results in their delamination from the substrate surface. Annealing the substrate either during deposition or after deposition significantly reduces the developed stress, but as temperature favors grain growth, many of the functional properties are adversely affected.

Bombardment by energetic ions during the time of deposition is found to relieve residual stress in these coatings. The sputtered target atoms are neutrals and it is not possible to control their flux to the substrate unless they are ionised. Biasing the substrate to a suitable voltage, DC or negative pulse, will increase the energetic ion flux to the substrate. In the present investigation, an additional plasma source (inductively coupled RF plasma), is introduced between the planar magnetron and the substrate. It is expected that the RF auxiliary plasma will ionise a fraction of the sputtered neutral atoms and a suitable substrate bias will energise them, increasing the flux of energetic particles bombarding the substrate surface. The coatings are characterized using X-Ray Diffraction (XRD) techniques.

In the present investigation, copper was used as the target material in the magnetron and Lexan as substrate. Copper coatings were deposited for the same duration (1 hr.) with various deposition conditions. The coatings were characterised using XRD techniques. The shifting of the peak positions indicated the nature of the residual stress. Information regarding the microstructure of the film were obtained using the Williamson – Hall integral breadth method. Proper corrections to account for the instrument broadening were applied using a Silicon standard crystal. All coatings show presence of compressive stress, as indicated by the shift towards the lower 2θ side in the XRD data. The combination of auxiliary plasma and substrate bias produces coatings with highest shift, and therefore having the highest value of compressive stress. Also it is observed that the crystallite size is larger as compared to other coatings, indicated by narrower peaks. The shift in the peak position indicate the amount of compressive stress present in the coatings. It is concluded that the auxiliary plasma influences the microstructural properties of the coatings and significantly controls the formation of residual stress in the coatings. Hence it is possible to deduce that a proper combination of substrate bias along with the auxiliary plasma can be employed to control the formation of residual stress in PVD coatings.

Nanocomposite $\text{Nd}_{4.5}\text{Fe}_{77-x}\text{Mn}_x\text{B}_{18.5}$ alloys for permanent magnet applications.

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Nanocomposite magnets composed of hard and soft magnetic phases with grain size in micrometer range exhibit excellent permanent magnetic properties. These materials, also known as exchange coupled magnets have attracted considerable interest in recent years. Strong coupling between the soft and hard magnetic grains leads to a high remanence in these materials, which is otherwise not achievable in fine grained isotropic magnets. A nanocomposite consisting $\text{Nd}_2\text{Fe}_{14}\text{B}$ hard magnetic phase along with $\text{Fe}_3\text{B}/\text{Fe}$ soft phase(s) has been studied in the recent past. Magnetic properties and the degree of exchange coupling in nanocomposite magnets are strongly dependent on microstructural parameters, such as crystallite size, phase distribution and volume fraction of the hard and soft magnetic phases. Efforts are being made to synthesize these magnets by melt-spinning, mechanical milling, thin film techniques etc. It has also been suggested that some magnetic as well as nonmagnetic additives can improve the desired properties further.

In the present study, the effect of partial substitution of Mn for Fe on the magnetic properties of $\text{Nd}_{4.5}\text{Fe}_{77-x}\text{Mn}_x\text{B}_{18.5}$ ($x = 0, 1, 2, \& 5$ at %) melt spun ribbons has been studied using differential scanning calorimetry, X-ray diffraction and magnetic property measurements. The samples were prepared by single role melt spinning as amorphous ribbons followed by heat treatment to develop a nanocrystalline microstructure. The crystallization temperature and thermal stability of amorphous phase is found to decrease on the Mn addition. X-ray diffractograms confirm the presence of the hard magnetic $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase and soft magnetic $\text{Fe}_3\text{B}/\text{Fe}$ phase(s) in the heat treated alloys. Enhancement of coercivity (H_c) and remanence (M_r) was observed for 1 at% of Mn addition. $\delta M-H$ measurements exhibit the presence of strong exchange coupling between $\text{Nd}_2\text{Fe}_{14}\text{B}$ and Fe_3B phases in the nanocomposite magnet. The Effect of annealing on the magnetic properties of these alloys are presented and discussed with respect to the Mn contents,

Laser Surface Modification Of Ti-13Nb-13Zr Using Nano TiO₂

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Titanium alloys are widely used in aerospace, marine, medical devices etc mainly because of their excellent specific strength and good corrosion resistance. However they are currently restricted to non-tribological applications owing to their poor friction and wear resistance. To overcome the above problem, presently nano TiO₂ and nano Al₂O₃ coatings are being given to the biomedical alloy Ti-13Nb-13Zr, using laser. We expect improved tribological properties of the above alloy. The microstructure and variation in the mechanical property such as hardness of the surface modified materials will be presented in this paper.

Electrochemical supercapacitors based on carbon nanotubes and related materials

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Electrochemical capacitances of various types of carbon nanotubes have been examined. Single-walled carbon nanotubes possess the highest double-layer capacitance of ~ 64 F/g. We have studied nanocomposites of SWNT with conducting polymers such as polyaniline and polypyrrole and significant enhancement (400-500% increase) in the capacitance has been observed. Several other nanostructures are being examined for supercapacitor applications.

Tuning the Size and Optical Properties in Molecular Nano/micro Crystals

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Fluorescent molecular crystals in the nano and micro size regimes form a thrust area of contemporary research because they are amenable to considerable variability and flexibility in terms of materials synthesis and nanoparticle fabrication and are promising materials for several optical, nonlinear optical and biological applications. Materials which exhibit strong fluorescence in the solid state are of great current interest in view of their potential application in the field of light-emitting diodes (LEDs) and sensors. The fabrication of novel molecular nanoparticles and exploitation of their size-dependent optical properties are of interest from the fundamental and application perspectives. The origin of the size-dependence of the optical properties in molecular nanocrystals is a relatively less explored area. We are investigating primarily, the fabrication of novel molecular nanomaterials and their size-dependent optical properties. We have developed a simple protocol to fabricate nano/micro crystals of a series of novel zwitterionic diaminodicyanoquinodimethane molecule which show a range of interesting size dependent photophysics. We have focused attention on 7,7 -bis(4-chloroanilino)-8,8-dicyanoquinodimethane (BCADQ). Crystal structure and microscopy characterizations, spectroscopic investigations and semi empirical quantum chemical studies lead to a viable model which espouses the progressive manifestation of hierarchical intermolecular interactions in these molecules. We have also investigated the solid state fluorescence property of tris(4-cyanophenyl)amine (TCP A). It shows strong blue fluorescence in the solution as well as in the colloidal and solid state. We have fabricated highly monodisperse nano/microcrystals of TCPA with well-defined morphology. Based on crystal structure and computational investigations the strong fluorescence in the colloids and solid state are attributed to J-aggregate structures. Preliminary explorations indicate that the molecular nano/micro crystals developed in our study are of potential interest in nonlinear optical applications such as optical limiting.

Adhesion And Mechanical Investigations of Nanostructured Si-C-N Thin Film Deposition by RF Magnetron Sputtering at Different Substrate Temperatures

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Nano-composite ternary Si-C-N materials have recently drawn interest due to its potential novel properties compared to those of crystalline Si_3N_4 and SiC mixture. These materials can possess properties such as high hardness, wide band gap characteristics, a wide transparency window, promising field emission characteristics, high temperature oxidation resistance, chemical inertness and promising wetting behaviour.

Although various deposition techniques like PECVD (Plasma enhanced chemical vapour deposition), Pulsed laser deposition (PLD), Ion Beam sputtering deposition (IBSD), Magnetron Sputtering etc. have been used to prepare nanocrystalline Si-C-N compounds as low temperature depositions, better adherence and easy scaling up is possible. Moreover it is comparatively much cleaner process. The present paper discusses the deposition of nano-SiCN thin films deposited by RF Magnetron sputtering from SiC target under Ar/ N_2 atmosphere of 1×10^{-2} mbar in plasma at different substrate temperatures (100-500°C) on different technologically important substrates such as silicon, glass and steel. Si-C-N

Nano-composite coatings are potential materials for wear resistance and high temperature applications. Beside the effect of different microstructure evolution, understanding of mechanical and adhesion behaviour for such nano-composite thin film is still under investigation. Adhesion, mechanical and film failure behaviour are very important for actual application of the coatings.. Failure of the film occurs when the coating starts to get peeled of from the substrate. The failure behaviour of the coatings is dependent on the hardness of both the coating and the substrate. This process can be quantified in terms of the critical load if we can detect the abrupt change of tractional force taking place during this event. In the present investigation the adhesion behaviour of nano-composite SiCN thin film on silicon, steel and glass substrates deposited at different substrate temperature is reported. The film thickness was measured of the order of 2.4-8.4 micrometer depended on the deposition conditions. Nanoindentation studies showed hardness and modulus values of 21GPa and 230 GPa respectively. TEM & AFM studies revealed amorphous nature of SiCN film when deposited at lower temperatures (up to 100°C) but at higher temperature (500°C) films showed crystalline grains in amorphous matrix. $\beta\text{-C}_3\text{N}_4$ phase formation was confirmed An appreciable critical load between 2-24 Newtons was required to detach the films from the substrate which was very much dependent on substrate temperature.

Development Of Multilayer Nanocomposites for Data Storage Applications

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In the last two decade; recording media technology has been continued to change from particulate to thin film media, because of better magnetic properties and resulting recording media. Recording media is composed of several layers, each of which has its own specific role to play in the production of magnetic recording media. The top magnetic layer is in contact with underlayer which in turn is in the contact with seedlayer, if present on the substrate. The conventional substrate material is Al-4%Mg alloy. But we had used Glass substrates because they are considered to be superior to aluminum-4%Mg alloy for lower flying height, which gives enhanced signal to noise ratio. One of the most successful seed layer so far is Ni-Al. But we used Ni-P as seed layer on glass substrate. Although Ni-P seed layer is deposited widely by sputtering by many researchers, but we preferred to use the process of electroless coating in acidic medium. Since the cost involved in seedlayer formation is cheaper, when compared to the sputtering and also it is easy to vary phosphorus content of Ni-P coating in Electroless technique. We used acidic medium for seedlayer formation since the amount of Phosphorous content in the Ni-P layer is more than when it compared with phosphorous content in alkaline medium for the composition of electroless bath. We preferred the deposition of Ni-P seed layer at different temperature to vary the phosphorous content and to examine how the content of phosphorous influences the microstructure and magnetic properties of the resulting storage media. Also we need more phosphorous content to make thin Ni-P layer in amorphous state, which is able to control the crystallographic texture and grain size of the underlayer. The underlayer is the key layer to control the grain size and preferred orientation. The best underlayer for HCP structure Co alloy is a Cr alloy with BCC structure.

In this study, first we deposited amorphous Ni-P on glass substrate by Electroless technique at different temperatures and then characterized Ni-P coating on glass substrates with the help of scanning electron microscope (SEM) images, Atomic Absorption Spectroscopy (AAS) and XRD. AAS was used to find out the composition of Ni-P coatings. In this investigation we found that with increasing electron microscope (SEM) images, Atomic Absorption Spectroscopy (AAS) and XRD. AAS was used to find out the composition of Ni-P coatings. In this investigation we found that with increasing temperature, phosphorus content was decreasing. For the preparation of sample, we then sputtered Cr, Co respectively on glass substrate. Then the role of amorphous Ni-P containing different amount of phosphorus content as a seedlayer in Co/Cr/glass substrate thin film media had been studied at two different argon pressures of sputtering chamber. It has been found that varying both the phosphorus content of amorphous Ni-P seedlayer as well argon pressure in sputtering chamber has a strong effect on grain size reduction. Both scanning electron microscope (SEM) images and XRD pattern images reveal a large reduction of the average grain size of the resulting media, which means an increase in recording density.

Effect of surface alloying on the surface plasmon properties of composite films of Ag-Cu nanocrystallites embedded in DLC matrix

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Diamond-like carbon films containing Ag and Cu in nanocrystalline form were deposited onto SnO₂-coated glass substrates by using electrochemical technique. Salts containing silver and copper in the electrolyte and the current density were adjusted to obtain films with different crystallite size while the volume fraction of the metal nanocrystallites were altered by varying the dilution of the solution containing the salts. Raman studies indicated the presence of two peaks located at ~1350 cm⁻¹ (D-line) and 1566 cm⁻¹ (G-line) for all the films and the relative intensity of these peaks changed with the amount of metal incorporation in it. The FTIR spectra were seen to be dominated by a peak at 975 cm⁻¹ for C-H out of plane deformation along with peaks for C-H bending, C-H stretching and C-C stretching modes at 858 cm⁻¹, 1113 cm⁻¹ and 1189 cm⁻¹ respectively. The optical absorption spectra of these nanocomposite films showed a single plasmon band instead of two characteristic bands for Ag and Cu. We ascribe this alloying to the interfacial reactions in nanophase limited at the Ag-Cu interface. The peak position shifted significantly to higher wavelength region from both the peak positions of individual constituent metal nanoparticles. This clearly indicates that the free electrons from the individual nanocrystallites participating in plasmon resonance lose their individual identity. Experimentally observed surface plasmon band could be faithfully explained by the Mie theory with the incorporation of the modifications of the expression for the dielectric constant and the refractive index.

Controlled growth of ZnO nano-dots to nano-rods and their optical properties

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We report synthesis and optical properties of ZnO nanocrystals and controlled growth of nanorods using these crystals as the seed. The size and microstructure of the nanocrystals (avg. size 5-20 nm) obtained by chemical route are determined by Transmission electron microscope (TEM) and X-ray diffraction (XRD) analysis. Nanocrystals show excitonic emission in the UV region (~365 nm) as well as strong luminescence in the blue green region (~540 nm) arising from defect states. The intensity of visible emission is very sensitive to the excitation energy, size and surface modification of the nanocrystals.

These nanocrystals of various sizes are then used as seed layer for the controlled growth of single crystal ZnO nanorod (dia~100-400 nm) via self assembly of ZnO nanoparticles. Seeding by the nanocrystals is responsible for the growth of aligned nanorods of various average diameters as seen by the Scanning Electron Microscope (SEM) and XRD analysis. Effects of other growth parameters such as growth time and growth temperature are also investigated. These nanorods have band gap of 3.3 eV as in the case of bulk crystals and show sharp excitonic emission in the blue region (405 nm). The visible emission at 540 nm is not seen, unlike the ZnO nanocrystals. When excited with the sub band gap energy (~355 nm), visible emission in the blue region (434 nm) is observed. Our observations are important in the viewpoint of realizing ZnO based heterostructures and superlattices for many optoelectronic applications.

Enhanced electrocatalytic reduction of oxygen on a poly(o-phenylenediamine) modified carbon nanotube electrode

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Carbon nanotube modified glassy carbon electrodes are being rapidly exploited in the development of electrochemical biosensors and also in other electroanalytical applications. Particularly, the advancements accomplished towards the functionalization of carbon nanotubes resulting in their enhanced solubilization in aqueous solutions have helped in the preparation of stable carbon nanotube electrodes. Composites of carbon nanotubes with several conducting polymers have been prepared using a variety of chemical and electrochemical polymerization techniques and have been shown to exhibit superior performance especially in hybrid – supercapacitors, electrochemical sensors and photovoltaic devices.

There have been some recent reports on the reduction of oxygen at carbon nanotube modified electrodes. To our knowledge, there has been only one very recent report on the use of a conducting polymer modified carbon nanotube electrode for oxygen reduction. Recently, we have reported that a nearly a seventy fold increase in the oxygen reduction current could be obtained on the platinum nanoparticle incorporated poly(o-phenylenediamine) electrode compared to bulk platinum electrode. In this presentation, it is proposed to highlight some new results obtained for the reduction of oxygen at a poly(o-phenylenediamine) modified carbon nanotube electrode.

Commercial sample of multiwall carbon nanotubes was functionalized by a simple oxidative acid treatment to prepare an aqueous dispersion. A known quantity of the dispersion was then cast on a glassy carbon electrode. Poly (o-phenylenediamine) was then electrodeposited on the carbon nanotube electrode. The morphology of the deposit was studied by SEM. The reduction of oxygen was studied on bare glassy carbon, carbon nanotube modified glassy carbon, poly(o-phenylenediamine) modified glassy carbon and poly(o-phenylenediamine) modified carbon nanotube electrodes. The cyclic voltammetry and chronoamperometry data indicate that the poly(o-phenylenediamine) modified carbon nanotube electrode is the best electrocatalyst among the four electrodes studied by showing a favourable potential shift of more than 500 mV and a five-fold increase in current. Rotating disc electrode voltammetry was used to determine the number of electrons involved in the charge transfer as two. The electrocatalytic effect is due to the synergistic effect of the carbon nanotube and poly(o-phenylenediamine) which is explained on the basis of a polymer redox mediated reaction.

SESSION P1

POSTER PRESENTATIONS – NSTI PROJECTS

Carbon Nanotubes and Graphene: What is new?

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This talk will bring out our new results on single walled carbon nanotubes (SWNT) and recently discovered Graphene. We will address the question if water enters the nanotubes and what is its dynamics. We will show that the dynamics is single file diffusion. The second part of the talk will discuss our recent experiments on the electronic transport in the SWNT in the field effect transistor geometry. In-situ Raman experiments as a function of gate voltage to tune the Fermi level will be described. The last part of the talk will describe our most recent results on the Raman fingerprinting of single and a few layers of Graphene.

Phase transformation in embedded nanoparticles produced by non-equilibrium processing

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The interfaces influence the phase stability of small particles. For embedded particles, the interface among the phases present within the particles and the matrix contribute significantly to the free energy and hence influences the phase stability at small sizes. Our results show that upon rapid cooling, we obtain a combination of larger two-phase alloy particles consisting of β - and γ - phases and very fine precipitates of In or Sn. The insitu results suggest that the β -rich phase gradually dissolves before melting and the particles retain the facets much above the melting temperature of the alloy particle. In case of two phase lead-tin alloy of nanometric sizes, electron diffraction studies coupled with composition analyses reveals that the two phases corresponding to Pb and Sn respectively separated by a structurally sharp interface. However, compositionally the interface is diffuse and asymmetric with broadening in the Sn side. During heating the two phases intermix and gradually yield to a single phase solid solution which melts at higher temperature.

In an alternate strategy, Two phase microstructure consisting of a fine dispersion of bismuth metal particles in a silver matrix was achieved by mechanical alloying. The estimates of average crystallite size using X-ray diffractometry indicate a size reduction of Bi and Ag grains to 15nm respectively. The measured Ag lattice parameter indicates the formation of solid solution after 12 hours of milling. Thermal analysis of milled samples showed two distinct melting events. The two peaks can be identified with melting of elemental Bi and eutectic melting of Ag-Bi alloy. The results can be directly correlated with the formation of the interphase interface during milling of the elemental mixtures.

Conductance Properties of Nanoscale Devices and Stability of Nanoclusters

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Systems at the nanoscale provide exciting and novel challenges for understanding the structure and property relationship. A major focus in the field of nanoelectronics is to design single-molecular electronics. Based on our theoretical studies, we have been able to elucidate the parameters that will enhance the conductance in single-molecular devices. Our model explains the recent observation of negative differential resistance (NDR) in oligo-phenyl-acetylenes. We have also made a significant contribution towards the design of novel nanoclusters with large electronic and spin delocalizations. These clusters have been studied for advanced non-linear optical properties. We are also actively involved in the processes of electron transfer within DNA base-pairs. The theoretical calculations on these systems will be discussed in details.

Synthesis and photocatalytic activity of nano TiO₂ and nano Ti_{1-x}M_xO₂

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Nanocrystalline TiO₂ and TiO_{1-x}M_xO_{2-δ} (M = Pd, Pt, Ag, Cr, Mn, Fe, Co, Ni, Cu, Rh, Ru) are synthesized by solution combustion using titanium nitrate solution and glycine as the fuel. TiO₂ doped with metal ions crystallize in anatase phase for small concentration of M ions. Structure is confirmed by XRD and Rietveld analysis. Photocatalytic degradation of methylene blue, rhodamine B, rhodamine B base and pigment violet with pure titania and metal substituted titania were studied under UV exposure. Rate of photocatalytic degradations of pollutant dyes is generally lower with transition metal substituted TiO₂. Lower photocatalytic activity is correlated with lower photoluminescence of Ti_{1-x}M_xO₂ compared to TiO₂. This is due to finite electron density of M (*d*) electrons in the band gap of TiO₂. However, 1 atom % Pd²⁺/TiO₂ in the form of nano Ti_{0.99}Pd_{0.01}O_{1.99} with oxide ion vacancy shows better NO reduction by CO than unsubstituted TiO₂ as well as Pd metal impregnated nano TiO₂.

The photocatalytic NO_x reduction by CO at room temperature with UV light was investigated. The optimum concentration of Pd in TiO₂ was found to be 1 atom %. The reduction of NO was carried out both in presence and absence of CO. Despite competitive adsorption of NO and CO on the Pd²⁺ adsorption site, the reduction of NO was two orders of magnitude higher than the unsubstituted TiO₂. A detailed mechanism and kinetics was developed to model the experimental data. It was shown that enhanced CO oxidation at Pd²⁺ ion sites and O₂ or NO photo dissociation at oxide ion vacancy is responsible for the enhanced catalytic activity. Nano Ti_{0.99}Pd_{0.01}O_{1.99} is only material which shows high photo dissociation and photo reduction of NO_x at room temperature. Photocatalytic reduction of NO with Ag⁺ substituted TiO₂ also showed higher rates compared to TiO₂.

Stability and fluctuations in metallic nanowires and interconnects

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We are investigating the stability of metallic interconnects of lateral dimension from submicron to few tens of nanometer for use as leads and as interconnects. The material used for the work has been grown by vapor phase (grown in UHV chamber using effusion cell) as well as electrochemical route and uses template as well as e-beam lithography. The films and nanowires were extensively characterized by XRD, SEM, TEM and electrical measurements.

We have used these wires as leads for electric field directed growth of nanowires. We have investigated the stability of these nanowires when they carry a D.C current using noise spectroscopy as well an in-situ method using a Scanning thermal microscope. we made a direct observation of the evolution of temperature inhomogeneity and the resulting atomic migration in a metal film (Ag on Si)stressed by a direct current. The experiment was carried out by stressing the film and imaging it with a Scanning Thermal Microscope that allows simultaneous temperature map as well as topography imaging when the film is being stressed. We observe that the temperature of the film becomes significantly non-uniform over time due to current stressing and this inhomogeneity nucleates atomic migration leading to creation of voids and hillocks. Significant damage (as measured by resistance) occurs when there are appearance of regions with significant temperature deviations form the mean temperatures.

We have also investigated fluctuations and stability of nanowires grown in templates. In this presentation we show that mesoscopic fluctuations leads to instabilities in metallic nanowires. These fluctuations in turn lead to noise in electronic conduction in these nanowires. We detect these excess noise and the mesoscopic fluctuations through sensitive noise measurements as well as direct observation through TEM .The experiments were carried out in Ag and Cu nanowires (with diameters down to 15nm). The wires were single crystalline and have only twinning defects as revealed by TEM. We found that at higher temperatures (~220K) large electrical noise sets in which we explain as arising from Rayleigh instability and confirm that from TEM images. At much lower temperatures (30K-50K) we detect yet another instability that arise due to martensite strain accommodation in these FCC metals which in certain diameter ranges show an additional 4H phase.

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Synthesis, Characterization and Application of Nanosized Oxide Materials

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The studies carried out on the products obtained by the hydrothermal and the combustion routes are discussed separately as part I and part II.

Part I: In the present investigation, hydrothermal method has been used for the preparation of ZnO, MoS₂ and CdSO₄ nanomaterials by varying the precursors' concentration, temperature and duration. These nanomaterials were characterized using XRD, UV-visible spectroscopy, photoluminescence and XPS. UV-visible spectrum of the ZnO nanorods shows blue shift compare to bulk ZnO. Photoluminescence spectra show strong UV emission at different wavelengths. XPS results show the peak positions of S(2p) and Mo(3d_{5/2}) for MoS₂ is in good agreement with reference to MoS₂ powder. CdSO₄ nanotubes/wires prepared at 180 °C for several hours possesses an intense UV emission at 372 nm compared to the bulk CdSO₄ (392 nm).

Part II: The porous nanocrystalline metal oxides; MgO, CaO and ZnO have been prepared through combustion process using metal nitrates as oxidizer and glycine as fuel. These simple combustion derived metal oxides are employed as adsorbents for the removal of fluoride in ground water and, COD and colour from industrial effluents. From the result it was found that the fluoride removal capacity of combustion derived nanocrystalline MgO (as made) is ~ 97%. It is observed that the COD removal from paper mill effluents by combustion derived nanocrystalline CaO is ~ 93 %. As prepared nanocrystalline MgO was also employed as adsorbent for the removal of colour and COD from the paper mill effluents.

Perovskites such as LaMnO₃ and La_{1-x}A_xMnO₃ (where A= Ca, Sr and Ba) have been prepared by low temperature combustion process using corresponding metal nitrates as oxidizers and oxalyl dihydrazide (ODH) as fuel. The crystal structure of manganites is directly correlated to Mn³⁺/Mn⁴⁺ ratio. The Mn⁴⁺ content in as-formed samples is high (~34 %) and this favors cubic phase. In calcined (900 °C, 6 h) samples, Mn⁴⁺ content is reduced to ~ 28 % and resulting into rhombohedral phase. A broad exothermic peak around 900 °C in differential thermal analysis (DTA) curve and gradual weight loss from 650 °C in thermo gravimetric (TG) curve is correlated to the reduction of Mn⁴⁺ to Mn³⁺. The SEM micrographs of combustion derived samples show that the powder products are voluminous and porous. As a result of high temperature (>1000°C) during combustion process and partial sintering, agglomerated circular shaped primary crystallites were formed.

The combustion derived samples exhibit a broad metal-insulator transition including LaMnO₃. The T_{M-I} values are shifting to lower temperature side on doping and these values are lower compared to the samples prepared by high temperature method (solid-state). The MR measurement is carried out on sintered pellets in a liquid helium cryostat vary from 300 K down to 70 K with magnetic field vary from 0 - 7 T. It can be seen that the resistance decreases with increasing magnetic field and that of T_{M-I} shifts towards higher temperature due to magnetic field induced delocalization of charge carriers.

Magnetic and Electrical Properties of Novel Nanostructured Magnetic Materials

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The magnetic properties of permanent magnetic materials such as $\text{Nd}_2\text{Fe}_{14}\text{B}/\alpha\text{-Fe}$ and $\text{Sm}(\text{Co}, \text{Fe}, \text{Cu}, \text{Zr})_7$ and also the magnetic and electrical properties of nanostructured Ni-Zn, Mn-Zn and Co- spinel ferrites are reported in this paper. The influence of grain boundary anisotropy on the exchange coupling and the maximum energy product of the nanocomposite $\text{Nd}_2\text{Fe}_{14}\text{B}/\alpha\text{-Fe}$ and the effect of grain size on the coercivity of $\text{Sm}(\text{Co}, \text{Fe}, \text{Cu}, \text{Zr})_7$ will be discussed. The role of grain size and the cation distribution on the magnetic, electrical conductivity and dielectric properties of Ni-Zn, Mn-Zn and Cobalt spinel ferrites has been studied in detail using various techniques such as impedance analysis, Mössbauer spectroscopy, EXAFS and thermal analysis and the results are presented.

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Functionalized carbon nanotube for chemical and biosensor

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In the past decade, the rediscovery of carbon nano tubes has opened new frontiers in the field of nano technology and nano science. The unique structural, mechanical and electronic properties of CNTs were initially exploited in the field of material science. Depending on their atomic arrangements, CNTs behave electrically as metal or as a semiconductor. The subtle electronic properties, the excellent conductivity, the high aspect ratio and the large specific area suggest that CNTs have the ability to enhance the electron transfer reactivity when used as an electrode material in chemical sensors and nanoscale electronic devices. Most of these applications require targeted chemical modifications of the nanotubes, e.g. to make the tube surface compatible with polymer matrices, to avoid bundling of tubes if high surface-area is desired, to link tubes together for active circuits in nano electronics.

Thus functionalization of carbon nano tubes were carried out to introduce functional groups such as -COOH, to which different redox mediators like toluidine blue, thionin and neutral red were coupled through an amide linkage using thionyl chloride and carbodiimide routes in this study. The functionalized carbon nano tubes were characterized by scanning electron microscopy (SEM), Transmission Electron Microscopy (TEM), Fourier Transform Infrared Spectroscopy (FTIR), UV-visible spectroscopy, Diffuse reflectance UV-vis spectroscopy (DRUV) and by thermal analysis. Modified electrodes were fabricated through mechanical immobilization of the functionalized carbon nano tubes for the construction of chemical sensors. Electrochemical characterisation of the modified electrodes was carried out with cyclic voltammetry. The modified electrodes were employed for the catalytic reduction of hydrogen peroxide. The parameters such as scan rate, pH and background electrolyte were optimized for the determination of H_2O_2 . Methods have also been developed for the application of these modified electrodes in flow systems for the determination of H_2O_2 . The modified electrodes have been applied for the determination of H_2O_2 in real samples also.

Functionalized nanotubes will be further immobilized with enzymes like glucose oxidase (GOx), Horse Radish Peroxidase(HRP) and laccase for Biosensor Fabrication. The redox mediator and enzyme incorporated carbon nanotubes will be mixed with silane precursors to get composite material. This composite material will be transferred to electrode surface and the electrodes will be characterized by electrochemical techniques. Based on the results, amperometric sensors will be developed for the determination of compounds of environmental and biological interest.

Enhanced catalytic activity of nanoscale platinum Islands loaded on SnO₂ thin film for sensitive LPG gas sensors

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The recent emergence of concern over environmental pollution and accidental leakages of explosive gases has increased awareness over a need to monitor such gases. To meet this demand, considerable research into the development of sensors using novel design and tailored material properties is underway. Consistent efforts have been made to enhance the performance of semiconductor metal oxide gas sensors through nanoengineering. Besides metal oxides, metal nano particles as a catalyst have attracted much attention for vapor- and gas-sensing applications. Recently as the usage of LPG gas has increased, the frequency of accidental explosions due to leakage has also increased sharply. From the available literature it is inferred that LPG gas sensors are based on tin oxide materials and show a low sensitivity (ranging from 2-20) operating at high temperatures (320 – 800 °C).

In the present study different catalysts (~10nm thick) including metals, noble metals and their oxides were loaded in dotted islands form over SnO₂ thin film for LPG gas detection. Platinum dotted islands over SnO₂ thin film deposited by rf sputtering not only enhanced the sensitivity (~ 742) but also reduce the operating temperature (~280 °C). Different characterization techniques have been employed, such as Atomic Force Microscopy (AFM), X- Ray diffraction (XRD) and UV-VIS spectroscopy, to study the surface morphology, grain size and optical properties of the deposited film. The results suggest the possibility of utilizing the sensor element with novel dispersal of catalyst for the efficient detection of LPG. The sensor response speed characteristics as a function of varying concentration of LPG have been studied.

Metal oxide/polyaniline nanocomposites: Cluster size and composition dependent structural and magnetic properties.

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The properties of magnetic nano particle system are known to be dominated by the size of individual nano particle, cluster size of these particles and the magnetic interparticle interactions. The role of magnetic interparticle interactions can be best probed in particles dispersed in matrix where the volume concentration can be systematically varied.

Nanocomposites of iron oxide, Nickel Ferrite/ conducting polymer in the form of powder and self standing sheets with varying compositions have been studied to understand the above variations. Single crystalline phase viz α - Fe_2O_3 and NiFe_2O_4 were observed through X-ray Diffraction (XRD). The presence of conducting polymer was confirmed through fourier transform infrared spectroscopy. The amount of polymer present in the composite, the transition temperature of iron oxide and thermal stability of polymer was determined through thermo gravimetric and Differential Thermal Analysis. The degradation temperature of polymer was higher for self-standing sheets as compared to powders. The transition temperature of iron oxide (ferromagnetic to paramagnetic phase) was found to decrease in its composite form. The particle size was estimated to be 10-20nm from the XRD and Transmission Electron Micrographs. The cluster size was found to reduce with increasing polymer concentration and chains of particles were observed for a particular concentration. Fibrous structures were observed for polymer films where as clusters were observed for composite films as seen from the Scanning Electron Microscopy. The room temperature magnetic hysteresis measurements show reduction in saturation magnetization with increasing polymer concentrations. The low value of coercivity ~ 160 Oe was observed for low polymer composites. On increasing polymer concentration the coercivity and remanence becomes negligible indicating super paramagnetic phase. Susceptibility measurements show a reduction in blocking temperature with increasing polymer concentration. Beyond a certain composition, system shows paramagnetic behavior. This is also confirmed through zero field cooled-field cooled measurements.

Investigation of complex metal - based nanosize oxides synthesized using the reverse micellar route

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Transition metal oxide nanoparticles have been obtained by the controlled decomposition of nanorods of transition metal (Cu, Ni, Mn, Zn, Co and Fe) oxalates. These nanorods have been synthesized using a reverse – micellar technique. These oxalate nanorods have been shown to be an ideal source for obtaining monophasic and homogeneous nanoparticles of the nanosize oxides at low temperatures of 450°C. Grain size of oxide nanoparticles could be controlled by optimizing the nature of non-polar solvent and surfactant. The metal oxalate precursor could be decomposed in suitable environment to yield various metal oxides as single phases (from the same precursor), for example, from the Mn-oxalate precursor, the following oxides could be obtained as nanoparticles (MnO, Mn₂O₃ and Mn₃O₄).

A modified route (with neutral surfactants) using reverse micelles, avoiding the expensive metal-alkoxides, has also been developed to obtain a large number of dielectric oxide nanoparticles like MTiO₃ and MZrO₃ (M = Sr, Ba, Pb). A detailed study of the entire solid solution of nanosized particles of Ba_{1-x}Pb_xZrO₃ (0 < x < 1) has been investigated and there is found to be a maximum dielectric constant at the X=0.5 composition. Our studies show marginal increase in size of the nanocrystalline grains on sintering even at temperatures of 1200°C. Apart from oxide nanoparticles we have also obtained chalcogenides and bimetallic alloy nanoparticles.

Growth and Study of Aging Phenomenon in CdTe and CdS_xSe_{1-x} Quantum Dots Embedded in Borosilicate Glass Matrix

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The quantum dots (QDs) of group II-VI compound semiconductors embedded in glass matrix have drawn considerable attention due to their strong nonlinear optical properties, ultra fast response time, and high potential for developing new optoelectronic devices such as optically bistable elements, optical switches, transistors, modulators, laser diodes, optical harmonic generators and optical memories. To enhance the non-linear optical properties of these QDs, the average size of the quantum dots should be smaller than exciton Bohr radius (a_B), their size dispersion should be low and the volume fraction should be high. In the present paper, quantum dots of CdTe and CdS_xSe_{1-x} embedded in borosilicate glass matrix have been grown using Double-Step (DS) annealing method with optimized growth parameters, viz. annealing temperature and annealing duration. Optical characterization of the QDs has been done through the combinative analysis of optical absorption and photoluminescence (PL) spectroscopy at room temperature. The optimum nucleation temperature for CdTe was found to be 550°C and optimum annealing duration 16 Hrs. For CdS_xSe_{1-x} these figures were found to be 475°C and 72 Hrs, respectively. After the nucleation process was completed CdTe samples were annealed at 590°C for 16, 32 and 54 Hrs to obtained QDs of various size and different volume fraction. Similarly, CdS_xSe_{1-x} samples were annealed at 575°C for duration 3, 5, 7 and 9 Hrs. For comparison, the CdTe and CdS_xSe_{1-x} QDs were also grown using conventional Single-Step (SS) annealing method. The radii of quantum dots, number of quantum dots, volume fraction and Gibbs free energy of quantum dots have been estimated by comparing the experimental absorption curves with the curves generated using Effective Medium Theory. It has been shown that QDs grown using DS annealing have lower average radius, strong quantum confinement, lesser size dispersion, higher volume ratio and higher decrease in bulk free energy as compared to quantum dots grown conventionally. The size dispersion of typical CdTe quantum dot sample decreases from 12.9% (SS) to 11.7% (DS). Aging studies on various parameters of CdS_xSe_{1-x} QDs in semiconductor doped glasses (SDGs), such as, changes in particle size, size distribution, number of quantum dots, volume fraction, trap related phenomenon and Gibbs free energy of quantum dots, have been explained on the basis of the diffusion-controlled growth process, which continues with passage of time even at room temperature. It has been seen that the system attains almost a stable nature after 24 months of aging. Annealing study shows that the size-dispersion in quantum dots reduces with the increase in annealing duration, but at the cost of quantum confinement effect. Therefore, a trade off has to be done between the size-dispersion and the quantum confinement. The PL study shows that the low energy value of the PL peaks are not due to band edges but because of shallow surface state and the decrease in the PL intensity with increase in particle size with time, may be attributed to the fact that bigger is the nanocrystallites smaller is their surface area to volume ratio. As a result of this, contribution of surface states induced defects is lower, which may be due to the decrease in density of shallow-trap centers with passage of time.

Decreasing trend of photoluminescence intensity with aging further confirms the trap elimination.

Studies on Effect of Mineral Nanofillers on the Mechanical and Processing Properties of Polymers and Their Industrial Applications

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Nano particles of CaSO_4 , $\text{Ca}_3(\text{PO}_4)_2$, CaCO_3 and $\text{Mg}(\text{OH})_2$ were synthesized in various sizes by in-situ deposition technique by varying the amount of poly ethylene glycol (PEG). Nano sizes of particles were confirmed by XRD and TEM. CaSO_4 was prepared of 12 and 22 nm sizes, and $\text{Ca}_3(\text{PO}_4)_2$ was of 13 and 24 nm sizes. The composites of polypropylene (PP) with nano and commercial CaSO_4 and nano $\text{Ca}_3(\text{PO}_4)_2$ were prepared by taking their 0.1 to 0.5 wt %. Transition of α to β phase was observed in case of 0.1 to 0.3 wt % of nano CaSO_4 and $\text{Ca}_3(\text{PO}_4)_2$ PP composites and CaCO_3 and, nano $\text{Mg}(\text{OH})_2$ HIPS composites. It was confirmed by the FTIR.

The increases in tensile strength, % elongation and Young's modulus observed in machine direction for 16 nm and 29 nm of CaCO_3 were greater than transverse direction up to certain loading followed by decrement on further addition. The continuous decrement in % elongation at break was observed in case of 9 nm CaSO_4 and increment in 29 nm of CaCO_3 . In cases of nano $\text{Mg}(\text{OH})_2$ and $\text{Ca}_3(\text{PO}_4)_2$, increments in tensile strength and Young's modulus were observed up to certain loading followed by decrement on further addition. Decrement in mechanical properties after certain wt.% loading of $\text{Ca}_3(\text{PO}_4)_2$ and continuous decrement for nano $\text{Mg}(\text{OH})_2$ in mechanical properties might be due to disordered exfoliation of the nano particles in the matrix. Anisotropic nature of the annealed polymer shows different properties in transverse as well as machine directions. The properties like tensile strength and young's Modulus showed higher value in machine direction, while % elongation at break showed lower value in machine direction. Since composites sheets are processed in extrusion method, molecules of matrix are highly oriented in the direction of pulling/machine during annealing.

Experimental variables such as torque, shear viscosity, shear stress and shear rate of nano filled PP composites were measured using torque rheometer and MFI. Torque vs time, Shear viscosity vs wt % and MFI vs wt % were plotted to investigate the rheological behavior of nano filled composites. Cross Williamson (CW) model was simulated using MATLAB simulation package to study thinning behavior of PP composites. Experimental results showed decrease in shear viscosity with increase in wt % of filler. Shear-thinning in molten PP composites was comparatively greater with reduction in nanosize of CaSO_4 and $\text{Ca}_3(\text{PO}_4)_2$. This kind of behavior was confirmed by N parameter determined from CW Model. Simulation of experimental data also showed similar trends as in theoretical data. At certain stage violation of theoretical data was observed. This is due to practical limitations of equation, as equation does not imagine physical situation of chain entanglements. The change of α phase to β phase, which is stable form, is responsible for improvement in mechanical and thermal properties. Thus very less amount of nanofillers increases mechanical properties several times in comparison to virgin polymer (PP). The lowering of viscosity with decreasing the nanosize of filler is responsible to provide more out put with greater mechanical properties.

Biomimetic route to hybrid nanocomposite scaffold for tissue engineering

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Hydroxyapatite-poly(vinyl) alcohol-protein composites have been prepared by a biomimetic route at ambient conditions, aged for a fortnight at $30\pm 2^\circ\text{C}$ and given a shape in the form of blocks by thermal cycling. The structural characterizations reveal a good control over the morphology mainly the size and shape of the particles. Initial mechanical studies are very encouraging. Three biocompatibility tests, i.e., hemocompatibility, cell adhesion, and toxicity have been done from Shree Chitra Tirunal, Trivandrum and the results qualify their standards. Samples are being sent for more biocompatibility tests. Optimization of the blocks in terms of hydroxyapatite and polymer composition w.r.t the applications and its affect on the mechanical strength have been initiated. Rapid prototyping and a β -tricalcium – hydroxyapatite combination in composites are in the offing.

The studies on crystallization behaviour and mechanical properties of Al-Ni-La metallic glasses

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Increasing demand for high performance engineering components continuously drives the development of new advanced materials. Amorphous and nanocrystalline alloys are examples of such materials. Al-based metallic glasses have attracted considerable attention in last two decades due to the occurrence of a primary crystallization reaction that yields a microstructure consisting of uniformly dispersed Al-nanocrystals embedded in an amorphous matrix. These alloys possess high specific strength coupled with good ductility, high hardness, good wear and corrosion resistance. However, these favourable properties fall off if the alloys crystallize to grain size that exceeds the nanometer range. Among the Al-based metallic system, Al-Ni-La alloys are interesting because of their good glass forming ability and wide glass formation range. Alloy ingots of compositions (6-8) at.% Ni, (4-7) at.% La and rest Al were prepared by induction melting in a purified Ar atmosphere. Each ingot was inductively re-melted and rapidly solidified ribbons were obtained by ejecting the melt onto a rotating Cu wheel in an Ar atmosphere. As-melt-spun and subsequently annealed ribbons were investigated by means of differential scanning calorimetry, X-ray diffractometry (XRD), transmission electron microscopy and micro hardness testing.

XRD studies confirmed that all the ribbons were fully amorphous. $Al_{90-x}Ni_6La_{4+x}$ systems showed a two-stage crystallization processes whereas $Al_{86}Ni_8La_6$ alloy showed three-stage crystallization processes on annealing. Crystallization kinetics was analysed by Kissinger and Johnson-Mehl-Avrami approaches. In Al-Ni-La alloys the crystallization pathways depend on the La concentration. The first stage corresponds to the formation of either fcc-Al (at low La concentration) or a mixture of metastable bcc phase and fcc-Al (at high La concentration). Microhardness of all the ribbons was examined at different temperatures and also at different time at a desired temperature and correlated with the corresponding structural evolution. Studies were also undertaken to examine the influence of other minor alloying elements (e.g., Zr) on the microstructure and crystallization behaviour of Al-Ni-La metallic glasses. The initial microstructure and the crystallization temperature change noticeable when a small percent of Ni is replaced by Zr.

Soft chemistry for nano-material synthesis

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We have developed the commercial process for making nano-sized TiO_2 and nano-sized BaTiO_3 , SrTiO_3 and their alloys as an efficient white pigment from Ilmenite.. Nano-sized BaTiO_3 , SrTiO_3 and their alloys have no chalking effect and are photo chemically inert and are promising material for white pigment . More over it is cheap. The By products of the process are NaOH and Fe_2O_3 both find commercial use. The cost of production is less than existing one for TiO_2 . Ba and Sr titanate is a new concept in pigment industries.
(The process has been filed for patent right by IIT, Kharagpur)

We have developed a reagent for making mesoporous Zr- phosphate / Zr silicate of various kind / Sn -phosphate / Sn silicate / Zr - molybdates / Zr Vanadate / Zr tungstate / Cr-phosphate . All the processes are very cheap and viable for commercial production. The materials are important for catalytic reactions in chemical industries.

Besides all these we have developed the processes for making

- 1) Nano-sized yellow pigment comprising TiO_2 and NiWO_4 .
- 2) Nano-sized yellow pigment comprising ZrO_2 and PrO_2
- 3) Nano-sized Bi_2Te_3 for thermo-electric device
- 4) Surface modified nano- Fe_2O_3 for cancer cell detection
- 5) Surface modified nano- Fe_2O_3 for protein separation
- 6) Nano sized ferro-electric niobates , tantalates , titanates and PZT.

Tailoring of room temperature excitonic luminescence in $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{SiO}_2$ nanocomposites and Fabrication of electroluminescence devices

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The basic objective of this research work was to fabricate $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ based quantum dots (by sol-gel technique) having highly intense excitonic UV luminescence compared to the visible defect related luminescence by embedding the semiconducting nanoparticles within a SiO_2 matrix. The dangling bonds or surface states associated with the $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ nanoparticles were tried to be reduced with a view to reduce the nonradiative pathways so that it may lead to increase in room temperature excitonic luminescence compared to the visible defect related luminescence. For tailoring the properties of quantum dots, Mg content (x value) and particle size along with other parameters were controlled during fabrication process and post deposition annealing treatments of the composite films.

Optical transmittance, Raman effect and photoluminescence measurements of the $\text{Mg}_{0.05}\text{Zn}_{0.95}\text{O}/\text{SiO}_2$ composites indicated effective capping of the $\text{Mg}_{0.05}\text{Zn}_{0.95}\text{O}$ nanoparticles (radii 1.61-1.68 nm) in the host showing practically no variation of particle size with the post deposition annealing treatments. The blue shift of the band gap (4.29-4.23 eV) from that of bulk $\text{Mg}_{0.05}\text{Zn}_{0.95}\text{O}$ indicated strong carrier confinement for samples annealed at $T \leq 873$ K. Highly intense UV emission (~ 4.14 eV) compared to that of defect related emission (2.59 eV) at room temperature was obtained by incorporating 0.05% Mg in ZnO.

The composite films, thus obtained, were characterized by microstructural (TEM, AFM), electrical and optical measurements so that the best quality films could be utilized for fabrication of electroluminescent devices in both homojunction and heterojunction configurations.

Synthesis and Luminescence Properties of Doped Nanostructures: Role of Shape, Size and Crystal phase

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We will demonstrate simple solution based method for preparing different doped nano-materials with distinct and well-defined morphologies, including spherical, hexagonal, tetrapod and rod, by controlling the reaction conditions and understanding their optical properties with changing shape, size and crystal structure. The mechanism related to morphology control of LaPO₄: Eu nanorods/ nanoparticles are proposed and discussed. We describe the “oriented attachment” growth mechanism for nanorod-to-nanoparticles transformation with increasing the temperature of heating. Our results also suggest that the diameter of the nanorod may be a critical determinant factor in governing the resultant shape of the product nanomaterials. The role of surface coating, doping and heating on the modification of crystal structure of ZrO₂, local structure of Zr and Eu and their effect on the photoluminescence properties of Eu₂O₃ doped and coated ZrO₂ nanocrystals will be discussed. X-ray absorption fine structure measurements were carried out to understand the local environment surrounding Zr and Eu ions in Eu doped and coated ZrO₂ nanocrystals. It is found that the local structure play most important role on the modifications of luminescence properties observed in Eu-doped and coated ZrO₂ nanocrystals.

Nano dielectrics with giant permittivity

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Nanodielectrics, is the subject of study related to dielectric phenomena of nanoscopic materials having morphology of particles, sheets, wires and tubes etc. During the last two decades numerous research efforts have been published in different areas of nanotechnology, such as, carbon nanotubes, nanowires, nanodiodes, single electron transistors, molecular data storage and drug delivery etc. but surprisingly, the area of nanodielectrics is relatively unexplored, although, there is enormous scope to use this material in power electronics industry and as gate electrodes in thin film transistors.

Although, some works on dielectric composites and organic dielectrics have been carried out, the field of nanodielectrics with giant permittivity value remains in its infant stage to be used in ultracapacitors for energy storage. In 1965, Gor'kov and Eliashberg predicted an enormously high permittivity value of a sufficiently minute metal particle having discrete energy levels¹. Later, this result was modified with interrupted metal strand instead of particle due to depolarization field². In the last decade few works have been done in composite materials in which high permittivity value has been reported. It is only recently reported³ by the present author, a giant (10^{10}) permittivity value in an assembly of ultra fine silver metal particles as a result of quantum confinement of the electronic wave functions.

Organic dielectric gate in organic thin film transistor is a great challenge due to lack of suitable materials with high permittivity value. A giant dielectric response ($\epsilon \sim 10^5$) is also observed as a result of Gor'kov-Eliashberg effect in conducting polypyrrole nanorods synthesized by chemical route in nanoporous template⁴. These nanorods essentially comprise of metallic chain segments interrupted by chemical defects, cross-linking and entanglement of the chains. Dielectric modulus spectra of the samples show a (KWW) exponent β equal to 1. This unusual result is ascribed to the structural order in the metal segment of the aligned polypyrrole chain.

These materials with extremely high dielectric permittivity will be useful as ultracapacitors for energy storage if the loss factor is controlled by tuning the disorder for electron confinement. Therefore, it is not difficult to speculate that an emerging area of nanodielectrics with a new class of materials having ultra high permittivity is imminent to be used in the future application in energy storage and ultra sensitive transducers.

As an application, a nanocapacitor with ultra high capacitance (718 ± 0.2 pF) has been fabricated using electro-deposited Au nanowires manipulated between two Au microelectrodes by the dielectrophoresis technique⁵. A high value of the dc resistance (~ 100 M ohm) and nonlinear current-voltage characteristics indicate the formation of a dielectric interface between the nanowires. From frequency dependent conductivity, it is seen that the interface exhibits a giant dielectric permittivity ($\epsilon \sim 1.8 \times 10^7$), which shows no frequency dispersion over the range from 30 Hz to 1 MHz. The enhancement of this permittivity value is attributed to the formation of a disordered interface containing gold atoms disrupted from the surface of the Au nanowires.

Applications of Nanostructured Metal Modified Electrodes in Catalysis and Sensor

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Nanostructured Pt, Au and Cu modified glassy carbon (GC) and indium tin oxide (ITO) electrodes were prepared using polyelectrolyte polymer and aluminosilicate clays. The AFM images of the Pt_{nano} deposited electrode surface (GC/Nf/Pt_{nano}) revealed that the clusters of electrodeposited Pt particles consist of a number of nanocrystallites. The GC/Nf/Pt_{nano} electrode showed selective electrocatalytic oxidation of dopamine and serotonin in the presence of interfering molecules such as ascorbic acid and uric acid. The GC/Nf/Pt_{nano} electrode showed a linear relationship for dopamine oxidation in the range of 3×10^{-6} - 60×10^{-6} mol dm⁻³ with a detection limit down to 1×10^{-8} mol dm⁻³ (10 nM) dopamine. It has been also shown that the GC/Nf/Pt_{nano} electrode can be used as a sensor with high selectivity, sensitivity and detection of submicromolar concentrations of dopamine and serotonin. The practical applications of GC/Nf-Pt_{nano} electrode in the determination of dopamine in real samples, like blood plasma and dopamine injection solution were also carried out.

Nanostructured Cu deposited GC electrodes (GC/Cu_{nano}) were prepared. The GC/Cu_{nano} modified electrode was used for the simultaneous detection and determination of uric acid (UA) and homovanillic acid (HVA) in the presence of excess concentrations of ascorbic acid (AA) and for the electrocatalytic reduction of hydrogen peroxide. Linear calibration curves were obtained for AA over the concentration range of 1 to 40 μ M in the presence of 50 μ M UA and 20 to 50 μ M UA in the presence of 50 μ M AA at physiological pH with a detection limit of 10 nM in the presence of 10-fold excess concentrations of AA or UA. The practical utility of the GC/Cu_{nano} modified electrode was demonstrated.

The hydrogen peroxide reduction was catalyzed by a redox cycle involving the Cu(I)/Cu(II) couple at the GC/Cu_{nano} electrode. The calibration curve was found to be linear upto 100 μ M H₂O₂ with a detection limit of 10 nM at the Cu_{nano} modified GC electrode. The electrocatalytic activity of Cu_{nano} doped polymers such as polypyrrole (PPy) and Nafion (Nf) film modified GC electrodes (GC/PPy/Cu_{nano} and GC/Nf/Cu_{nano}) towards oxygen reduction was investigated in 0.1 M phosphate buffer containing saturated oxygen. The electrodeposited Cu_{nano} in polypyrrole film was characterized by AFM, XPS, EIS and cyclic voltammetry and used for the oxygen reduction studies.

Gold nanoparticles (Au_{nps}) dispersed Nafion modified electrodes (GC/Nf-Au_{nps}) were prepared and characterized by electrochemical methods. The phenosafranine (PS⁺) dye was incorporated into the GC/Nf-Au_{nps} electrode (GC/Nf-Au_{nps}/PS⁺). The electrochemical and *in situ* spectroelectrochemical behavior of the incorporated PS⁺ dye at the Au_{nps} nanoparticles immobilized Nafion coated electrodes (GC/Nf-Au_{nps}/PS⁺) were studied by using absorption spectrophotometer, cyclic voltammetry and emission spectrophotometer.

The Au_{nps} deposited TiO₂ nanoparticles were prepared and characterized by the surface plasmon of the Au_{nps}. The TiO₂-Au_{nps} dispersed Nafion membrane was prepared and used for photoelectrochemical investigations.

CdS/ CdSSe quantum dots in glass matrix

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The compositions containing 55% and 60% silica have been formulated for preparation of glass filters having sharp cut off at 475 and 575 nm in UV-Visible. To achieve cut off at these wavelengths the glasses have been doped with CdS/CdSSe and melted at 1200-1300°C. The glass samples were transparent and pale yellow colored due to presence of CdS/CdSSe tiny particles. The dopant were grown thermally by reheating these glass samples at temperature near to it's glass transition temperature. The thermal treatment leads to controlled in-situ growth of CdS/CdSSe nano crystals, which impart the yellow/orange/red color to these glasses. Optical characterization using UV-visible spectrometer shows that, as prepared glasses show optical cut off in the range of 350-370nm. The thermal striking to these glasses leads to the shift in optical cut off to visible region (Red shift). The optical filter having cut off at 475 nm can be prepared by doping CdS whereas CdSSe has to be doped for preparation of cut off filter of wavelength 575nm. Both the glass filters have been characterized by TEM for distribution and morphology of CdS/CdSSe nanoparticles. The TEM results show that the CdS/CdSSe crystals ranging from 2-5nm is uniformly distributed into the glass matrix.

Synthesis and Photochemistry of Composite Metal-Semiconductor Nanostructured Materials

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Nanocolloids of semiconductors and metals have been synthesized and characterized by employing different analytical techniques. The core-shell nanostructures consisting of PbS, ZnS/PbS and PbS/ZnS were synthesized by interfacial exchange of Zn²⁺ by Pb²⁺ from ZnS and interfacing ZnS on PbS, respectively. In mixed colloids PbS particles consists of relatively much smaller average size (6 nm) compared to those of ZnS particles (14 nm). In these materials ZnS and PbS were found to be present in the wurtzite and face centred cubic (fcc) forms, respectively. These samples were further analyzed by IR, electronic and fluorescence spectroscopy. The addition of Pb²⁺ to ZnS causes the quenching of emission due to ZnS along with a simultaneous development of emission in varied wavelength range due to formation of Q - PbS of different size and at its high concentration relatively a strong emission band is developed in the red region at 710 nm. The dynamics of charge carriers in both pure and mixed colloids has been followed by time correlated single photon counting technique. An initial addition of Pb²⁺ ($< 1 \times 10^{-4} \text{ mol dm}^{-3}$) reduces the $\langle \tau \rangle$ at 460 nm to subnanosecond range along with a simultaneous increase in $\langle \tau \rangle$ at 710 nm due to formation of PbS from about 7.5 ns to 23.8 ns. In these nanosystems the extent of charge separation and the dynamics of charge carriers could be manipulated by their surface modification. Under varied experimental conditions the optical absorption and emission could be manipulated in the wide spectral.

Development of nanograined materials by mechanical alloying and gas reduction

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Nano-materials are increasingly gaining importance in modern technological advances due to their unique properties as well as the efforts to miniaturizing systems. In nanocrystalline materials, majority of grain size is in range from 1~ 50 nm and offer a large surface that could be of a greater importance for tailoring various physical and mechanical properties. Currently there are several methods being employed to produce nanograined bulk materials. The two processes namely ball milling and gas-solid reduction and with case studies presented. The high energy ball milling (HEBM) has successfully been employed to produce nano sized powders. The method has also been used to extract aluminium from its chloride. In this work, an attempt has been made to produce intermetallic compound of TiAl based nanocomposite by using mechanical alloying method. Electroless Ni-P coated graphite powder is been mixed along with titanium and aluminium powders to study the effect of this inclusion. An attempt has been made to optimize the process parameters so as to achieve uniform structure in the nano range. The parameters studied are weight percentage of graphite (1-4 wt. %), time of milling and RPM upto 400 of the milling.

Nanograined intermetallic materials like Fe₂Mo and PbTe are produced by reducing the required metal oxides by hydrogen gas. The advantages of this process include the environmental friendly reaction product as H₂O and the amount of the substantial product quantity. A fluidized bed reactor is designed and fabricated to have the temperature of reaction up to 900°C. Then the thermodynamic and kinetic calculations are made to see the feasibility for the products formation in the reactor. In case of Fe₂Mo, the starting materials are Fe₂O₃, MoO₃ and Fe which then are milled to produce Fe₂MoO₄. Hydrogen gas is allowed to pass through Fe₂MoO₄ in the reactor 700-1000 °C for 0.5- 10 h. The cold pressed pellets of the same when observed under TEM revealed nano-grains with magnetic domains. The X-ray analysis further confirms the formation of nanograined Fe₂Mo of the size ~100 nm. The saturation magnetization of Fe₂Mo is found to be 93.868 Gauss with the maximum applied magnetic field of 9 Kilo- Gauss. PbTe, a potential candidate for thermoelectric and optoelectronic device applications has also been produced by reducing a mixture of Pb₃O₄ and Te powders by hydrogen gas reduction method. Besides producing the intermetallic, another aim of the experiment was to optimize the conditions that lead to the maximum production of PbTe. These conditions include temperature, composition of the reactant mixture and time for reaction. Requisite amounts of the reactant powders were taken and then mixed in an agate mortar at ~150 rpm for ~ 1 h. The X-Ray diffraction pattern corresponds to the rock-salt structure of PbTe, clearly verifying the formation of the lead-telluride intermetallic. SEM and TEM results show the presence of average grain size of these particles in the range of 50-100 nm.

Electroless ni-p nano coating technology

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Nanocoatings are defined to have either the thickness of the coating or the second phase particles that are dispersed into the matrix in the nanosize range. Electroless, EL (without using electricity) is one of the classical coating technology in which deposition is purely systematic chemical process i.e. sensitization, activation, nucleation and growth of nanosized alloy globules first vertically then horizontally during the reduction process onto the catalytic surface of the substrate. This study will ascribe an understanding to know EL nano coating technology in terms of thickness of layer of metal, alloy, and composite nanocoatings and the characteristics of embedded second phase particles.

In metallic coating the deposition starts with atomic level that further transform into layer on nm range with in few seconds of deposition time by controlling the process parameters. On the other hand in the case of alloy (Ni-P) deposition, first the Ni atoms nucleate on the nucleation sites of Pd ions (less than 1 nm) developed onto the surface of substrate under study during activation process. P atom easily goes into the Ni lattice to form Ni-P alloy nano sized (1-2 nm) globules then further growth took place in all possible directions in autocatalytic manner that increases the globular size from few nm to ten to hundred nm size results into the uniform coating layer within 10 to 60 sec. Bonding mechanisms of EL coatings has been studied for metallic and alloy deposition. An empirical model has been developed to understand the relation between deposition rates.

In EL Ni-P nanocomposite deposition the second phase nanoparticles are co-deposited/co-precipitated into the Ni-P matrix by two ways. In the first case, external addition of second phase particle (X) i.e., conventional method while in the second case specific reactions by-products results into precipitations that follow to co-deposition as a second phase along with the Ni-P deposition to form Ni-P-X nanocomposite coatings. The various nanocomposites Ni- P-X coatings (second phase particles like; X=ZrO₂-Al₂O₃-Al₃Zr, hexaferrites, ferrites, ZnO, Al₂O₃-TiO₂ etc.) are studied for various applications. The application part of these nanocomposites coating depends upon the second phase particles that are embedded in the Ni-P matrix. A few applications have also been outlined which may reveal the capabilities of the EL Ni-P nanocomposite coating technology to the relevant industries with the emphasis on tribological, corrosion, magnetic behavior etc.

Structural Characterization of Copper Nanoparticles

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Nanomaterials in the form nanoparticles or nanocrystalline thin films have been a source of great interest due to their novel electrical, optical, physical, chemical and magnetic properties and are experiencing a rapid development in recent years due to their existing and/or potential applications in a wide variety of technological areas such as electronics, catalysis, ceramics, magnetic data storage, structural components etc. Their uniqueness arises from their high ratio of surface area to volume (aspect ratio), as these materials typically have diameters of 100 nm or less. The properties of nanometer-scale metallic particles differ from those of the same material in bulk. These differences arise due to their small size effect, surface effect, quantum size etc. Recently Copper nanoparticles have attracted much attention due to their unique properties, resulting in a wide range of applications in the field of metallurgy, nanofluids, nano- and optoelectronics. In this paper, we report on the structural characterization of the nanocrystalline copper metal powder prepared by dc magnetron sputtering. Liquid nitrogen cooled cold finger arrangement have been used to prepare nanocrystalline powder. The particle size, crystal structure and morphology of the samples were characterized by In situ High Temperature X-ray diffraction, TEM and AFM. Results showed that the copper nanoparticles are not only stable at room temperature but at high temperatures too. It was observed that highly oriented (111) phase becomes randomly oriented at higher temperature with a systematic shift in peak positions towards lower 2θ values due to change in lattice parameters. Temperature dependence of lattice constants under vacuum shows linear increase in their values along with increase in size of the grains. A red shift in the plasmon resonance peak of copper with increase in particle size was also observed.

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Doped Barium Titanate nanoparticles

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We have synthesized nickel/Iron ion doped BaTiO₃ nanoparticles through a chemical route using polyvinyl alcohol (PVA). The concentration of dopant varies from 0 to 2 mole % in the specimens. The particle diameters in the specimen decreases with increasing dopant concentration. The lattice parameters 'a' and 'c', obtained by employing Reitveld's powder structure refinement method, show an unusual lattice contraction of BaTiO₃ due to incorporation of dopants. It is also seen that the dielectric permittivity in doped specimens is enhanced compared to that of undoped BT ceramics. The dielectric permittivity shows maxima in the specimen containing a specific dopant concentration.

Optical and Morphological Investigations of Nanoparticles Using Scanning Near Field Optical Microscopy (SNOM)

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In the present project structural and optical properties of chemically synthesized metal and semiconductor nanoparticles as well as core-shell particles are investigated. Highly monodispersed and stable particles were obtained. Along with the spherical structure different morphologies such as fibers, rods and tubes could also be obtained in some cases. Doping of elements such as manganese in semiconductor nanoparticles such as CdS, ZnS and ZnO has been carried out.

Room temperature ferromagnetism could be observed in the investigations carried out on Mn doped ZnS and CdS nanoparticles. In addition, intense cathodoluminescence could also be detected from Mn doped ZnS and ZnO nanoparticles.

Furthermore field emission application of semiconductor materials viz. ZnO and SnO₂ has been studied. It has been shown that chemically grown oriented field emitters are quite stable and prove to be a promising material for field emission applications.

Biological application of core-shell nanoparticles (silica @ Ag) is also demonstrated. The core-shell particles prove to be very useful in detection of E. Coli. present in water as well as for rapid detection of antibodies.

Investigation on the liquid crystalline phases of polycation induced compacted nanostructured DNA : implications on gene therapy

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Aim of this project is to develop novel cationic polymer vectors for gene delivery application. Human disease may be treated by the transfer of genetic material into specific cells of a patient in order to correct or supplement defective genes responsible for the disease. Several systems can be used to transfer foreign genetic material into the human body such as viral (adeno- and retrovirus) and non viral vectors. Endocytosis of DNA can be achieved if it can be condensed to 100 nm or less in diameter, because access to tumor tissue from the vasculature is limited to particles less than 70 nm in diameter. Condensation of DNA under suitable conditions gives rise to the collapse of extended DNA chains into compact orderly particles. The limitations of viral vectors, in particular their relatively small capacity for therapeutic DNA, safety concerns, difficulty in targeting to specific cell types have led to the evaluation and development of alternative vectors based on synthetic, non-viral systems. Cationic liposomes and polymers have been accepted as effective non-viral vectors for gene delivery with low immunogenicity. To be effective, polymer vectors should be cationic, biodegradable, non toxic and hydrophilic in character. Two novel polymer vectors possessing these properties are synthesized and used to induce the compaction of DNA to nanoparticle. One is a depolymerized chitosan and the second one is a block copolymer of spermine with amino acids (aspartic acid and glutamic acid) made water-soluble with polyethylene glycol (PEG). The physicochemical properties of the complexes were investigated by means of FTIR, scanning electron microscopy (SEM) and atomic force microscopy (AFM). The effect of molecular weight and the degree of deacetylation of chitosan, a biodegradable and biocompatible polymer on the condensation behavior of high molecular weight calf thymus DNA and plasmid DNA was investigated. High molecular weight chitosan was depolymerized by oxidative degradation with NaNO₂ at room temperature. It was then characterized by first derivative UV spectrophotometry. The results indicated that low molecular weight chitosans exhibit high charge density and thereby strong binding affinity than the high molecular weight chitosans. Very low molecular weight chitosans formed aggregates easily even at very low charge ratios, hence chitosan having medium molecular weight and high degree of deacetylation was chosen. Condensation experiments were done using plasmid DNA with medium molecular weight chitosan, and a molecular weight of 49 KD and DD% of 94% was found to be the optimum for the DNA compaction. Synthesis of water-soluble block copolymeric carriers of spermine ASSP and GLSP was prepared by the direct polycondensation spermine with acidic amino acids such as aspartic and glutamic acid. The copolymer was synthesized in a mixture of asymmetrical ionic liquid (butylmethylimidazolium hexafluorophosphate) and triphenyl phosphite, both as solvent and condensing agent. The cationic polyamides were highly hydrophobic and to make it hydrophilic it was coupled with PEG using ionic liquid as solvent. The product obtained was about 90% yield with aspartic acid and 76% of yield with glutamic acid.

Construction of an Optical Tweezer for Nanometer Scale Rheology

Dr. Sharath Ananthrmurthy

Bangalore University

a) Infrastructural Work: (Phase 1)

As we started the work with absolutely no infrastructure except for a laboratory space within the department, we had to spend the initial phase undertaking extensive infrastructural work.

Work carried out:

- Lab partitioning, plumbing, painting and air conditioning to achieve dust free and an isolated laboratory environment.
- Moreover to minimize electrical noise in sensitive measuring equipment, new electrical wiring with separate earthing lines was prepared using high grade copper wire.

b) Design and Construction of the Tweezer Set Up: (Phase 2)

- Detailed literature survey of experimental and theoretical work pertaining to research using optical tweezer. Based upon these, design of an optical tweezer setup was prepared. Setup has open microscope configuration and is modular so that any components may be added or removed without having to change the entire setup.
- Prime equipment identified and procured. Building of single beam optical tweezer setup.
- Careful calibration of prime components of the set up.
- Measurements carried out: Trap stiffness of the optical tweezer using quadrant detector and with video microscopic technique.

c) Rheological studies of Viscoelastic Materials: Material under focus: SILK (from Bombyx Mori Silk Worm) (Phase 3)

This material has various commercial and industrial uses (as a biosensor)

- Measurement of viscoelastic moduli of regenerated silk fibroin (RSF) solution, using optical tweezer and video microscopy.
- characterizing the frequency-dependent viscoelastic response of the material at different concentrations.
- Characterizing the micro-level inhomogeneity, and thereby, the differences in viscoelastic response in different regions of the material.

Aligned Carbon Nanotubes Films Grown on Large Area of Quartz Substrates By Floating Catalyst Chemical Vapor Deposition Method

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A simple method has been developed for the growth of aligned multiwall carbon nanotubes (MWNTs) on a large area of quartz substrate through floating catalyst chemical vapor deposition with ferrocene-xylene solution. High density CNTs were vertically aligned on quartz plate. The effect of reaction parameters such as gas flow rate, catalyst concentration, reaction temperature and reaction time on the structure and yield of the vertically aligned carbon nanotubes films have been studied. Thermo gravimetric analysis of purified films showed only 3 wt % catalyst impurities present in the sample. The SEM analysis purified deposited films reveal that the CNTs are multiwall structures and the films thickness of few microns to 1.1 mm. The films have uniform growth of CNTs with few stacking of nanotubes layer within the film. The diameter of synthesized CNTs varies from 20 nm. to 60 nm. The bulk densities of purified MWNTs film were about 0.45 gm/cm³ and the average growth rate of film synthesis was about 11 μm/min. The films obtained were further densified with bulk carbon by chemical vapor infiltration (CVI) using methane to get carbon composite materials. SEM analysis shows good infiltration of bulk carbon into the space between CNTs. However, the complete infiltration could not be achieved due to mouth blockage at the upper end of nanotubes film. These composites were evaluated for thermal properties especially thermal conductivity and were compared with the thermal conductivity of pitch/nanotubes composites. Latter materials exhibit higher thermal conductivity than former materials.

Instability Route to Patterning of Soft Films(*)

Vijay B. Shenoy, N. Ravishankar

Soft films are prone to many morphological instabilities due to many competing energy scales present in them. Recent work has shown that a new kind of morphological instability can be induced in a soft film that interacts with a contactor (via, for example, van der Waals forces). In this work we present results of electric field induced morphological instabilities in films. We show that electric field can be used to control the morphologies and present a phase diagram showing various morphological phases. Experimental realization of these are discussed.

(*) Work done in collaboration with J. Sarkar, N. Arun, K. S. Narayan and A. Sharma.

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Nanodevices Using Organic Molecules

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We have fabricated and characterized two types of nanodevices using organic molecules.

(i) Single organic molecule based nanoelectrodes have been developed using simple and reliable method for making electrical contacts to small organic molecules with thiol endgroups. Nanometer-scale gaps between metallic electrodes have been fabricated by passing a large current through a lithographically-patterned Au-line. The passage of current breaks the Au-line, creating two opposite facing electrodes separated by a gap comparable to the length of small organic molecules. Current-voltage characteristics have been measured both before and after deposition of short organic molecules. The resistance of single 1,4-benzenedithiol and 1,4-benzenedimethanedithiol molecules were found to be $9\text{ M}\Omega$ and $26\text{ M}\Omega$, respectively. The experimental results indicate strong electronic coupling to the contacts and are discussed using a relatively simple model of mesoscopic transport. The use of electrodes formed on an insulating surface by lithography and electromigration provides a stable structure suitable for integrated circuit applications for future nanoelectronics.

(ii) There is increasing interest in solid-state memory in two terminal devices based on organic semiconductor. In particular, the two terminal nonvolatile memory devices based on organic semiconductor sandwiched between two metal electrodes have attracted much attention for their advantage due to low power consumption, relatively simple fabrication technique and absence of technological bottleneck on miniaturization. We have studied the electrical field induced conductance transition in thin film of Perylenetetracarboxylic dianhydride sandwiched between two metal electrodes, from an insulating state to conducting state with a high ON-OFF ratio. This has been possible by creating a metallic nanowire using electromigration inside semiconductor based on organic molecules. Temperature dependence of resistivity shows semiconducting behavior in OFF-state, but it shows metallic behavior in the ON-state. This suggests that conducting pathways are responsible for the electric field induced conductance transition.

Solvation and migration of charge defects in hydrogen bonded nanoclusters and in nanotubes: A quantum simulation study

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The solvation structure and migration of charge defects in hydrogen bonded nanoclusters have been a topic of current interest from both theoretical and experimental points of view. In this study, we carry out ab initio quantum simulations to investigate the solvation structure and diffusion of protonic defects with an excess proton and also with a proton less in water clusters of varying size and also in water-filled nanotubes of varying radius. We have also investigated the localization of an excess electron both in presence and in absence of metal counterions in water and water-ammonia clusters at finite temperatures. The structural and dynamical aspects of hydrogen bonds in the context of solvation and migration of charged solutes and their connections to recent ultrafast spectroscopic studies are also discussed 1,2. The quantum simulations are carried out by using the ab initio molecular dynamics method where the forces on the nuclei are obtained directly from 'on the fly' ultrafast electronic structure calculations 3. Since no predefined interaction potentials are used in this scheme, it is ideally suited to study complex chemical systems like the ones considered here which involve substantial dynamical rearrangement of their electronic structures at finite temperatures.

Dendritic Nanoreactors

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Dendrimers are monodisperse macromolecules built with the highest level of synthetic control over structure. The high level of synthetic control makes it possible to synthesize metal nanoparticles with high loading and superior catalytic properties. Dendritic architecture consists of connectors and symmetrical branching units, built around a core, which could be an atom, a small molecule or a linear polymer with reactive terminal groups. The consecutive sheaths that are subsequently synthesized around the core are called dendritic generations. As we proceed from lower to higher generations, the molecule, which is initially not much more than a branched organic molecule begins to take a more defined shape. We have used poly amidoamine dendrimers with ethylene diamine core for our investigations. We can choose dendrimers with different exterior functional groups. Hydroxyl, amine and carboxyl terminated dendrimers are available in the market. In the present project, amine terminated Poly amidoamine dendrimers, which belong to fourth generation, and carboxyl terminated polyamidoamine dendrimers, which belong to 4.5 generation, have been used for the investigations. These dendrimer molecules have been used to prepare dendrimer encapsulated Pt nanoclusters by chemical method and dendrimer encapsulated copper nanoclusters by electrochemical method. This work describes an innovative approach for the preparation of metal-dendrimer nanocomposite and a new strategy for the electrode modification with the dendrimer-metal nanocomposite. Three different methodologies have been developed to prepare metal-dendrimer nanocomposites. New protocols have been developed to link the dendrimer encapsulated nanoclusters onto the electrode surfaces and they have been evaluated for the electrocatalytic oxidation of small molecules like methanol and for the electrochemical recognition of copper ions. where picomolar detection limit has been achieved. The results will be presented under three heads

- A. Platinum –dendrimer nanocomposite monolayers on gold surfaces for Electrocatalysis:
- B. PAMAM dendrimers as adhesion promoters for the preparation of electrocatalytically active thin films:
- C. Electrochemical preparation of copper-dendrimer nanocomposite: detection of Cu^{2+} ions at picomolar level

Preparation and characterization of nanosized cathode materials

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A motivation in nanoscience is to try to understand how materials behave when sample sizes are close to atomic dimensions. Nanometer clusters belong to a state of matter in the transition region between molecules and bulk solids. These materials due to their extremely small size and large specific surface area show unusual physical and chemical properties compared to their bulk counterparts. When the characteristic length scale of the microstructure is in the 1- 100 nm range, it becomes comparable with the critical length scales of physical phenomena, resulting in the so-called "size and shape effects." This leads to unique properties and the opportunity to use such nanostructured materials for novel applications and devices. The main synthesis techniques for nanostructures include template directed growth methods and soft chemistry methods such as sol-gel routes, hydrothermal methods, chemical precipitation methods etc. Recently our group has investigated the nanoparticle sized cathode active materials prepared by a simple low-temperature solid-state route. Today lithium based ceramic oxides are getting attention due to variety of applications such as lithium-ion batteries, cellphones, camcorders, pacemakers, memory chips etc. In this investigation simple, low-temperature, ecofriendly and inexpensive solid-state reaction method is adopted for the synthesis of $\text{LiM}_{1-x}(\text{M}=\text{Co or Ni})\text{N}_x(\text{N}=\text{Mg or Ca or Ba})\text{O}_2$ with urea as igniter and glycerol as binding material to result in nanoparticle sized materials. Nitrates of lithium, cobalt/nickel and magnesium/calcium/barium were mixed in appropriate quantities together to form a uniform mixture. Required quantities of urea and glycerol were added to this mixture to form a paste. The paste was heated to 150°C initially and finally to 600°C for 8 hrs. The product obtained was subjected to TG/DTA and XRD analysis. The SEM/TEM analysis was carried out to confirm the particle size. To confirm the composition of the materials, SEM with EDAX measurements were made. A 2016 coin type button cell was assembled with $\text{LiM}_{1-x}\text{N}_x\text{O}_2$ (where, $\text{M}=\text{Co or Ni}$; $\text{N}=\text{Mg or Ca or Ba}$) as cathode and graphite as anode containing polypropylene separator and a solution of 1M LiBF_4 dissolved in 1:1 (EC+DMC v/v ratio) mixture as the electrolyte. Charge/discharge studies were conducted to establish the viability of a reversible cell and to understand the advantages of the doping in the ceramic matrix on nanoscale.

Size-selective electrodeposition of metal, metal oxide and conducting polymer nanoparticles and their nanocomposites for technological applications

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a) Size-selective electrodeposition of conducting polymer nanostructures

The objective has been to prepare uniform and oriented nanostructured conducting polymers by a templateless method using the concept of controlled nucleation and growth on soft electrode substrates like platinum. Experiments carried out with polyaniline, poly(*N*-methylaniline) and poly(*o*-phenylenediamine) in the presence of sulphuric acid have resulted in the formation of clusters of size of about 100 nm. Further experiments with highly oriented pyrolytic graphite on the preparation of nanostructured conducting polymers in the presence of organic sulphonic acids for better control of the growth event are in progress.

b) Investigation of oxygen reduction and methanol oxidation at poly(*o*-phenylenediamine) – Pt nanocomposite electrode in acid medium

The electrochemical reduction of oxygen at poly (*o*-phenylenediamine) (PoPD) modified platinum electrode was studied. Platinum nanoparticles with a diameter of about 10-35 nm were electrodeposited onto the polymer matrix. The platinum loading was varied from 3.9 to 175 mg / cm². Experiments have also been carried out on unmodified platinum electrode and platinum particles deposited platinum electrodes for direct comparison. The films were characterized by AFM. Rotating disc electrode experimental data indicated a one step four electron reduction. It is demonstrated that nearly a seventy - fold increase in the oxygen reduction current can be obtained on the platinum nanoparticles incorporated PoPD electrode compared to the bulk platinum electrode. The experiments on methanol oxidation are in progress.

c) Electrochemical synthesis and characterization of poly(*o*-phenylenediamine) – carbon nanotube composite in a surfactant solution

Detailed experiments have been carried out on the electrochemical preparation of poly(*o*-phenylenediamine) – carbon nanotube composite in a surfactant solution and the composite is characterized by IR, Raman, SEM, XRD, DLS and AFM techniques. Fine microtubules of the composite are obtained by this method and further experiments are in progress to assess its performance in electrocatalysis and supercapacitors.

d) Enhanced growth and redox characteristics of some aromatic and heterocyclic conducting polymers on carbon nanotube modified electrodes and their applications in fuel cell reactions

Experiments on the polymerization of aniline, (*o*-phenylenediamine), *N*-methylaniline and *N,N*-dimethylaniline on carbon nanotube modified electrodes have shown enhanced electrochemical growth and redox characteristics. The poly(*o*-phenylenediamine)-carbon nanotube composite electrode showed a high catalytic effect for oxygen reduction and methanol oxidation. The enhancement in the electrochemical properties are not due to the surface area effects but due to specific interactions between the carbon nanotube and the polymer. No such enhancement was observed in the case of polypyrrole.

Design of New and Novel Nanoconstruction Tools

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In the past few decades synthetic chemists have learned how to synthesize highly complex molecules (eg. cubane, dodecahedron and palytoxin) using novel strategies and sophisticated reagents. The drive towards higher level of achievement in organic synthesis, both in terms of methodology and complexity of target remains unabated. The sizes of the targets are generally less than 10 \AA (1 nm) with molecular weight ≈ 400 Dalton. Because these molecules are on nano dimension and they possess well-defined and characteristic shapes, they are considered as nanoscale objects or simply "nanostructure". These nanostructures have important applications in material sciences and life sciences. Our objective is to develop a new and novel synthetic method for the construction of molecules of nano dimension. In this regard we have adapted trimerization of carbonyl compounds and Suzuki coupling strategy to prepare polyaryl dendrimer, C_3 -symmetric dendrimers, highly functionalized tetraphenylmethane (TPM) derivatives and we plan to display our findings during the poster session.

Use of nanomagnetic materials for targetted drug delivery

Prasad Tamhankar, Manoj Sharma, A M Kulkarni and S C Watawe*

The microwave assisted combustion synthesis has been conventionally used for the synthesis of nanocrystalline ferrite materials with the advantage of reduction in sintering time and temperature while the conventional double sintering ceramic technique does not have the control on grain growth and also requires larger time and temperature. The ferrites can be conventionally used as magnetic carriers for targeted drug delivery where they can be directed using external magnetic field gradients. The toxicity of the ferrite materials has to be taken care of by coating them with biocompatible polymer material. We report here the polymer coating of the ferrite nanoparticles with aniline, Oelate and alginate. The coating has been done using chemical methods involving vigorous and constant stirring to initiate proper coating of the sample. The characterization by XRD and IR clearly indicates the formation of ferrite structure and also coating of the sample with polymer material. The SEM micrographs indicate the uncoated ferrite sample to have particle size in the range of 50 to 60 nm and for coated sample in the range 70 to 90 nm. This size is suitable for targeted drug delivery as even after the coating of drug on the sample size can be maintained below 200nm, which is critical.

Metal nanocluster doped coloured coatings on glasses and plastics using sol-gel technique

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Several noble metal nanoparticles doped sol-gel derived thin coloured films have been synthesized and characterized. These are pure (Ag, Au, Cu and Pt), mixed Ag–Cu and alloy (Au–Cu, Au–Ag, Au–Pt) nanoparticles in SiO₂, Au in mixed SiO₂-TiO₂ and SiO₂-ZrO₂, Au and Ag nanoparticles in inorganic-organic hybrid film matrices etc. This investigation leads to the development of tailor-made coloured coatings by tuning the SPR band positions of embedded nanometals on glass and plastic substrates. The following points are noteworthy:

(i) The SPR absorption position of nanometals was tailored by controlling the refractive index of the embedding matrix. Using this idea different coloured coatings on ordinary sheet glasses were prepared by incorporating Au nanoparticles in SiO₂-TiO₂ and SiO₂-ZrO₂ having different refractive index values ranging from about 1.41 to 1.94. As for example the Au-SPR can be tuned from 540 nm to ~600 nm on going from SiO₂ to SiO₂-TiO₂ (3:7) matrix, and as a consequence, different coloured coatings (pink, magenta, violet, royal-blue and blue) were obtained.

(ii) A new two-layer (TL) approach has been developed for the generation of Au–Ag alloy nanoparticle doped SiO₂ films on glass. In this approach Au–Ag alloy nanoparticles of tunable atomic ratios were generated by UV- and heat-treatment of two successive overlapping coating layers obtained from Au- and Ag-ion incorporated sols respectively. The alloy nanoparticles (<D> ~2.5-4.5 nm) were formed through the interlayer diffusion showing Au–Ag nanoalloy SPR absorption bands in between Ag- (410 nm) and Au-SPR (540 nm). This new TL approach also works well in Au–Cu system. In this case oriented 2D Au–Cu nanoalloy particles of variable atomic ratios were formed.

(iii) In another development, *in situ* generation of Ag nanoparticles in the refractive index controlled inorganic-organic hybrid host (SiO₂-TiO₂-PEO) leads to the formation of abrasion resistant coloured coatings (yellow to pink) on plastic substrates. In case of ‘Au nanoparticles in SiO₂-TiO₂-PEO’ system the Au-SPR can be tuned with respect to the UV light of different energies, used for the purpose of curing. In this case the red shifting of Au-SPR is initially controlled by the refractive index of the matrix and finally due to the change in interparticle distance/coalescence of nanoparticles causing plasmon coupling of Au nanometals.

(iv) The nonlinear optical (NLO) studies were done in collaboration with *Univ. of Hyderabad*. The mixed Ag–Cu nanoparticle doped SiO₂ films showed self-defocusing nonlinearity and a good NLO absorption leading to the optical limiting (OL) behaviour. Au nanoparticle doped SiO₂-TiO₂ films having refractive index controlled tunable Au-SPR exhibit good optical switching behaviour. It has been observed that the refractive indices of the matrices around the Au-nanometals play an important role in modulating good photo switching.

Nanocrystalline Spinel Ferrites by solid state reaction route

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We have explored a technique by ceramic processing route with doping in which spinel ferrites like NiFe_2O_4 , MnFe_2O_4 , $(\text{NiZn})\text{Fe}_2\text{O}_4$, CoFe_2O_4 are developed. Particle diameters are found to decrease with increasing dopant content. The substitution Nb^{5+} or Ti^{4+} ions essentially break up the ferromagnetically active oxygen polyhedra and the size of the grains are confined. Magnetic parameters depend strongly on the size of the ferrite grains. Saturation magnetizations vary linearly with the inverse diameter of the magnetic phases. Superparamagnetic splitting is observed from Mossbauer spectra if the particle size is reduced. Electrical characterizations of the specimens show that the DC resistivity decreases by at least five orders of magnitude compared to pure sample. This is ascribed to the presence of an interfacial amorphous phase between the sites.

The new set of nanostructured materials shows very uncommon dielectric behavior. We have reported the unusual dielectric behavior of nanocrystalline CoFe_2O_4 and $\text{NiZnFe}_2\text{O}_4$ synthesized using the same doping technique. Dielectric constant from nanostructured CoFe_2O_4 specimens show a peak at ~ 430 K. Similarly a peak at ~ 480 K is observed from $\text{NiZnFe}_2\text{O}_4$ specimens. This is believed to arise due to the presence of a phase in between the ferrites phases. The former has a lattice symmetry lower than cubic which probably causes the presence of dipole moment in the unit cell. This implies that there is transition of the phase to one with cubic symmetry at that particular temperature.

Understanding the Atomic Force Microscope : Instabilities in cantilever motion

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We investigate the instabilities in the Atomic Force Microscope (AFM) introduced by non-linear forces (in our case, the attractive van-der-Waals force). We show that this leads to many of the observed effects in force-distance curves, which form the basis of operation of the AFM. We also show that these instabilities can equally well explain effects which have till now been attributed to adhesion. Finally we show how these instabilities can lead to a new way of calculating the Hamaker constant of materials.

Thermal and Electrical conduction in nano-fluids

Prof. Sarit Kumar Das (Principle Investigator), Prof. T. Pradeep, Prof. T. Sundararajan, Dr. A. Dasgupta, Dr. N. Dasgupta

Two state of the art equipments for measurement of thermal conductivity of nanoparticles suspensions and pure liquids have been developed using the principles of transient hot-wire method and temperature oscillation method. These apparatus are not available in the country. BARC and TRDDC have shown interest in these apparatus.

An equipment has been setup for electrical conductivity measurement of nanofluids.

Experimental setup for evaluation of convective heat transfer in nanofluids has been developed.

Experimental setup for evaluation of boiling heat transfer in nanofluids has been developed.

Experimental setup for cooling of electronic equipments using nanofluids has been developed.

Characterisation of nanoparticles using TEM and XRD had been carried out.

Experimental studies on thermal conductivity of oxide, metallic and carbon nano-tubes based nanofluids have been done and are being carried out.

Experimental studies on boiling heat transfer of nanofluids of different particle sizes with heating surfaces of varying surface roughness have been done.

Experimental studies on cooling of electronic chips using nanofluids are under progress.

Theoretical studies

A theoretical model for thermal conductivity of nanofluids using the concept of surface area increase and Brownian motion of particles has been proposed.

A further refined model of thermal conductivity enhancement using micro-convection around particles has been developed.

A theoretical model for CNT nanofluids using percolation through chain has been developed.

A computational model for convective cooling using nanofluids has been developed and applied to a practical chip cooling situation.

Investigation of the dissolution kinetics of some nano sized catalysts

Gurmeet Singh

The main objective of the project is to find out and prepare transition metal catalysts of nanometer size to have enormous surface area. These nano sized catalysts may corrode in the reaction media and therefore their uses are limited. Hence, the related objective of the proposal is to study the change of electrode potential of various metal catalyst nanoparticles with the adsorption of different nucleophiles and electrophiles species. One of the most interesting aspects of the study of metal nano particles is their size-dependent properties which have been observed to be equally important from the fundamental as well as from an application point of view. With these objectives in mind recently great deal of interest has been shown in procedures for the preparation of colloidal metallic particles and semiconductor crystallites. The major limitation of the method used for nanoparticles preparation is that AOT/Non-Polar system is having limited solubilisation of the ionic solution and thus decreased yield and stability results. Therefore, an alternate system composed of AOT + SDS/hexanol/cyclohexane/water has been deployed for preparation of Cu and Au nanoparticles. Copper nanoparticles have been prepared in the aqueous core of AOT + SDS/hexanol/cyclohexane/copper sulphate system by reduction. The study on the stability of the colloidal system, size of the particles obtained and interfacial rigidity of the microemulsion has been carried out. These particles have been prepared and characterization has been done by TEM, DELS and other techniques. The study related to change of electrode potential of various metal catalyst nanoparticles with the adsorption of different nucleophiles and electrophiles is in progress. In addition, seeing the importance of semiconducting materials and realizing the fact that only few elements out of 92 naturally occurring elements can be used as semiconducting material, an attempt has been made to synthesis and characterize the CdSe quantum dots. The method used here is at 300°C as against the normal method which is carried out at 1100°C. Another achievement here has been to replace the conventional dimethyl Cadmium with a more easy to handle precursor CdO. Moreover, capping of these CdSe quantum dots at 300°C with trioctyl phosphine oxide facilitates stabilization against particle growth and this method yields very well size controlled CdSe nanocrystals. These have been characterized by XPS, TEM and XRD. Cd/Se input precursor ratio is varied to form colloidal TOP/TOPO capped CdSe nanoparticles. An optimum input precursor ratio is determined where stoichiometric yield, efficiently capped smallest sized (~ 5 nm) CdSe nanoparticles with superior optical, structural and morphological properties are obtained. Electron Diffraction and deconvolution of XPS-core-levels enables the identification of the different compositional regimes of CdSe nanocrystallites. For non-optical precursor ratios, the presence of Cd- and Se-related oxides are observed. The multi-technique approach has enabled us to pictorially model the compositional, structural and morphological aspects of TOP/TOPO capped CdSe nanoparticles.

Efficient Utilization of Platinum Nanoparticle Enriched Substituted Polyaniline Network Composite Electrodes towards Electrocatalytic Applications

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Fuel cell reactions viz., oxygen reduction, methanol oxidation, hydrogen oxidation occur at membrane electrode, which is a composite of Pt-incorporated-polymer matrix. Literature shows that only 20 percent of the noble metal catalyst is used-up under operation leaving behind 80 percent of expensive Pt unused. The present project has been initiated with the objective of achieving the total utilization of the Pt catalyst by realizing the following two factors regarding the present polymer film containing 3-dimensionally distributed Pt catalyst particles: (1) the catalytic efficiency can be enhanced by depositing nano-sized Pt by electrochemical methods, (2) the overall electrocatalytic reaction current is a manifestation of several associated film processes, like, electron transport, substrate diffusion, and catalytic reaction between the embedded catalyst particles and the substrate, all occurring in the coated film. As a consequence of the later mechanism, estimation of reaction rates corresponding to the individual processes is essential for formulating optimization protocols for designing nano Pt-polymer composite electrodes with maximum catalytic efficiency with minimum effective loading of Pt nano particles. It is realized that a conducting polymer like polyaniline (PANI) is the best choice as a polymer matrix to support Pt nano particle catalyst.

The first part of the work has been devoted to standardize the electro-polymerization conditions to obtain a good quality PANI film on glassy carbon electrode (GCE) from sulfuric acid containing aniline monomer. Potential cycling method was employed for preparing PANI film. The film property-controlling experimental parameters, like, electrode substrate (GCE, Pt, Au, Ag, ITO), sulfuric acid concentration, aniline monomer concentration, potential scan rate, film formation cycle number etc., have been varied and their effects studied. Film stability test has been used to monitor the quality of the film. From the above results we established that a highly stable, good quality PANI film possessing the characteristic Leucoemeraldine to Emeraldine and Emeraldine to Pernigraniline transition peaks can be obtained when the PANI films are prepared over 15 cycles with following experimental conditions: 0.1M of aniline, 0.5M of H_2SO_4 , 50 mV s^{-1} scan rate, and -200 to 1200 mV (SCE) film formation potential window.

Subsequent to this, work related to nano Pt particle deposition into PANI film from $\text{K}_2[\text{PtCl}_6]$ solution by electrochemical methods has been undertaken. Four different methods have been used here viz., single pulse potentiostatic method, double pulse potentiostatic method, potential cycling under stationary or hydrodynamic conditions. In each method, a set of electrochemical deposition parameters is varied and their effect on Pt particle size and conductivity of the film by Electrochemical Impedance Spectroscopy (EIS) technique are followed. For certain samples physicochemical characterizations by TEM, SEM, EDAX, XRD, XPS and AFM are also carried out. These and other results will be presented and discussed.

SESSION P2

POSTER PRESENTATIONS - STUDENTS

Carbon doped boron nitride nanotubes: a first principle study

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We study the atomic and electronic structures of armchair and zigzag boron nitride nanotubes (BN-NTs) of different sizes in their two possible forms: bundled and isolated. Comparison between the properties of the pristine isolated and bundled BN-NTs allows us to characterize the intertube interaction. We compare and discuss the electronic structures of the pristine and carbon-doped BN-NTs. Carbon substitution in either a single boron or a single nitrogen atom site in a BN-NT can induce carriers in the insulating pristine boron nitride nanotubes. However, co-doping of even number of carbon atoms at neighbouring B and N sites allows the BN-NT to remain insulating. Our results show that the induction of carriers for carbon doped either in B or N position can be attributed to the pi conducting channel of carbon atom.

Solvothermal synthesis of nanorods of ZnO, N-doped ZnO and CdO

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ZnO nanorods with diameters in the 80-800 nm range are readily synthesized by the reaction of zinc acetate, ethanol and ethylenediamine under solvothermal conditions. The best products are obtained at 330°C with a slow heating rate. Addition of the surfactant Triton®-X 100 gave nanorods of uniform (300 nm) diameter. By adding a small amount of liquid NH₃ to the reaction mixture, N-doped ZnO nanorods, with distinct spectroscopic features are obtained. CdO nanorods of 80 nm diameter have been prepared under solvothermal conditions using a mixture of cadmium cupferronate, ethylenediamine and ethanol at 330°C. Similarly, Zn_{1-x}Cd_xO nanorods of a 70 nm diameter are obtained under solvothermal conditions starting with a mixture of zinc acetate, cadmium cupferronate, ethanol and ethylenediamine.

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Nanolithography on modified Si surfaces using conducting AFM probe

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The process of conducting tip induced local anodic oxidation commonly known as LAO, has emerged as a fine lithographic technique for creating oxide patterns at the nanoscale on semiconductors surfaces. Due to proximity of the tip, the substrate is subjected to local oxidation under the intense electric field ($\sim 10^8$ V/cm), leading to well defined nanometric protruded patterns of the relatively less dense oxide (SiO_x). This presentation deals with two aspects of our research activities related to LAO. We have carried out a comparative study of LAO on Si (100), (110) and (111) substrates employing negative tip voltages of 5, 8 and 10 V. The nature of the oxide formed has been related to the surface densities of the substrates, the (110) surface being dense requires more voltage to initiate oxidation but produces voluminous oxide. Nanoindentation on the LAO pattern yielded a hardness value of 4.34 GPa. The oxide patterns could be washed away with HF leaving trenches on the surface. We have also examined the effect of a polymer barrier on the LAO process. With Si substrates coated with PVP (polyvinylpyrrolidone) films (~ 30 nm), a tip voltage of -12 V produced neat trenches (upto 100 nm wide, 5 nm deep), in the polymer film. These trenches can potentially act as stencils for nanopatterning desired materials such as metals and semiconductors. Following developing in water, the SiO_x patterns formed beneath the polymer film were clearly visible. In another study, instead of neat PVP, nanocomposites of PVP with metal nanoparticles as well as ionic precursors have been tried out.

Nanoscale patterning of metals and inorganic materials by Electron Beam Lithography

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Electron beam lithography (EBL) has become inevitable in Nanotechnology. A focused electron beam with energy in the range of 1-200 kV, with a beam spot of few nanometers can work like a 'pencil' to write patterns on e-resists, thus producing the desired masks in nanolithography. In our Laboratory, we have employed commonly available polymer resists such as polystyrene to produce line gratings with pitches down to 200 nm. The Au metal was cast into gratings by a simple electroless process. As our method uses electron beam in the 'imaging mode', large areas extending to few mms can be easily patterned. A similar method was followed to produce gap electrodes down to 200 nm, along with large contact pads. The utility of such electrodes is demonstrated by measuring the resistance of a nanometal conduit. Circuits have also been made on SiO_x/Si substrates using physical vapor deposition of metals. Furthermore, we have found a zwitter resist behavior- the polymer alternating between negative and positive behavior with increase in e-dose, which was related to its chemical nature. We have also used EBL technique innovatively as a direct write method to create nanopatterns of various inorganic materials. These include magnetic iron oxide and metals such as Pd. Patterns of submicron size have been obtained and the chemical species have been characterized using spectroscopy techniques.

Core-Shell Nanoparticles Based on an Oxide Metal: $\text{ReO}_3@Au$ (Ag) and $\text{ReO}_3@SiO_2$ (TiO_2)

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Core-shell nanoparticles based on metallic ReO_3 nanoparticles have been prepared for the first time. The nanoparticles with the metallic shell viz. $\text{ReO}_3@Au$ and $\text{ReO}_3@Ag$ were prepared by the reduction of metal salts over ReO_3 nanoparticle seeds. $\text{ReO}_3@SiO_2$ and $\text{ReO}_3@TiO_2$ core-shell nanoparticles were prepared by the hydrolysis of the organometallic precursors over the ReO_3 nanoparticles. The core-shell nanoparticles have been characterized by transmission electron microscopy, optical absorption spectroscopy, energy dispersive X-ray spectroscopy, X-ray diffraction and Raman spectroscopy. The $\text{ReO}_3@Au$ and $\text{ReO}_3@Ag$ core-shell nanoparticles show composite plasmon absorption bands comprising contributions from both ReO_3 and Au (Ag) whereas $\text{ReO}_3@SiO_2$ and $\text{ReO}_3@TiO_2$ show shifts in the plasmon bands depending on the refractive index of the shell material.

Studies on electrical and magnetic behaviour of nanostructured cobalt ferrite

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Cobalt ferrite is one of the most important ferrites having the highest coercivity and hence it is suitable for applications in information storage system, ferrofluid technology, magnetocaloric refrigeration and medical diagnostics. We have synthesized nanocrystalline (8 run) cobalt ferrite by a conventional co-precipitation technique and studied in detail its electrical conductivity and magnetic behaviour. The as-prepared ferrite has been heat treated to attain various grain sizes (92, 102, 123 run). The samples were characterized for their structural, electrical and magnetic properties using various techniques like X-ray diffraction, impedance and Mossbauer spectroscopy. The effect of grain size on the electrical conductivity and magnetic properties of nanocrystalline CoFe_2O_4 is discussed. The activation energies for conduction, both at grain and grain boundaries were determined from the Arrhenius plots. The activation energy values suggest that the conductivity is due to hopping of electrons and holes. The paper in particular discusses in detail the reason for the observed decrease in conductivity when grain size is increased to 92 run. This observation is attributed to variation in cation distribution, wherein Fe^{3+} ions migrate from octahedral to tetrahedral positions as is evident from in-field Mossbauer studies.

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Size Dispersion Reduction in CdS_xSe_{1-x} Quantum Dots Embedded in Borosilicate Glass Matrix Due to Aging

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Quantum Dots of CdS_xSe_{1-x} embedded in borosilicate glass matrix have been grown using Double-Step annealing method. Optical characterization of the quantum dots has been done through optical absorption at room temperature. The changes in particle size, size distribution, number of quantum dots, volume fraction and Gibbs free energy of quantum dots, has been explained on the basis of the diffusion-controlled growth process, which continues with passage of time. For a typical case, it was found that after 24 months of aging, the average radii increased from 3.05 to 3.12 nm with the increase in number of quantum dots by 190% and the size-dispersion decreased from 10.8% to 9.9%. After that no significant change was found in these parameters for the next 12 months. This shows that the system attains almost a stable nature after 24 months of aging. It was also observed that the size-dispersion in quantum dots reduces with the increase in annealing duration, but at the cost of quantum confinement effect. Therefore, a trade off optimization has to be done between the size-dispersion and the quantum confinement.

Tunable physical properties of nanoporous AuFe alloys by electrochemical charging

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The present work is focused on the study of electronic tunability of the electrical, magnetic, and mechanical properties of nanoporous materials by electrochemical charging. Hitherto, the approach was to tailor the properties of materials by conventional methods such as alloying, introducing lattice defects etc. The limitation of such methods is that changes once made cannot be reverted back i.e. modifications are permanent. The work being reported here is based on the proposition of Gleiter, who suggested that the properties of materials can be modified in their nanophase state by inducing surface charge on them. The property of the entire material is influenced because the surface to volume ratio is high in the nanomaterials.

We studied the effects of charging on the following bulk properties in-situ: a) volume change by dilatometry b) variation in mass magnetization by magnetometry, and c) electrical conductivity. At the microscopic level, the hyperfine interaction parameters were measured by in-situ Mossbauer spectroscopy. Nanoporous powders of the alloy Au₅₀Fe₅₀ were prepared by inert gas condensation. The samples were characterized by X-ray Diffractometry and Scanning Electron Microscopy. In-situ measurements were carried by making the sample as a working electrode and by using 1M lithium perchlorate in ethyl acetate as electrolyte.

Resistivity measurements were carried out in a custom designed electrochemical cell using dc four-probe method. The observed relative change in resistivity was 2.6 percent. It was also observed that there was a negligible influence of surface reconstruction during charging and de-charging because of the presence of iron.

From field-cooled and zero field-cooled measurements, the magnetic state of the sample was characterized to be super-paramagnetic and a blocking temperature of 65K was observed. For in-situ charging measurements of the magnetic moment, an extraction magnetometer (Quantum Design PPMS) was used in DC extraction mode, while flushing the sample environment with helium. It was observed that there was a relative change in mass magnetization with charge of 1.5% and the magnetic moment increased at negative charging.

A reversible relative change in strain of 0.17% was observed by in-situ dilatometry studies using a pushrod dilatometer. These results were similar to strain measurements on nanoporous Pt black.

The Mossbauer spectrum of the bulk polycrystalline sample showed a sextet, whereas the spectrum of the nanoporous alloy gave a doublet in conformity with magnetic measurements. In-situ Mossbauer measurements showed a small and systematic change in isomer shift as well in the quadrupole splitting.

Polyelectrolyte Templating Strategy for the Fabrication of Langmuir-Blodgett Films Capable of Stable and Enhanced Optical Second Harmonic Generation

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Langmuir-Blodgett (LB) films have been explored extensively in recent years because they facilitate control of the construction of functional organic materials at the molecular level. Some of the fundamental problems that have limited their applications are instabilities of Langmuir films at the air-water interface, unfavorable deposition sequences and postdeposition rearrangements in the LB films. We have developed a 'polyelectrolyte templating methodology' that provides a simple and efficient strategy to address some of these problems. The technique relies primarily on the electrostatic interaction between ionic amphiphilic molecules and water soluble polyelectrolytes at the air-water interface. The advantage of this technique is that the choice of amphiphilic molecule and the polymer are quite general and that the molecular organization and LB film deposition can be controlled to a large extent by varying the combination of complexing partners. It was demonstrated in our laboratory that polyelectrolyte templating effectively suppresses the aggregation of cationic hemicyanine based amphiphiles in monolayer LB films leading to stable and enhanced optical second harmonic generation (SHG). Laser induced decay of SHG in the LB films was also effectively arrested through the polyelectrolyte templating. We have now employed this technique to fabricate multilayer LB films of N-n-octadecyl-4-[2-(4-dimethylaminophenyl)ethenyl]pyridinium bromide (ODEP+Bf).² Different polyelectrolytes such as poly(4-styrenesulfonic acid), deoxyribonucleic acid and carboxymethylcellulose were employed in this study. It is found that the nature of the polyanion employed influences strongly the multilayer deposition sequence resulting in significant variations in the SHG response. Carboxymethylcellulose is identified as an optimal polyelectrolyte template that facilitates favorable z-type deposition of the amphiphile and formation of stable multilayer films, showing the expected quadratic increase of SHG with the number of layers.

Determination of local spin structure and characteristic magnetic length in field-annealed VITRO PERM by resonant γ -ray and microwave absorption techniques

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Resonant γ -ray absorption (Mossbauer effect) at room temperature and resonant microwave absorption (ferromagnetic resonance) at temperatures ranging from 77 K to 325 K were measured for the samples S₂₀ and S₁₅₀ of Vitroperm with nominal composition Fe₇₃Cu₁Nb₃Si₁₆B₇, supplied by Vacuumschmelze GmbH, Hanau. The samples S₂₀ and S₁₅₀ (in the form of melt-spun ribbons) were annealed at 580 and 560°C for 1 hour in a magnetic field (H) directed along the width in the ribbon plane. 'Field-annealing' induces uniaxial magnetic anisotropy with easy axis in the direction of H and produces a nanocomposite consisting of ferromagnetic nanocrystalline grains (volume fraction \sim 90 %) of mean size $d = 20(2)$ nm embedded in a ferromagnetic amorphous matrix. The sample S₁₅₀ (S₂₀) exhibits a magnetic permeability of $\mu = 150,000$ (20,000). While nearly 60 % of the nanocrystalline grains have a cubic DO₃ Fe₃Si-like structure with actual Si concentration of about 22 %, the remaining 40 % nanocrystalline grains have hexagonal Fe₂Si and tetragonal Fe₃B structure. Consistent with the uniaxial nature of the magnetic anisotropy, which constrains the magnetization vector to lie within the ribbon plane along the width, Mossbauer effect results clearly demonstrate that the magnetic moments on most of the Fe sites point along the easy direction of magnetization. However, at certain Fe sites, the direction of magnetic moments deviates substantially from the direction dictated by the field-induced uniaxial anisotropy. The dispersion in the direction of magnetic moments is more in the case of the sample S₂₀ with the result that the permeability of this sample is an order of magnitude smaller than that in S₁₅₀.

An elaborate lineshape analysis of the dP/dH versus H curves (where P is microwave power absorbed) taken at different temperatures yields the resonance field, Landé splitting factor 'g' and saturation magnetization. At a given temperature, uniaxial anisotropy field is directly determined from the difference between the observed values of the resonance field when H is applied along and perpendicular to the easy axis. Resonant microwave absorption studies reveal the importance of magnon-magnon interactions in the thermal renormalization of the spin wave stiffness, the origin of 'in-plane' anisotropy field and the characteristic magnetic (exchange correlation correlation) length, which decreases with increasing temperature. These results lend support to the random anisotropy model in that larger the exchange correlation length compared to the nanocrystallite size, more effective is the averaging of the magnetocrystalline anisotropy of individual nanocrystalline grains.

Crystallization kinetics and mechanical properties of Al₈₉Ni₆La₅ metallic glass

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Past one decade has seen a rise in interest in amorphous and nano-crystalline Al-based alloys. These alloys have attracted considerable attention among the researchers as possibly light-weight, novel mechanical properties, wear and corrosion resistance materials. The high strength can be achieved due to the occurrence of uniform dispersion/precipitation of Al-nanocrystals in an amorphous matrix.

Among the Al-based amorphous alloys, Al-Ni-La system shows wide composition range for glass formation and possesses good glass forming ability. In this paper, the mechanical properties and crystallization kinetics of Al₈₉Ni₆La₅ alloy were reported.

Ingots were prepared by induction melting in an argon atmosphere. Rapidly solidified ribbons were obtained by single roller melt spinning technique. As-melt-spun and annealed ribbons were investigated by means of X-ray diffractometry (XRD), Transmission electron microscopy (TEM), hardness measurements. Crystallization behaviors were investigated by differential scanning calorimetry (DSC) and electrical resistivity measurement. XRD studies revealed that the ribbons are fully amorphous in the as-melt-spun state. DSC studies showed that crystallization proceeds in two stages. The phases responsible for these stages were identified. The first stage is responsible for precipitation of fcc-Al while the second stage is responsible for precipitation of Al₃Ni and Al₁₁La₃. Growth rate of fcc-Al is very slow prior to the second stage of crystallization. Crystallization kinetics was analyzed by Johnson-Mehl-Avermi approaches. Activation energy for the crystallization was measured by isochronal and isothermal studies. Microhardness of the ribbons was examined at different temperature annealed for 10 minutes and correlated with the corresponding structural evolution. The microhardness results showed increase of hardness up to the onset of second crystallization stage (~290°C) due to precipitation of nanoscale fcc-Al in amorphous matrix followed by sharp drop of hardness due to decomposition of amorphous matrix.

Preparation of nanofibers of poly vinyl alcohol and poly caprolactone by electrospinning for biomedical applications

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Electrospinning has developed as a unique and versatile process to fabricate ultrathin fibers in the form of non-woven meshes or as oriented arrays from a variety of polymers. In the present investigation, we focus on the preparation and characterization of nanofibers of biocompatible and biodegradable polymers such as polyvinyl alcohol and polycaprolactone and their blends. The fibers were spun on stationary copper electrodes as well as on designed mandrels. It was observed that the orientation of nanofibers varied with the rotational speed of the collecting electrode. The parameters such as flow rate, electrode separation, viscosity of polymer solution and applied electric field were found to be crucial in deciding the diameter of the nanofibers. The structural properties of these individual as well as blend nanofibers were compared using scanning electron microscopy (SEM), atomic force microscopy (AFM) and Fourier Transform Infrared (FTIR) spectroscopic techniques.

Direct observation of protein residue relaxation dynamics in nanoenvironments

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Dynamics of relaxation of chromophores attached to a protein by amino acid residues in comparison to that by water molecules has remained a long-standing problem in the field of protein solvation dynamics. An attempt to unravel the existing controversy has been made by studying the solvation dynamics of dansyl labeled proteolytic enzyme alpha-chymotrypsin in both native and denatured state. In the native state the dansyl probe at the surface of the protein interacts largely with the hydration water while in the denatured state the solvation relaxation of the probe in the randomly oriented polypeptide chain is mainly governed by the polar amino acid residues of the protein. A significant structural perturbation of the protein upon denaturation due to which the probe finds itself in a non-polar environment of the peptide residues is also evident from steady-state fluorescence, circular dichroism (CD) and dynamic light scattering (DLS) experiments. High-resolution streak camera has been employed in order to study dynamic fluorescence Stokes shift of the dansyl probe due to hydration water and protein residues. The time scale of solvation by polar peptide residues is found to be an order of magnitude slower than that by bulk type water molecules. In order to show the effect of environmental restriction on the solvation dynamics, the protein in both native and denatured states have been encapsulated inside reverse micelles of varying degree of hydration (w_0). Simple theoretical models have been proposed in order to qualitatively understand the experimental findings. This study might invoke further research in the field of protein solvation.

Size and Shape-dependent Electron-Hole Relaxation Dynamics in CdS Nanocrystals

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The dynamics of photoluminescence (PL) in CdS nanocrystals (NCs) with various sizes and shapes dispersed in water-in-oil microemulsions (reverse micelles) are studied with the picosecond resolved time correlated single photon counting (TCSPC), streak camera and nanosecond resolved gated PL spectroscopic techniques. The time resolved PL-spectra exhibit several discrete features, which are not pronounced in steady state PL spectra. In quantum dots (QD), slower carrier recombination dynamics are observed in smaller sized NCs. The relaxation of the excited state carriers in a quantum rod (QR) is found to be slower at early time and faster in the longer time scales compared to those in QD with similar volume. The signature of thermoluminescence (TL) of CdS QR in low temperature (77K) is clearly evident from our studies. We also study the effect of the shape of the NCs on their PL-anisotropy. The steady state and time resolved PL-anisotropy of a QR show significantly different behavior compared to those of a QD with similar volume. The results of the NCs are important in the context of designing better, more effective physical and biological PL probes.

Large area growth of patterned two-dimensional arrays of gold nanoparticles

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A method of preparing large area patterned 2D arrays of gold (Au) nanoparticles using self-assembly has been developed. The pattern has been formed using uncapped Au nanoparticles. The Au nanoparticles were synthesized via a standard toluene/water two phase system using a reducing agent and colloidal nanoparticles were produced. These nanoparticles have been prepared without using any kind of capping agent. Analysis by TEM and AFM showed discrete Au nanoparticles of diameter around 4 nm (measured by TEM and AFM). These nanoparticles formed self-assembled coherent patterns with dimensions in excess of 500 nm. We find that these islands of Au nanoparticles can be arranged in a pattern as described below.

We were able to arrange these islands of Au nanoparticles into larger patterns by spin coating on Si substrate. These patterns form due to self-assembly that is controlled by a combination of alignment forces. The patterns can be controlled by surface treatment and spin-coating speed. There is a critical value of the spin-coating speed at which these patterns form. The pattern formation depends on the hydrophilic nature of the Si substrate and when the surface is made hydrophobic no such patterns form.

In the process of spin-coating, the centrifugal forces cause the liquid to drain radially off the edge of the substrate until solvent evaporation leaves a solute-rich liquid. The solute-rich phase is too viscous to flow readily and ultimately forms large concentric arrays of liquid droplets. The droplets contain the Au nanoparticles, which then grow into an array within the droplets. The pattern thus obtained contains arrays of islands (~30nm-400nm) each of which is an array of Au nanoparticles.

Bulk modulus enhancement in semiconductor nanocrystals

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Semiconductor nanoparticles have been intensively studied in recent times because of the dependence of their properties on nanoparticle size, an effect that has tremendous technological implications. In this study we focus on a specific set of properties the modification of the bulk modulus with size. Studies on semiconductor nanocrystals have been found to have an enhanced bulk modulus compared to values for the bulk. It is difficult to study the renormalization of the mechanical properties experimentally. One does not always have a homogeneous distribution of particles. Further their sizes vary over several percent. In this context theoretical calculations, which can simulate the ideal situation, would provide valuable insight into the modifications as a function of size. We have examined within first principle calculations, the bulk modulus enhancement in the elemental group IV semiconductors as a function of size for particles with diameters upto 30 Å. In the case of Si, a cross-over to almost bulk-like values for the bulk modulus is seen for particles sizes in the range 25-30 Å. For particles with diameter larger than 15 Å, we had a scaling of the bulk modulus, which is in very good agreement with the scaling relation derived in general for bulk semiconductors. The results for other systems will be contrasted with "bulk-motivated" models in an attempt to formulate a general picture for the modifications.

Spherical self-assembled particles with Mn and Cr co-doped ZnO nanocrystals

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Doped ZnO has been receiving considerable attention recently due to the presence of ferromagnetism in a semiconducting oxide. The successful synthesis of well defined nanostructures of these materials provides an opportunity to develop a wide variety of applications. Hence in the present work co-doped ZnO nanocrystals were synthesized by a soft chemical technique at low temperature, which also facilitates self-assembly into highly ordered structures. The synthesis process is based on hydrolysis of the acetate precursors which were dissolved in diethylene glycol (DEG) and heated under refluxing conditions. The XRD analysis reveals that the Mn, Cr: ZnO samples crystallize in a wurtzite structure with a crystal size of ~ 10-15 nm. The lattice constant is found to be larger than that of pure ZnO which confirms that Mn^{2+} and Cr^{3+} substitute Zn^{2+} in the ZnO structure. SEM micrographs show spherical particles of diameter in the range of 100-400 nm, larger than the crystal size obtained by XRD. To clarify this ambiguity of size, TEM was performed and it is clearly observed that the spherical particles are well-defined, discrete and porous. Each sphere is made up of spatially connected numerous nanocrystals of average diameter 10-15 nm in agreement with the crystal size obtained from XRD. These fine nanocrystals self-assemble due to electrostatic interactions into highly porous polydisperse spherical particles. The selected area electron diffraction pattern (SAED) can be indexed to the wurtzite structure of ZnO. The thermal stability of the self-assembled spherical particles has been investigated by heating them to 300 °C for 1 hour. TEM of the heat treated particles does not show any significant changes in either the overall morphology or size of the nanocrystals in the spherical particles. The co-doped ZnO sample exhibits a shift in the absorption edge (red shift) compared to that of pure ZnO nanocrystals. This is mainly due to the sp-d exchange interactions between the band electrons of ZnO and the localized d electrons of Mn^{2+} and Cr^{3+} which are present at the Zn^{2+} sites. The ESR spectrum exhibits a broad resonance at room temperature, a characteristic of ferromagnetic resonance (FMR). In addition to the broad resonance, a very weak six-line splitting pattern is observed in external fields in the range of 3.0-3.5 kOe with a g-value of 2.0035 and hyperfine splitting constant of $74.6 \times 10^{-4} \text{ cm}^{-1}$. These results indicate that Mn is in 2+ oxidation state and it occupies the tetrahedral sites originally occupied by Zn^{2+} . A detailed characterization of the magnetic behaviour of co-doped ZnO is currently in progress and these results will be discussed together with the optical absorption results.

In-situ high temperature XRD studies of ZnO nanopowder prepared via cost effective ultrasonic flame pyrolysis

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We report the preparation and characterization of ZnO nanopowder grown by using ultrasonic flame spray pyrolysis technique. The particle size, lattice parameter and crystal structure of ZnO nanopowder are characterized by *In situ* High temperature X-ray diffraction (XRD), Transmission Electron Microscopy (TEM). The optical properties are observed using UV-visible spectrophotometer. The influence of high temperature vacuum annealing on XRD pattern is systematically studied. Results of high temperature XRD showed prominent 100, 002 and 101 reflections among which 101 is of highest intensity. With increase in temperature a systematic shift in peak positions towards lower 2θ values has been observed, which may be due to change in lattice parameters. Temperature dependence of lattice constants under vacuum shows linear increase in their values. Diffraction patterns obtained from TEM are also in agreement with the XRD data. By using UV-visible spectrophotometer the band gap of the ZnO nanopowder is found to be greater than the band gap in case of bulk powder.

Reverse Micellar route to the synthesis of oxalate/carbonate precursors of Ce and Zr and their decomposition to CeO₂ and ZrO₂ nanoparticles.

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Nanorods of transition metal oxalates have been synthesized via the reverse micellar route. The particles synthesized are homogeneous and monodispersed. Morphology of the product can be controlled by changing the composition of the microemulsion system. Here we report the synthesis of oxalate and carbonate precursors of cerium and zirconium, prepared using reverse micelles as nanoreactors. Thermal decomposition of these precursors led to the formation of their respective oxides. The precursors and the oxides obtained from them were characterized by PXRD, TEM, HRTEM, and TGA/DTA. Mixture of nanorods and nanoparticles of cerium oxide (nanoparticles of 10 nm and nanorods with 7 nm diameter and 30 nm length) were formed by the decomposition of cerium oxalate precursor. Cerium oxide with crystallite size of 10 nm was obtained from cerium carbonate precursor. Monodispersed nanoparticles of zirconia with an average size of 3-5 nm and 12 nm were obtained from the oxalate and carbonate precursor, respectively.

Synthesis and Characterization of Quantum Dots for Bioapplications

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The coupling of biomolecules with semiconducting nanoparticles known as Quantum Dots (QDs) attracts substantial research efforts directed to the development of new imaging, labeling and sensing system. This is motivated by the favorable fluorescence properties of quantum dots as compared to conventional organic dyes. Furthermore, the stability of (QDs) towards photodegradation and photobleaching turns the particles to be an attractive material for analytical purposes. However the controlled interfacing of hydrophilic organic molecules with the inorganic surface of nanocrystals is an important challenge. Our group is actively involved in optimizing various conditions for the efficient labeling of biomolecules such as proteins, antibodies with QDs for their applications in diagnostic/bioimaging.

Synthesis of Amorphous Cobalt and formation of nanocrystalline hcp-Co by A Novel Annealing Process

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The work reported in this paper demonstrates, for the first time in the literature, a simple hydrothermal annealing (HTA) approach to obtain phase pure stable nanocrystalline hexagonal cobalt particles for magnetic applications. Ultrafine particles of pure amorphous cobalt were chemically synthesized by borohydride reduction of a cobalt salt in aqueous condition. This material when subjected to a controlled annealing in aqueous medium at 80 °C for about an hour yielded phase pure nanocrystalline particles of cobalt with a hexagonal close packed (hcp) structure as revealed by an X-ray diffraction (XRD) analysis. The estimated particle size was 17 nm. Differential scanning calorimetry (DSC) studies and subsequent XRD analysis of the samples after a DSC cycle, carried out both on amorphous and HTA cobalt, showed that while amorphous cobalt on heating crystallizes into a hcp+fcc mixture having dominant fcc phase with a crystallization temperature of 485 °C, the annealed cobalt particles of phase pure hcp structure are stable up to 374 °C beyond which a partial phase transition to fcc is observed. Thermogravimetric measurements under bar magnet yielded an amorphous Curie temperature of 275 °C for the as-synthesised Co and established the phase transition temperature of 375 °C for hcp-Co. The magnetic properties of the amorphous and annealed samples obtained from Vibrating Sample Magnetometer (VSM) measurements are also discussed in the paper.

Synthesis of rare–earth doped nanophosphors through soft chemistry

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Semiconductor nanocrystals show unique optical, electronic and chemical properties which make them ideal for a number of applications ranging from inorganic bio-labels to lasers. Luminescent nanocrystals based on CdSe, CdTe, or CdSe/ZnS core/shell materials have been one of the most studied nanosystems particularly for bio-applications. However, recent *in vivo* toxicity studies revealed that these nanocrystals are acutely cyto-toxic due to the liberation of free radicals of Cd⁺ and Se⁻ into the blood-stream. Specifically, the surface oxidation of nanoparticles through variety of biological pathways causes the release of chemically reduced cadmium leading to the cell death. These findings indicate the serious limitation in the application potential of heavy-metal containing chalcogenide nanocrystals and it is important to develop new non-heavy metal luminescent nanocrystals with essential bio-compatible surfaces.

In the present work , we report a simple aqueous wet-chemical method for the preparation of rare-earth doped nanophosphors of Y₂O₃ doped with Eu³⁺ and Tb³⁺ rare earth elements have been successfully incorporated into the host Ytria lattice during slow crystallization process under wet-chemical conditions. The reaction pH, post-synthesis crystal growth ,host optimized in order to obtain bright emission colors in green 543nm and red 612nm from Eu³⁺ and Tb³⁺, respectively. One of the most interesting feature of the process is that the nanoparticles are easily surfaces conjugated with a number of important bio-molecules such as mercaptoacetic acid/acrylic acid /dextran/Folic acid, etc. The XRD studies show formation of phase pure cubic yttrai with ~ 20nm size, derived using Debey-Sherrer equation. The photo-luminescence studies clearly indicate radiative involving f-f orbitals of rare-earth elements in yttria.

On the Modeling of Nanostructure Formation

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For the design of materials with precise physico-chemical properties, mathematical models with excellent predictive capabilities to correlate synthetic conditions with final size, shape and compositions of nanostructures are required. Towards this goal, we have been working on the developing mechanisms of formation and modeling of nanostructures like single component and multicomponent (core-shell) nanoparticles, nanorods etc.

Firstly, the formation of single component nanoparticles is one of the colloidal templates, water-in-oil (w/o) microemulsions, is modeled using deterministic Population Balance Equation (PBE) model and stochastic Monte Carlo (MC) simulation. These models are based on time-scale analysis of elementary events consisting of reactant mass transport, solid reactant solubilization, reaction, coalescence-exchange of drops, and finally nucleation and growth of nanoparticles. For another different kind of process involving mixing of two w/o microemulsions, each containing a pre-dissolved reactant in the drops, we developed a bivariate PBE model and a limiting univariate PBE model for low reactant concentrations.

Secondly, a two stage mechanism for the formation of two-component core-shell nanoparticle is developed from our own experimental findings. The first stage consists of core nanoparticle formation via coalescence-exchange of drops, reaction, nucleation, growth and coagulation of nanoparticles while the second stage includes the growth of shell on the core particles. Our predictions from MC simulation of this mechanism compares well with the temporal evolution of experimental mean size and shell thickness of CdS-ZnS core-shell nanoparticles for various drop sizes.

Finally, a PBE based model is presented to explain the formation of nanorods from a colloidal suspensions of pre-formed spherical nanoparticles. Our model shows that linear pearl-chain aggregates form by oriented attachment (OA) of nanoparticles during the early stages of synthesis, since it occurs with a time-scale much smaller than coalescence time-scale of nanoparticles present within an aggregate.

Fabrication of Fe(II)/Fe(III) loaded multi-walled carbon nanotube-poly(2,5 dimethoxyaniline) composite modified electrodes for electrocatalysis of ascorbic acid

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Modified electrodes were fabricated by the deposition of films of multi-walled carbon nanotube (MWCNT)-poly (2,5dimethoxyaniline) (PDMA) composite through cyclic voltammetry and loading further with an electrochemical inclusion-exclusion type Fe(II)/Fe(III) redox species on the surface of glassy carbon electrode (GCE). Also, modifications of the surface of GCE were done with a layer of MWCNT-PDMA composite or pristine MWCNT or pristine PDMA and also with an incorporation of Fe(II)/Fe(III) redox moieties. Surface morphology of the modified electrodes was examined through scanning electron microscope (SEM). Electrochemical impedance measurements were performed to study the interfacial properties of the modified electrodes. The electro catalytic behaviour of the modified electrode were tested for the oxidation of ascorbic acid in phosphate buffer (pH = 7) solutions. The electro activities of the GCE/MWNT-PDMA (Fe(II)/Fe(III)) are compared with other electrodes. Cyclic voltammetry, chronoamperometry and double potential chronoamperometry were used for obtaining a comparative evaluation on the electrocatalytic behaviour between these modified electrodes.

A novel GMR material of Ag-coated CrO₂ nanoparticles in form of thin fibrils derived through a polymer template

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The interest in ferromagnetic chromium dioxide (CrO₂) has undergone a renaissance in the recent years due to its promising potential for applications in the emerging fields of spintronics and photonics. Being a half-metal, with only Cr 3d spin-up band at the Fermi energy E_F , CrO₂ has the highest measured spin polarization (~100 % at 5 K) of all materials to date. This distinctive property of total polarization of charge carriers together with a high Curie temperature of ~ 114°C, makes it the most apposite to be utilized not only in ultra-high-density magnetic recording, high frequency magnetic sensors, magnetic tunnel junctions and spin polarizers for current injection into semiconductors, but also to increase the efficiency of optoelectronic devices and even in self-assembled quantum computers.

Despite these attributions, CrO₂ is a metastable compound, which irreversibly starts to degrade into antiferromagnetic Cr₂O₃ at the surface at an early temperature as 200°C and a complete CrO₂ → Cr₂O₃ conversion lies at temperatures above 400°C according to microstructure. Such Cr₂O₃ surface layer, if not stabilized and controlled, propagates and destabilizes the CrO₂ phase. However, a dense and uniform stable CrO₂ surface layer of Cr₂O₃ (or other diamagnetic coating materials of ceramics, polymers, or metals such as silver, gold, etc.) plays an ideal role of tunnel barrier in spin-dependent intergranular tunneling of electrons in CrO₂, which is the basic mechanism behind giant magnetoresistance (GMR), as well as optical and other useful properties. Different research groups have tailored CrO₂ ceramics in various forms to optimize these properties by improving the electrical and magnetotransport behaviors, which are strongly, influenced by different parameters, such as shape anisotropy, particle size, grain boundaries, defects present at the grain boundaries, etc. In this regard, diluted CrO₂ composites, e.g., CrO₂-Cr₂O₃, CrO₂-TiO₂, or CrO₂-polymer have spurred much attention in studying the functional role of grain boundaries in the intergranular tunneling process. This type of two phase composites of CrO₂ are technologically very smart, since GMR and other properties can be precisely manipulated and controlled by the modification of the grain boundaries in presence of the dia/antiferro magnetic phase. We have developed thin fibrils (average diameter 300 nm) of Ag-coated CrO₂ nanoparticles with a preferred nucleation and growth in [001] direction, using a polymer template of reactive molecules of poly vinyl alcohol (PVA) in hot conditions at 50 - 60°C in aqueous solution. X-ray diffraction with the X-ray beam facing the fibril surfaces, thus lacks the (00l) diffraction peaks, which has a significant intensity in XRD in the virgin Ag-coated CrO₂ nanoparticles. SEM microstructure confers the results of the preferred growth. The fibrils have a tetragonal crystal structure of modified lattice parameters $a = 0.4426$ nm and $c = 0.2950$ nm, with an enhanced 4.85 g/cm³ density over 4.83 g/cm³ in the virgin Ag-coated CrO₂ nanoparticles of $a = 0.4429$ nm and $c = 0.2950$ nm. The directional growth in the fibrils is led by the surface anisotropy that imposes (and drives) a shear stress over growing crystallites (within it) along the [001] surface at elevated temperature.

Self-assembled Growth of Ge Islands on Si (001) using Molecular Beam Epitaxy

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Self-organized growth and self-assembly at surfaces can serve as an efficient and versatile tool for creating low-dimensional nanostructures. Stranski–Krastanow growth mechanism by molecular beam epitaxy (MBE) is potentially attractive as a rich system for exploring the behaviour of strongly interacting nanocrystals. Here we report the shape, size distribution and characteristics of self-assembled Ge islands grown on Si (001) surfaces by solid source molecular beam epitaxy at substrate temperatures varying from 480-630°C. A typical growth started with the deposition of a Si buffer layer using electron gun followed by 14 monolayer Ge film using a heated Knudsen cell. The grown samples were characterized by *ex situ* atomic force microscopy (AFM), high-resolution XRD, micro-Raman scattering and Rutherford back scattering (RBS) measurements. A variety of coherently strained, defect-free, heteroepitaxial Ge nanoislands morphologies have been experimentally observed in our study. These 3D islands are produced spontaneously on top of a thin Ge wetting layer during lattice-mismatched heteroepitaxial growth, as a result of the competition between strain and surface energy. At a low growth temperature (<500°C), we observed elongated nanocrystals bounded by four {105} facets known as *hut* clusters. These hut clusters are metastable in nature and tend to disappear during thermal annealing, leaving the surface populated with small {105}-faceted *pyramids* having square base, larger multifaceted *domes* and still larger dislocated islands known as *superdomes*. Thus the shape of the hut clusters is kinetically controlled instead of mass transport, and the equilibrium shape of {105} faceted islands is found to be pyramids. The elongated hut base results from a larger barrier to nucleation of additional atomic planes onto {105} facets. Continued cluster growth results in a transition to octagonal-based domes bounded by steeper facets making a ~25° contact angle with the substrate. The evolution of the shape and size distributions of MBE grown Ge islands on Si (001) during post-growth annealing has been studied. The islands are found to coarsen for a range of annealing times at a representative temperature of 650°C. Detailed analysis of the coarsening is complicated by the presence of two different island shapes. While smaller islands are pyramidal, the shape changes to a more complex, faceted structure as the islands grow. The larger domes and smaller nanocrystals are found to coexist throughout the annealing sequence. The intermixing of Si with Ge islands at the studied temperature allows larger pyramids to be stable, greatly affecting the shape of the islands during prolonged annealing. Thus, the evolution of the island size depends on both the kinetics of coarsening processes and intermixing, as well as the lowest energy size of both the pyramids and domes. Both the alloy composition and strain in the islands have been estimated by micro-Raman scattering, high-resolution X-ray diffraction and Rutherford backscattering analyses. A correlation between strain relief and island shapes / sizes has been established in the study.

Control of Nanocrystallization in Silicon from (SiH₄+He+H₂)-Plasma in RF-PECVD

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Helium dilution to the SiH₄-plasma is one of the well established approach to enhance the growth rate of Si:H network when deposited by plasma CVD. Helium as a diluent in the plasma produces ionized He⁺ and metastable He* which plays vital role in the dissociation of SiH₄ and produce a high density plasma that initiates high growth rate. However, at an average temperature around 200°C, the grown network is mostly amorphous in structure. On the contrary, high hydrogen dilution to the SiH₄ promotes crystallization to the network through generation of required properly hydrogenated precursors and thereafter by atomic hydrogen induced modulation to the network structure at the growth zone. However, atomic hydrogen induced etching at the interconnections significantly reduces the growth rate of the material. Aided by the high diffusivity of atomic hydrogen into the silicon network, medium range ordering prevails in the network and that produces large microcrystals in a crystalline-like growth condition. To restrict the crystalline growth within nano-dimensions in view of generating nanocrystalline silicon, presence of structural imperfections (defects) could be beneficial. Presence of helium in the plasma may provide required defect barriers, the associated high growth rate, in addition, weaken the crystallization process and thereby maintain the extent of crystal growth limited within nano-dimension. Thus strategically utilizing the individual advantages from helium and hydrogen plasma, the growth and control of nanocrystalline silicon from (SiH₄+He+H₂)-plasma has been illustrated.

Sol-gel synthesis and magnetic studies of nanophased CoFe_2O_4 and CuFe_2O_4

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Ferrimagnetic materials by the name ferrites have attracted the attention of chemists, physicists and technologists since they exhibit magnetic as well as semiconducting properties. At the same time these have well-established catalytic properties. Their high resistivity and low hysteresis loss makes them suitable to use in microwave applications and radio electronics. When prepared in the order of 1-10 nm sizes they show super paramagnetic behaviour. Nanometer clusters belong to a state of matter in the transition region between molecules and bulk solids. These materials due to their extremely small size and large specific surface area show unusual physical and chemical properties compared to their bulk counterparts. The usual ceramic method of preparing ferro spinels requires high calcination temperature and gives inhomogeneous and aggregate particles with low surface areas. To produce nanosized ferrite particles, various techniques like chemical co-precipitation, hydrothermal synthesis, sol-gel synthesis, hydrolysis of metal carboxylate in organic solvent, and aerosolisation have been developed. Here, in this study sol-gel method is utilized because of its advantage of good stoichiometric control and the production of ultra fine particles in a relatively short processing time at lower temperatures. Poly acrylic acid (P AA) has more carboxylic acid groups than other chelating agents like citric acid or poly vinyl alcohol to form chelates with mixed cations and to form cross-linked gel. The use of P AA as a chelating agent has got the advantage of reducing the calcination temperature since the heat of combustion of P AA is utilized for the crystallization of the particles.

Cobalt and copper ferrite (CoFe_2O_4 and CuFe_2O_4) nanoparticles (average particle sizes 18 and 12 nm) are synthesized by sol-gel method using PAA as the chelating agent. Structural and magnetic properties of the products are investigated using X-ray diffraction (XRD) and vibrating sample magnetometer (VSM) and the results showed that they are spinel ferrites with cubic symmetry and are super paramagnetic at room temperature. Scanning electron microscopy (SEM) observation showed that the nanoparticles formed are uniformly distributed in size.

Synthesis and characterization of albumin immobilized $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ nanoparticles for possible biomedical applications

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$\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO) is a mixed-valent room temperature ferromagnet with properties that can be explored for their application in biomedicine. In the present study LSMO nanoparticles were synthesized using citrate-gel method and then conjugated to bovine serum albumin (BSA) by using 1-ethyl-3-(3 dimethyl aminopropyl)-carbodiimide (CDI) as a coupling agent. FTIR study of the nanoparticle-conjugated system revealed electrostatic interaction between LSMO (O^-) and the N^+ site of the hydrolyzed ion formed due to interaction of BSA and CDI. The particle size of the conjugated nanoparticles was seen to be ~ 80 nm as observed by SEM, TEM and AFM.

Magnetization studies carried out with VSM and SQUID showed the saturation moment of the coated samples was substantially lower (14 emu/g for BSA-coated) than the uncoated one (55 emu/g). The magnetic transition temperature of the uncoated LSMO was 360K, which did not change upon conjugation with albumin.

For cytotoxicity studies, A-431 (human skin carcinoma) and HT-1080 (human fibrosarcoma) cell lines were used. Upon exposure to a dose of $20 \mu\text{g/ml}$ of BSA-coated nanoparticles, the maximum percentage cell viability for HT-1080 and A-431 cell lines was observed to be around 96%. On the contrary, uncoated nanoparticles showed a decreased cell viability of around 40% (HT-1080) and 70% (A-431). These results reveal potential applicability of such systems in the field of biomedicine, especially in drug delivery.

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Seed mediated synthesis of gold nanorods and their optical properties

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Metal nanoparticles offer a wide area of application owing to their size and shape dependent optical properties. Recently, there has been significant interest in gold nanorods due to their potential application in the field of biomedical imaging, photo thermal therapy and optoelectronics. Owing to their interesting properties, potential of gold nanorods has also been realized in the field of nanoelectronics and nanophotonics. Gold nanorods of different aspect ratios have been synthesized by various techniques with considerable success. However, achieving control over the shape of nanoparticles leading to proper tuning of longitudinal surface plasmon band in case of gold nanorods has been a difficult task. Aspect ratio of gold nanorods is found to be extremely sensitive to nucleation conditions which are further dependent on large number of experimental parameters involved in the seed mediated synthesis.

We have synthesized gold nanorods in aqueous solution by seed mediated growth method and studied the dependence of longitudinal plasmon band on various experimental parameters like temperature, pH, amount of seed, ageing of seed, molarity of surfactant and other experimental conditions. Subsequent changes in the plasmon band have been monitored by uv-vis spectrometer and aspect ratio of gold nanorods has been determined using TEM.

Sonicated low volume fraction Carbon Nanotube Reinforced Epoxy nanocomposites and the role of dispersion on its mechanical properties

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This paper represents the process of manufacture of low percolation level carbon nanotube reinforced nanocomposites in epoxy matrix by the process of sonication. The degree of dispersion of the Multiwalled carbon nanotubes in the polymeric continuous matrix at the time of sonication have been investigated using the optical micrograph and the mechanical properties like flexural modulus and fracture toughness have been calculated using INSTRON-1195 and a very good trend was obtained for good dispersion level. The highest value obtained for flexural modulus for well-dispersed samples are nearly 176 MPa and for poorly dispersed sample is 89.37 MPa.

Creation of nano-architectural pattern on electropolished aluminium surface

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In this work, periodically arranged nano-architectural pattern, self-organized in atomistic length scale has been developed on aluminium metal surface by electropolishing. Pure (99.99% pure) aluminium metal samples of nearly 15x15x2 mm dimensions are annealed at 400°C for four hours in order to get homogeneously distributed large grains of aluminium to favor high order pattern formation on the surface. The samples were electropolished using universal acidic electrolyte solution by controlling voltage and time. A new XRD technique has been developed to predict the topographical features of the electropolished surface. This technique is capable of providing two-dimensional cross-sectional view of the electropolished surface geometry. Analyses of XRD patterns have revealed the fact that during electropolishing, the most closely-packed (111) planes on aluminium metal surface reduce considerably compared to other crystallographic planes. AFM investigation has been carried out to get the vivid 3-D image of the predicted geometrical feature of the electropolished surface. Mainly, 'nano-channel' and 'egg-carton' like surface patterns appear on the electropolished surface depending upon the variation of parameters like electropolishing voltage and time. Furthermore, the mechanism of the nano-pattern growth during electropolishing has been explained mathematically by calculating the surface energies of different crystallographic planes of aluminium and modification of the surface energies by the applied electric field, as electropolishing is carried out under a constant electric field. The surface energies of different crystallographic planes of aluminium have been calculated by the help of ab initio plane wave pseudopotential density functional theory (DFT) as implemented in the CASTEP of Materials studio software package. This calculation shows that the energy of the (111) crystallographic plane of aluminium is less compared to that of the other planes. Therefore, from the thermodynamic point of view Al (111) planes should be more stable compared to other crystallographic planes and should not be preferentially attacked by the electrolyte solution during electropolishing. However, the XRD study clearly indicates that the rate of dissolution of the atoms in the Al (111) planes is faster than that of the other planes. In this context the effect of the applied electric field was incorporated and it was seen that under electropolishing condition Al (111) planes become unstable compared to other planes. It has been also established that the difference in the rate of the dissolution of the surface atoms and difference in the atomic displacement of different crystallographic planes of aluminium during dissolution and subsequent relaxation plays the key role behind the formation of ordered nano-pattern on aluminium metal surface.

Voltammetric investigations on composite of carbon nanotubes-silver prepared by electrophoretic methods

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Voltammetric investigations on composite of multiwalled carbon nanotubes (MWCNTs) with Ag is reported. The MWCNTs were prepared by a catalytic vapour decomposition (CVD) method. The nanotubes so prepared were having an average diameter ca. 70 nm (TEM analysis). These were purified by air annealing and functionalized them with COOH by refluxing them with concentrated HNO₃. Their composites with Ag (Ag-f-MWCNTs) were prepared by the electrophoretic dissolution of silver anode in aqueous dispersion of -COOH functionalized MWCNTs. The composition has been varied by controlling the various experimental parameters viz. duration, applied voltage and the temperature of the electrophoretic bath. These were characterized by XRD, FTIR, Raman and SEM.

For the voltammetric investigations, Ag-f- MWCNTs were dispersed in the phosphate buffer and the cyclic voltammograms (CVs) were recorded for different scan rates. In all the voltammograms two anodic peaks at ca. 0.35 V and 0.60 V and their complimentary cathodic peaks at ca. 0.11 V and -0.08 V were observed. Two pairs of complementary redox peaks, instead of one pair suggest that Ag associated with the composite is present in two different potential fields or environments; namely (1) nanotube surface and (2) core of the tube. This was further confirmed by Raman spectroscopy, SEM and TEM analysis. Higher over potential peaks (0.35 V and 0.11 V) could be assigned to the redox reaction of Ag/Ag⁺ present in the nanotubes core.

The application of Ag-f-MWCNTs have been tested successfully for the catalytic reduction of Rhodamine-6G. The reaction was found to be 300 times faster than the one reported to be catalysed with silver impregnated carbon. Further investigations are in progress.

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