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INVITED TALKS

Engineering Carbon Nanotube Architectures

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Carbon nanotubes are fascinating materials from the point of view of structure, form, growth and properties. The biggest challenge however is to assemble nanotubes into various architectures useful for specific applications. The talk will focus on the recent developments in our laboratory on the fabrication of carbon nanotube based architectures tailored for various applications. Various organized architectures of multiwalled and singlewalled carbon nanotubes can be fabricated using relatively simple vapor deposition techniques. The work in attaining control on the directed assembly of nanotubes on various platforms will be highlighted. Our efforts on the strategies of growth and manipulation of nanotube-based structures and in controllably fabricating hierarchically branched nanotube and nanotube-hybrid structures will be discussed. We have pursued several novel applications for these structures, for example, as nanostructured electrodes for sensors, electrical interconnects, unique filters for separation technologies, thermal management systems, multifunctional brushes, and polymer infiltrated thin film and bulk composites. A perspective of the field based on the work done by the author over a period of more than decade will be presented here with highlights from recent work and thoughts on future implications of the field.

Keywords: carbon nanotubes, sensors, composites

Towards Transparent Magnetic Materials—By Excitonic Confinement

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The prospect of finding transparent magnetic materials are very bright with the advent of nanoscience and nanotechnology. Nature does not produce magnetic materials and it has to be made by man. Transparent magnetic materials find innumerable applications in xerox technology, magneto-optical recording, magnetic field controlled optical modulators, magneto-optical displays and switching devices.

It is known that particles in the nanoregime exhibit superlative physical, magnetic,optical, chemical and electric properties with respect to their coarser sized cousins. In magnetic materials, finite size effects are manifested in the form of quantum magnetic tunneling, superparamagnetism, single domain nature and shift in optical absorption edges. Their large surface to volume ratio provides excellent scope for the modification of their properties due to the large reduction in their linear dimension and high lattice strain. Optical properties of magnetic materials change enormously including the bandgap due to small wave function overlapping. In order to study the excitonic confinement, ultrafine maghaemite particles are incorporated inside polystyrene matrix by the strong ion exchange process. It has been found that, in the weak field excitonic confinement, a maximum of 0.64 eV can be blue shifted and if the particle size can be further reduced to the ‘dot’ level, a maximum shift of 1.6 eV can be achieved. This augurs well for producing optically transparent magnetic materials. The alloying induced blueshift in magnetite based ferrofluids will also be dealt with. The details of the synthesis of magnetic nanocomposites and the blue shift by excitonic confinement are discussed in this paper.

Keywords: Magnetic Nanocomposites, Ferrofluids, Ferrites

New Insights of Inorganic Nanotubes

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Synthesis and analysis of inorganic nanotubes, not necessarily containing graphitic carbon, have become an intriguing research topic over the last several years. Nowadays, inorganic nanotubes with interesting properties and potential applications constitute an important domain of the nanostructural family. Among these material systems, the nanotubes made of boron nitride, Si, III-N compounds, II-VI compounds, metal oxides are particularly important because of their unique properties and potential technological applications compared with conventional carbon nanotubes. It is of great interest to explore new synthesis pathways to form nanotubes of these materials; however, the reported tubular structures are either amorphous or polycrystal forms, which would negatively affect their performance in real application. So, the synthesis of single-crystalline nanotubes from these materials and exploration of their properties are challenging tasks yet to be accomplished.

We report herewith on a wide variety of novel inorganic nanotubes (covering the above inorganic materials) most recently synthesized and thoroughly analyzed within our Laboratory. New properties of these inorganic nanotubes, including optical, electrical, thermal, mechanical, and gas adsorbing will be demonstrated. In particular, the effective functions of these nanotubes filled by other foreign materials, such as liquid metal will be highlighted. The authors will take an advantage of the state-of-the-art high-resolution transmission electron microscopy for the microstructure analysis and novel properties associated with these inorganic nanotubes.

Keywords: inorganic nanotubes, synthesis and analysis, TEM

Carbon Nanotube Based Interconnects

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CNTs are being evaluated as potential candidates for replacing copper as the interconnect material in many levels in microelectronic silicon die and die-package regions. In this talk, the opportunities and challenges for use of CNTs will be addressed.

Keywords: CNT, interconnects

Tools for Nano-Technology

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Nano-research requires the ability to form and characterize nanostructures. The precision and accuracy requirements to produce structures on the nm scale, to characterize them morphologically, structurally and chemically demands a tool set commensurate with those needs. This talk will survey FEI's most advanced tools and applications for nanotechnology designed to address the industries needs.

The versatility of dual beam systems (electron + ion beams) enabled the development of many applications, such as patterning 3D nanostructures by employing site specific deposition and milling techniques, as well as preparing cross sections and thin samples for S/TEM analysis.

Historically, the S/TEM has always supported development on the nano-scale, with its high resolution capabilities. Currently, S/TEM resolutions are well below the nm level. FEI's TEM technology lends itself to

nano-scale development by going well beyond the 0.1nm resolution mark, through a dedicated aberration corrected platform. FEI's mature digitized S/TEM platform enhances development cycles of nanostructures by providing embedded solutions such as tomography, chemical, electronic and structural analysis.

Finally, the use of scanning probe microscopy for 3D metrology and the fabrication of specialized diamond probe shapes by FIB will discussed.

Keywords: Dual Beam, Focused Ion Beam (FIB), TEM, STEM, profilometer

Imaging Spermatozoa using Atomic Force Microscopy – A Valuable Tool for Research in Contraceptive Development

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The ability to image living biological cells in three dimensions in their native environment at atomic resolution has made atomic force microscopy (AFM) a valuable tool for research in biology and related areas. One of the interesting applications of AFM is in the field of reproductive biology. Unstained, unfixed spermatozoa in their natural physiological surroundings provide extensive information on the morphological and pathological defects in sperm cells with precise topographical details. Sperm head defects and the acrosome at the tip of the head, responsible for fertilization, can be examined and correlated with the lack of functional integrity of the cell. Considerable amount of work has been done on sperm chromatin analysis using AFM. Rigorous research by our group over the past two decades has led to the development of a non-hormonal, reversible male contraceptive given the name RISUG® (an acronym for Reversible Inhibition of Sperm Under Guidance). Non-contact mode AFM was used to examine the morphological and topographical alterations on the sperm surface induced by this contraceptive, in vitro. An almost complete disintegration of the plasma membrane with subsequent rupture of the acrosomal membrane leading to dispersion of acrosomal contents was observed. Clustering of the mitochondria in the midpiece region and its fusion with sperm head indicated loss of functional competence of the spermatozoa. AFM, with its ability to provide morphological details and 3D topographical images of the spermatozoa at nano-resolution, appears to have a tremendous potential as an investigative research tool in facilitating contraceptive development and/or improving infertility management.

Keywords: atomic force microscopy, spermatozoa, acrosome, contraceptive

Precisely Variational Quantum Chemistry via Analytical Density Functional Theory

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First-principles quantum chemistry is one of the most powerful tools to provide definitive information on the energy, forces between atoms, and their manifestations in molecules and solids. However, due to the very nature of quantum interactions between (two-body) and among (many-body) charged particles, the solution of the mathematical statements of the physics becomes dauntingly challenging--especially if meaningful numerical results are needed. Historical developments made by J. C. Slater and S. F. Boys in the 1950's, which introduce mathematically tractable functions for numerical calculations in quantum chemistry, lead directly to what we call analytic density-functional theory (ADFT). Its variational parameters are 10's of linear combination of atomic orbitals (LCAO) coefficients rather than 100's of plane-wave coefficients or numerical values at 1000's of points per atom per molecular orbital. In ADFT quantum-mechanical matrix elements are computed to machine precision. Only an analytic theory guarantees that one can always apply the variational principle to achieve whatever accuracy is necessary.

For small calculations ADFT scales as the number of orbitals cubed rather than the fourth power scaling of Hartree-Fock. The only major problem of ADFT is the labor-intensive optimization of our toolbox of analytic functional forms to achieve optimal results. In this talk, the toolbox of functionals developed by our group at US

Naval Research Laboratory over the course of past 25 years will be described. We have used Perl scripts to optimize ADFT over the G2 and extended G2 sets of up to 148 molecules for various properties. The computer code is capable of rather accurate calculations of atomization energies, optimized geometries and dipole moments.

We use generalized Gaunt coefficients to speed up completely analytic, and thus precise, gradient calculations involving basis functions of high angular momentum. We have optimized the geometries of the most stable C240, C540, C960, C1500, and C2160 icosahedral fullerenes using a triple-zeta plus polarization orbital basis (6-311G*) and a matched basis for the Kohn-Sham potential that contains up to f functions. Even with a greatly simplified variational-quantum-chemical method calculations can still be challenging. Our largest calculation employing about 39000 basis functions could only be performed on a parallel-processing platform.

The Office of Naval Research, directly and through the Naval Research Laboratory, and the Department of Defense's High Performance Computing Modernization Program, through the Common High Performance Computing Software Support Initiative (CHSSI) Project MBD-5, supported this work.

Keywords: Variational Fitting, Analytic Density-Functional Theory, Functional Optimization

Protein Nanosensors for Multi-Scale Technologies

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The Multi-scale Technologies Institute at Michigan Technological University is focused on integrating technologies with characteristic dimensions that span many orders of magnitude. This presents many exciting opportunities and challenges requiring an interdisciplinary approach. One of these applications is a nanosensing platform that utilizes quantum dots, proteins, and single electron transistors (SETs) to form a chemical or biological detection system.

Quantum dots (QDs) are nanometer scale crystals of semiconductor materials. When excited by light of a wavelength shorter than their emission wavelength, the dots emit at a Stokes-shifted characteristic emission wavelength. By functionalizing the exterior of the QDs with environmentally sensitive molecules, such as amino acids, the emission characteristics of the QDs will change. This change can be optically detected. Bacteriorhodopsin (bR) is an optical protein extracted from the cell membrane of an extremophile bacterium. bR converts light to electrical charge very efficiently and with no cross-talk among adjacent molecules. bR serves as the optical-to-electrical transduction medium in the nanosensor system. To reduce the size and power of the sensing system, SETs will be used to sense the bR output. The bR, when coupled with the SETs, will form an array of nano-optical field effect transistors giving a small and very low power nanosenor system. The talk will focus on the system aspects of the application and report on progress to date.

Keywords: nanosensor, protein, quantum dot, multi scale technologies

Bioinspired Materials for Nanoelectronics

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The need for nanoscale structures in next generation electronic devices has directed attention toward the use of novel motifs for the construction of the essential interconnect networks. The formation of such nanowire assemblages directly confronts several challenges including scalability, self assembly and nanoscale patterning. Along with others, we have recognized that biomaterials may provide a potential solution. While biomaterials generally do not possess sufficient conductivity they may serve as templates for assemblage of conducting moieties such as aromatic rings or metallic components. Polypeptides are especially attractive templates as they fold by established rubrics, undergo intermolecular self-assembly, present a wide variety of functionality and are chemically robust. Of particular interest, β-sheet forming sequences have been long recognized to form well-ordered aggregates, and under some conditions form fibrillar structures, the best known representatives of which are amyloid fibrils. Adapting the pioneering work of Tirrell, a de novo genetically engineered family of polypeptide sequences has been prepared that self assembles to form nanofibrils that can be oriented via surface-directed assembly. These fibrillar structures have been adapted to 2-point electronic test circuits for electrical investigation. In addition, parallel efforts have investigated direct metallization of these fibrillar structures for the formation of hybrid nanowires to exploit the biological beta-sheet self-assembly.

Keywords: Polypeptides, beta sheets, fibrils, nanoelectronics

Novel Aspects of Property Control in Nanostructured Materials

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Materials science is based on the understanding of the role of defects on the properties of materials. Popular examples are point defects for diffusion processes, dislocations for the plastic behavior of metals and alloys and interfaces playing an important role in phase transformation and electronic properties. The basic idea of nanostructured materials about 25 years ago was the incorporation of localized planar defects (grain or phase boundaries) with a large volume fraction, corresponding to grain sizes in the nanometer range, that novel properties arise based on the different atomic arrangements in the interfaces or due to the strong grain size dependence of the materials properties. A different approach is the use of homogeneously disordered materials, such as metallic glasses. Over decades, materials science has concentrated on the detailed understanding of the role of defects and processes to incorporate such defects even in larger concentrations to tailor the properties of such materials.

In semiconductors, the influence of electronic effects at interfaces between dissimilar materials has been extensively used to obtain properties necessary for advanced electronic devices. The properties of semiconductors can be altered reproducibly by applying external electric fields. Such tunable properties based on external fields have not been observed in metals and alloys, as the charges at surfaces or internal interfaces are screened and thus, do not alter the properties of a bulk materials. Recently, it has been shown in nanoporous metals and in thin films that the mechanical and electrical properties can be tuned when the metal is exposed to an electrolyte by the application of an electric field. The space charge regions at the interface between the electrolyte and the metal surface result in a re-distribution of electrons at the metal surface, i.e. a change in the Fermi energy. This effect is responsible for the tenability of the properties. As an example, substantial changes of the electrical conductivity have been observed in a nanoporous Au-Fe alloy and in a thin Au-film on a substrate at small potentials of a few Volt.

Furthermore, a novel technique for the preparation of unstable solid alloys of metals and ionic crystals is presented. It involves the deposition of neutral atoms or molecules as well as the deposition of ions controlled by an electric field. In the presentation the well established concepts of materials science are presented and are put in contrast with the new opportunities possible by using man-made nanostructures.

Keywords: nanostructured materials, properties

Educating the Workforce for the New Nanotechnology Industry – the College of Nanoscale Science and Engineering at the University at Albany

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The University at Albany's College of Nanoscale Science and Engineering (CNSE) – the first U.S. college in nanoscale science and technology – has evolved into an internationally recognized education and research center due to it's eminently successful model for collaboration between industry, government and academia. The success of the NanoEngineering and NanoSciences graduate degree program relies on CNSE to continue to perform the critical function of providing an education to students of the highest quality equal or superior to that available in institutions of higher learning anywhere in the world. Moreover, CNSE is located in the most advanced research facilities of its kind at any university in the world. With a current net asset value in excess of U.S. $2 billion, the 450,000-square-foot complex attracts over 150 corporate partners from around the world and offers faculty and students a one-of-a-kind academic experience in an interdisciplinary environment. CNSE's unique education and research experience is it's integrated complex which currently houses over 1,000 faculty, researchers, and students from CNSE and its industrial partners, including IBM, Honeywell, GE, Infineon, SEMATECH, Applied Materials, and many others. As the college's new model matures and leadership advances, it continues to expand curricular offerings in Nanoeconomics, Nanobioscience and a dual Nano+MBA degree to participate in the development and implementation of CNSE's education, research, service, outreach and management programs to train the workforce of the nanotechnology industry.

Keywords:

Integrating and Accurate Positioning of 1D Nanowires in Devices and Circuits: Recent Developments, Current Challenges and Future Opportunities

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In the past few years, exciting developments in the synthesis and novel device demonstrations of one-dimensional (1D) semiconductor nanowires have given rise to an enormous optimism. Interesting characteristics such as high surface to volume ratio, quantum confinement, and simple and low cost synthesis process of nanowires are opening new frontiers in novel electronic and photonic devices. Despite a significant progress in nanowire synthesis and many promising single device demonstrations, nanowire applications have been stalled by our incapability to incorporate and precisely position them within devices and ICs. Several researchers have demonstrated a scheme of serially connecting metal electrodes to individual nanowires using slow and expensive e-beam lithography and explored numerous intriguing device opportunities. However, many of those methods are not likely candidates for cost-effective and mass-manufacturable integration process for reproducible fabrication of ultra-high density nanodevice arrays. This talk will give an overview of the recent developments, current challenges and future opportunities in the construction of large and complex systems with nanowires. We will present our novel *nano-bridging* techniques that can simultaneously connect a large number of highly directional metal-catalyzed nanowires between two pre-fabricated electrodes. The technique, for the first time, can help access individual nanowire based devices without using nano-probes or expensive lithography techniques. This method of connecting nanowires offers exciting opportunities of integrating III-V materials on Si wafer for ultra-fast nano-electronic and photonic devices. A novel technique for positioning large arrays of free-standing nanowires with uniform size and spacing will also be presented for the first time.

Keywords: nanowire, nanostructure positioning, mass-manufacturing, quantum wire, nano-electronics, nano-photonics

Applications of Nanoscale Sciences to Cell Wall Biotechnology in Trees

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Forest product industries produce thousands of wood products from trees that are vital for sustaining global economies and exploding human populations. Trees also mitigate the evil effects of increased green house gases by sequestering excess amounts of atmospheric carbon into wood for a long time. Thus biotechnological improvements in wood formation hold a tremendous promise from economical as well as ecological perspectives. Biologically, wood is nothing else but cell walls of dead xylem cells those help conducting water and minerals to the top of the tree and provide mechanical strength to tree trunks so that trees can withstand

environmental assaults for hundreds or even thousands of years. For over 300 million years, trees have been producing cellulose Nanofibrils that further interweave with themselves as well as other cell wall polymers such as hemicelluloses and lignin to produce Nanocomposites that we call wood. Our main goal is to first understand the molecular processes by which trees accomplish this feat and then genetically engineer wood formation to improve the end-products for human utilization. Towards this goal, we have dissected the contribution of several genes to wood formation and produced novel wood phenotypes. Little is known about the biological processes that dictate a variety of wood quality traits and ultra-sensitive Nanotechniques are required to catalogue the existing natural variations in wood traits. Finally, changes in wood gene expression at the single cell level must be monitored. Advancements in Nanotechnology could thus be harnessed for studying the process of wood formation at the Nanoscale level, for detection of physical changes in wood resulting from genomic modifications or natural variations, and for monitoring Nanochanges in gene expression levels by using whole genome-wide Nanoarrays based on carbon Nanotubes. Availability of such Nanochips will also open up new avenues in medicine, homeland security, and biology. Manipulation of the cell wall nanostructures of trees will allow us to create novel wood products that would possess superior qualities for end-utilization. An active cross-disciplinary cooperation among scientists and engineers is indispensable for attainment of this goal.

Keywords: Cellulose, Nanocomposites, Nanofibrils, Nanoarrays, Trees, Wood products

Introducing Nanotechnology Education in the Undergraduate Curriculum

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A team of faculty at Michigan Technological University (MTU) has developed a suite of educational and research experiences to introduce undergraduate students to the prospects and challenges of nanoscale science and engineering as part of a National Science Foundation Nanotechnology Undergraduate Education grant. Although open to all students, the program was designed in particular for engineering students whose curricula have relatively little flexibility. Activities were developed to fit into or to modestly supplement existing curricular frameworks, and were aimed at introducing students to three foundational aspects of nanoscale work: the underlying science, possible scientific and engineering applications, and the societal implications. A web site http://nano.mtu.edu was developed as central focal point for nano-related research and education activities at MTU.

The most successful activities included the creation of a new elective course on "Fundamentals of Nanoscale Science and Engineering"; a two-hour nanotechnology "exploration" for first-year engineering students and high school students; and summer research experiences for seven undergraduates. Beginning in the fall of 2005, a new interdisciplinary minor in "Nanoscale Science and Engineering (Nanotechnology)" became available to students. Major requirements for the minor include the above elective course, a new course in Societal Implications of Nanotechnology, a selection of approved elective courses outside of a student's major, and nanotechnology-related research or independent study.

This talk will outline these activities in more detail. Challenges, rewards, and lessons learned through the process of their development and implementation will also be presented.

Keywords: Undergraduate Education, Nanotechnology, Societal Implications

Biobased Organic Synthesis: Novel Building Blocks for Soft Nano Materials by Bottom-Up Design

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The self-assembly of low molecular weight building blocks into nanoscale molecular objects has recently attracted considerable interest in terms of the bottom-up fabrication of nanomaterials. The building blocks currently used in supramolecular chemistry are synthesized mainly from petroleum-based starting materials. However, bio-based organic synthesis presents distinct advantages for the generation of new building blocks since they are obtainable from renewable resources. This study is an effort to combine the philosophies of green chemistry and supramolecular chemistry, making use of renewable plant-derived resources as the starting materials (an alternate feedstock) for the noncovalent synthesis of meso- and nanoscale structures. The use of cardanol and its derivatives for various applications is well known. However its use in the synthesis of aryl glycolipids and their self-assembled nanostructures are new to the literature. The glycolipids are self-assembled to form a variety of well-defined nanostructures including liquid crystalline phases (thermotropic & lyotropic), vesicles, nanofibers, low-molecular weight gelators and nanotubes under suitable conditions, which could be of use in material applications. We have developed multiple systems based on biobased organic synthesis by chemical/biocatalytic methods for functional applications. These results will lead to efficient molecular design of supramolecular nanostructures and nanomaterials based on green chemicals, otherwise under-utilised. Also address the advances that have led to the understanding of chiral behaviour and the subsequent ability to control the structure of glycolipid nanostructures-derived from renewable resources-and the resulting impact of this on future material applications.

Keywords: self-assembly, soft materials, biobased organic synthesis, amphiphiles

Thermodynamics of Clusters : Size Sensitive Heat Capacities and Higher than Bulk Melting Point

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Recent experimental measurements on clusters in the size range of 20-200 have brought out a number of interesting features. Clusters of Tin and Gallium show melting point higher than bulk. The heat capacities of Gallium and Aluminium clusters show dramatic size sensitivity. We present results of ab initio molecular dynamics on a number of clusters. We establish a correlation between ground state geometry and the shape of heat capacity. Based on our extensive simulations we present our understanding of thermodynamics of finite size systems.

Keywords: clusters, ab initio molecular dynamics

Nanoscience and the Energy Challenge: The U. S. Department of Energy's Nanoscale Science Research Centers

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To support the synthesis, processing, fabrication and analysis at the nanoscale, the U. S. Department of Energy, Office of Science is developing, constructing and operating five new Nanoscale Science Research Centers (NSRCs). When complete, this network of five NSRCs will constitute the United States' premier User Facilities for interdisciplinary research at the nanoscale, serving as the basis for a national program that encompasses new science, new tools and new computing capabilities.

The Brookhaven National Laboratory Center for Functional Nanomaterials (CFN), slated for initial operations in April 2007, will contain clean rooms, nanofabrication laboratories and one-of-a-kind signature instruments such as advanced electron microscopes. In addition to offering advanced equipment to the scientific community free of charge, the CFN also provides scientific expertise for basic research in support of energy: energy conversion, energy storage and energy efficiency. CFN research is concentrated in the fields of Nanocatalysis, Biological and Soft Nanomaterials and Electronic Nanomaterials. Recent research results selected from the three CFN scientific theme areas will be highlighted.

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Keywords:

Multiscale Modeling with Carbon Nanotubes

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Technologically important nanomaterials come in all shapes and sizes. They can range from small molecules to complex composites and mixtures. Depending upon the spatial dimensions of the system and properties under investigation, computer modeling of such materials can range from first-principles Quantum Mechanics, to Forcefield-based Molecular Mechanics, to Mesoscale simulation methods, to Finite-Element computation of properties. We illustrate all of the above modeling techniques through a number of recent applications with carbon nanotubes (CNTs): (1) effect of adsorbates on CNT-based field-emission displays [1]; (2) CNT-strain-controlled nano electromechanical sensor (NEMS) devices [2, 3]; (3) the sensitivity of topological defects on CNT action as chemical sensors [4]; (4) assessing the quality of metal-CNT contacts [5]; and (5) mesoscale morphology of polymer-CNT composites [6, 7] and finite-element computation of electrical and thermal transport [8].

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Keywords: Multiscale modeling, displays, sensors, nanocomposites

Theoretical Study on Exciton Dynamics of Dendritic Systems

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Excitation energy transport is one of the essential processes in photosynthesis in green plants on earth and also finds an important application in photonics and biology. Although typical energy transport is observed in supramolecular antenna involved in green plants and their artificial polymeric mimics, most of them have disordered structures, in which energy transport is partially carried out by random walk, thermal activation and so on. On the other hand, efficient and controllable energy transport is known to be one of the fascinating properties of dendritic systems with ordered fractal-like architecture, which exhibits a directed, multistep energy transport of absorbed light. The mechanism of this energy transport, which originates in exciton migration, in dendritic aggregate systems is investigated using a quantum master equation approach including exciton-phonon coupling. It is found that the overlap of exciton distributions between adjacent generations is essential for the efficient exciton migration in addition to the multistep exciton states originating from the fractal architecture. We also extend this approach to the calculation of exciton dynamics of supermolecular systems, i.e., dendrimers, based on the ab initio molecular orbital (MO) configuration interaction (CI) method. We examine the effects of the variation in the excitation energy of the core molecule of nanostar dendritic systems on the multistep exciton migration from the periphery to the core based on the relaxation factors among exciton states.

Keywords: exciton, dendrimer, energy transfer, master equation

Surface Adsorption Effects on the Emission Properties of Single-Wall Carbon Nanotubes: A Density Functional Theory Study

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In order to explain field emission properties of single-wall carbon nanotubes (SWCNTs), we overview our theoretical work on the effects of surface adsorption, indicating that the results are consistent with experimental observations for O_2, in preliminary work also for O_3, and for Cs. Moreover, good agreement with experiment was obtained for changes in the Raman shifts upon alkali-atom adsorption in SWCNTs, and an understanding in terms of lattice expansion and charge transfer, further validating the calculations.

Keywords: single-wall carbon nanotubes, surface adsorption, density functional theory

Stability of Nanoclusters and NDR Phenomena in Molecular Systems

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We have recently proposed some novel inorganic charge transfer (CT) complex like hetero-metallic Al-clusters. These Al-clusters have polarization responses 10000 times more than the conventional organic systems due to charge-transfer.We have also theoretically proposed the experimental strategies to synthesize these clusters. Transport through organic molecular species have attracted much attention due to their potential applications. We have recently proposed the mechanism behind negative difference resistance (NDR) in some of the Tour molecules. The talk will deal with the stability and transport mechanism of some of the nanomolecular systems.

Keywords: Nanoclusters, Charge-transfer, bistability, NDR, Switching

Structure and Dynamics in a Self-Organized C_{60}–Fullerene Dyad

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Understanding the intermolecular interactions in carbon nanomaterials is an important step toward rational designing of functional nanoscopic architectures. Precise control of the geometry of the self–assembled structure allows fine-tuning of the functional properties of these materials in building nanoelectronics. A careful premeditated design of Fullerene[60] based donor–bridge–acceptor dyad systems aids in controlling their electronic properties and self–assembly for application in molecular electronics. The talk will focus on one such dyad system and its structure–property correlations leading to molecular rectification.

A novel methano fullerene dyad based on a hydrophobic – hydrophilic- hydrophobic network has been designed and synthesized. The *ab initio* geometry optimized structure with B3LYP / 3-21G* level of theory indicated a ground state intramolecular charge-transfer complex formation between the donor and the acceptor moieties of the dyad, further corroborated by the large magnitude of the calculated dipole moment, natural population analysis and the spatial electron density distribution of the dyad's HOMO. Concentration and solvent polarity controlled structure architectures from the self-assembly of the π-electronic amphiphile resulted in spherical fractal aggregates of ~10 μm when extracted from THF into water. Molecular dynamics simulations revealed the unit cluster to such a form involves an aggregation number ~90 with predominant soft associative molecular interactions, corroborating the octadecahedral model proposed for the cluster growth. A rectifying junction operating at an applied bias voltage of ± 3 V with an optimum rectification ratio of 158 at 3 V has been obtained from the LB monolayer film of the dyad with a verification of molecular rectification obtained from the symmetrical I-V curves from the centrosymmetric bilayers of the dyad.

Keywords: C_{60} Dyad, Fractal aggregates, MD simulation, Rectification

Characterization of Nanostructures with Single Atom Sensitivity through Aberration-Corrected STEM

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The aberration-corrected scanning transmission electron microscope (STEM) offers dramatically improved resolution and sensitivity for determining atomic arrangements, impurity concentrations and local electronic structure in nanostructured materials. Z-contrast images now reveal oxygen columns in perovskites, and individual atoms can be imaged and spectroscopically identified through electron energy loss spectroscopy. Coupled with density-functional calculations, the microscopic origins of many nanoscale properties are becoming understood. The location of charge carriers within the unit cell of the high temperature superconductor YBCO can be seen directly, the transfer of charge across a superconductor/ferromagnet interface relates to macroscopic properties, and spectroscopic imaging of charge ordering in manganese perovskites explains the nature of the phenomenon. The 3D shape and crystal polarity of high quantum yield semiconductor nanocrystals reveals their growth mechanism. Individual catalyst clusters can be imaged with single atom sensitivity, and theory reveals the room temperature catalytic activity of gold nanocatalysts originates from low-coordination sites. Individual Hf atoms can be located in 3D within a $Si/SiO_2/HfO_2$ gate dielectric structure to a precision of 0.1 x 0.1 x 1 nm, and the perturbed electronic structure can be linked to macroscopic device properties.

Keywords: high-resolution electron microscopy, scanning transmission electron microscopy, Z-contrast, electron energy loss spectroscopy, manganites, catalysts, nanostructure characterization, semiconductor devices, nanocrystals

Evolution of Materials Education - The Indian Scenario

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1923 marks the beginning of formal education in a materials related field, when the farsighted vision of Pandit Madan Mohan Malaviya led to the establishment of the first Department of Metallurgy in India at the Banaras Hindu University. In 1964 a school in Materials Science was organized in the Indian Institute of Technology, Kanpur and marked the broadening of materials programme in India. The advent of nanoscience in the late nineties has led to some tentative eforts at education in this field. We will survey these developments in India over the past eight decades and compare them with global developments. The slice of materials education will also be put in the context of higher technical education in India.

Keywords: mining, metallurgy, materials, nanoscience, Technical education, India

Electronics with Dyes

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Phthalocyanine (Pc) is a symmetrical 18 p-electron aromatic macrocyclic compound, having an alternating nitrogen atom-carbon atom ring structure closely related to the naturally occuring porphyrins. The Pc molecule is able to coordinate hydrogen and metal cations in its center by coordinate bonds with the four isoindole

nitrogenatoms. Therefore, a variety of phthalocyanine complexes exist. A major application of phthalocyanine pigments is in the production of cyan printing inks used for printing paper and packaging materials. Nowadays, both metal-containing pigments and metal-free phthalocyanine pigments are commercially available and compete with one another. Apart from their high thermal and photostability they show intense absorption in the UV and red/near-ir regions of the spectrum. More recently, it is noted that phthalocyanines themselves have a remarkable range of semiconducting, photoconducting, optoelectronic, and non-linear optical properties in their own right. In Grätzel's photovoltaic cells, a dye is anchored to a TiO_2 surface; incoming light photoexcites the dye and an electron is injected in the conduction band of the substrate and the dye can be certain phthalocyanine derivatives. Films of several phthalocyanine derivatives have been extensively studied as sensitive elements of gas sensors. We have also fabricated single layer memory devices based on spun cast film of lead phthalocyanine molecules. A unique type of formulation in which lead sulphide nanoparticles are integrated into a thin film of phthalocyanine has recently been achieved to form inorganic/organic nanocomposites.

Keywords: phthalocyanine, charge transport, sensors, solar cell

Energy-Related Applications of Carbon Nanotubes Synthesized Using Novel Alloy Hydride Catalysts by Chemical Vapor Deposition Technique

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The talk presents the synthesis of different types of carbon nanotubes by the pyrolysis of suitable hydrocarbons over selective novel alloy hydride catalysts by the chemical vapour deposition (CVD) technique. The advantages of this novel approach to catalyst preparation using hydrogen decrepitation with reference to the increase in the catalytic reactivity and active sites for the formation of different types of CNTs are high lightened. The results of the characterization of the as-grown and purified CNTs by XRD, BET surface area analysis, SEM, TEM, HRTEM, TGA and Raman spectroscopy are described. The dependence of the yield and the purity of the CNTs synthesized on the alloy hydride catalysts are discussed. The energy-related applications of CNTs such as the oxygen reduction catalyst support material for proton exchange membrane fuel cell (PEMFC) and hydrogen storage capacity are discussed. The experimental techniques needed for these applications are described. The results of the performance studies of PEMFC and the hydrogen adsorption capacity of the purified MWNTs are discussed along with the recent literature reports.

Keywords: Carbon nanotube, fuel cell, Hydrogen storage, CVD

Novel Effect of Electron Irradiation in Nanostructures

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It will be demonstrated, that irradiation exposure at elevated temperatures, can be used as an effective tool to covalently weld SWNTs in order to create molecular junctions of various geometries. We have fabricated "Y", "X" and "T-like" junctions that are stable. Tight binding molecular dynamics calculations demonstrate that vacancies, formed under the electron beam, trigger the formation of molecular junctions involving seven or eight membered carbon rings. We envisage that our results will pave the way towards controlled fabrication of novel nanotube based molecular circuits, nanotube fabrics and network architectures. In this context, novel super architectures, using carbon as building blocks will be proposed and their mechanical and electronic properties discussed, as well as their possible applications.

We will also show that the melting and solidification behavior of metal crystals can be drastically altered when they are encapsulated in fullerene-like graphitic shells. The melting temperature of low melting point metal crystals (e.g. Bi, Sn, Pb, etc.) inside graphitic shells is increased relative to the bulk melting point by a much larger amount than that observed for metal crystals embedded in other materials. It appears that graphite is the ultimate material for enhancing the melting/solidification hysteresis of small crystals or clusters. Therefore, metal clusters encapsulated by graphitic shells may be potentially advantageous in temperature-resistant crystalline composite materials.

Finally, we demonstrate that controlled irradiation of multiwalled carbon nanotubes can cause large pressure buildup within the nanotube cores, to the extent of being able to plastically deform, extrude, and break solid materials that are encapsulated inside. We further show by atomistic simulations that the internal pressure inside nanotubes can reach values higher than 40 GPa. Nanotubes can thus be used as robust nanoscale jigs for extruding hard nanomaterials and modifying their properties, as well as templates for other high-pressure applications at the nanoscale.

Keywords: Nanotubes, Electron Irradiation, Nanowires, Compression, interconnects

Theory of Mössbauer Spectrum of a Single-Walled Carbon Nanotube

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Identification of physical processes at the atomistic scale is necessary for characterization of nanomaterials, which is needed for their industrial application. Conventional methods of characterization of materials that depend upon their macroscopic response are not adequate for nanomaterials. We suggest that Mössbauer spectroscopy can be a valuable new tool for quantitatively characterizing the nanomaterials at the atomistic scale because it depends directly upon their phonon spectra. In particular, we show that the Mössbauer spectra of single-walled carbon nanotubes (SWNTs) have some unusual features that can provide a new insight into the physical processes in SWNTs. We have calculated the line shapes of one phonon lines in the Mössbauer spectrum of 57Fe in SWNTs of different chiralities and diameters using a phonon Green's function method which is also applicable to other nanomaterials. The phonons are represented in terms of causal Green's function that is calculated by using a Born-von Karman type model and the force constants derived from a recently constructed many body interatomic potential between carbon atoms in an SWNT. The effect of the Mössbauer isotope is represented by a change in the phonon Hamiltonian. The corresponding defect Green's function is calculated by solving the Dyson integral equation in the defect space. The phonon frequencies are calculated from the poles of the defect Green's function whereas the line shapes are obtained from its imaginary part. The line shapes can be measured and used to determine the chirality of SWNTs which can not be easily determined by any presently available method.

Keywords: chirality; Green's function; Mössbauer spectrum; phonons; single-walled nanotube

Nanotechnology and Next Generation Electronics

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The world is experiencing rapid advancement and progress in the ability to design and fabricate mechanical and electronic structures and devices with nanoscale dimensions. This ability stems from parallel advances in materials growth technology, patterning techniques, imaging and manipulation capability, and advances in characterization and testing. When taken together, these techniques form the basis for designing and fabricating electronic devices and structures with atomic level control. Nanotechnology permits the realization of new devices and structures with performance far exceeding that available from current systems and will keep electronic systems on Moore's Law. Materials research on the nano-scale offers the potential to produce materials that do not exist in nature, and with idealized and optimum properties, while parallel effort in nano-electronics presents the opportunity to fabricate devices and circuits with orders of magnitude increase in performance compared to present devices. As circuit size is reduced system speed can increase and it is possible for circuits to operate well into the high mm-wave frequencies. Some desired applications, particularly in sensing, require THz systems. The fundamental problem of interfacing circuits with free space presents interesting design challenges. Recent breakthroughs provide evidence of potential success. The rapid development in nanotechnology is predicted to generate progress in a diversity of areas and applications and this success will provide the basis for the next worldwide economic boom. Current trends in nanoelectronics are discussed and recent progress will be described.

Keywords: Nanotechnology, Nano-Electronics, Nano Sensors, THz technology

Nano-Ceramics by Chemical Routes

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he nano-ceramics are potential candidates for a variety of technological applications and hence their commercial value is increasing tremendously. Depending up on the final application, oxide ceramics are used in the form of sintered body having the desired shape, size and microstructure. Hence, the synthesis of powder with controlled and required characteristics is of the utmost importance. The shape, size, extent of agglomeration and purity are the important characteristics for deciding the powder quality. There are a number of methods for preparing the nanocrystalline materials viz., inert gas condensation, physical vapor deposition, laser ablation, chemical vapor deposition, sputtering etc. In addition, there are a number of chemical routes also. Among the available chemical routes, the combustion technique is capable of producing the nanocrystalline powders of the oxide ceramics at lower calcination temperature in a surprisingly short time, without any elaborate laboratory facilities. This process involves a combustion reaction between a fuel (e.g. glycine, citric acid, urea etc.) and an oxidizer (i.e., metal nitrates). Depending on the system, the selection of a suitable fuel is a crucial step to begin with. In our group a wide ranging functional materials, viz. nuclear materials, ionic conductors, catalysts and optical materials, have been prepared by combustion route. The specific examples are ceria, thoria, barium polytitanates, barium and strontium thorate, doped ceria, $SrCeO_3$, Sr_2CeO_4, $Zr_{0.8}Ce_{0.2}O_2$, YSZ, $La_{1-x}Ca_xCrO_3$, rare-earth ortho-ferrite. A number of techniques like XRD, HT-XRD, surface area analyzer, SEM, TEM, sinterability, Raman spectroscopy, dynamic light scattering, small angle x-ray/neutron scattering, dilatometer etc. were used for detailed characterization. It was shown to be a simple and cost effective technique, which results in the phase pure, nanocrystalline powders having high surface area and better sinterability. The crucial role of process parameters, especially fuel-to-oxidant ratio, on powder characteristics will be discussed in detail. This method could be extended to prepare thermodynamically metastable phases also, which are difficult to prepare by a conventional ceramic method. The effect of heating rates was found to have a strong bearing on sinterability of the nano-powders while retaining the sub-micron grain size. The versatility and capability of the combustion technique as a preparative method for a variety of nanocrystalline powders of oxide ceramics will be discussed in this talk. A few typical examples of their optical and electrical properties will also be elaborated.

Keywords: Nano-ceramics, combustion, powder properties

Carbon Nanotube Structures for Electronic Applications

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Single and multiwalled carbon nanotubes (CNTs) have attracted significant interest due to their unique physical properties. Furthermore, among the wide variety of their possible applications most importantly CNTs offer potential to serve as building blocks for future electronic device architectures; they may serve as active or passive electronic elements. Our work shows that larger CNT structures can unify the advantages of a nanosystem and the micrometer or millimeter scale devices, so they may serve as bridges between these size ranges.

In this talk, we demonstrate our state-of-the-art methods of tailored nanotube growth focusing on the resulted in nanotube structures which will be further investigated to explore their electrical properties as hysteresis,

modulations in the resistance at room temperature, noise, etc.

One interesting feature of our structures is their readiness to form composite materials. We report the fabrication and characterization of transferable and extremely flexible high-performance field emission devices using vertically aligned multi-walled carbon nanotubes in a transparent polymer matrix (PDMS). The devices are easy to prepare, re-usable and show remarkable mechanical and electrical stability under stress. Typical devices show very large field enhancement factors, in the order of ~10^4, and have breakdown fields less than 1V/μm. The high β and low breakdown fields are attributed to a field emission coming from single nanotubes in the device, and a very effective prevention of mutual screening from surrounding nanotubes due to the presence of the insulating polymer matrix.

Keywords: carbon nanotubes

National Science Foundation Support for Research and Education in Nanoscale Science, Engineering and Technology

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The emergence of nanoscale science, engineering, technology and education has led to revolutionary advances as drivers of the global economy. An increase in U.S. spending for nanotechnology over the past five years reflects the Administration's continuing support for expanding knowledge, strengthening the US economy, supporting national security and enhancing the quality of life for all citizens. The U.S. National Nanotechnology Initiative (NNI) is a long-term research and development program announced in January 2000 that coordinates 25 federal agencies and departments having a total budget of about $ 1.2 billion in fiscal year 2006, of which the estimated budget for the National Science Foundation (NSF) is $344 million. The NSF supports collaborative research and education in nanoscale science and engineering through single investigator research, interdisciplinary research and education teams, nanotechnology science and engineering centers, exploratory research, networks and user facilities. NSF also supports nanotechnology research and education through focused initiatives and core programs. These various support mechanisms will be presented. NSF's goal is to support fundamental research to catalyze synergistic science and engineering research and education in emerging areas of nanoscale science and technology. In the past five years nanotechnology has experienced considerable progress in expanding from passive nanostructured components to active nanosystems, and from scientific discovery to technological innovation. Challenges facing the nanotechnology community and its sponsoring agencies will be addressed.

Keywords:

Analytical Solutions for Next Generation Nanoscale Lithography using Fresnel Diffraction

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The ultra high resolution lithography technique (UHRL) using a Fresnel diffraction model that was proposed by Bourdillon et al [1] was based on diffraction solutions that were obtained using graphical methods. In this paper

we present analytical solutions as in [2] with which we will illustrate how the required solutions for Fresnel diffraction based UHRL, are obtained with greater ease. This analytical method also allows for greater flexibility during simulations.

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Keywords:

Devices and Architectures for THz-Frequency Spectral Sensing at the Nanoscale

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The U.S. Army Research Office (ARO) has strategic interests in advancing the state-of-the-art in nanoelectronic engineering towards new research applications that have relevance to national defense and security. Terahertz (THz) frequency spectral sensing has been one of these focus application areas for many years and one that is actively supported by the U.S. ARO, U.S. Army Edgewood Chemical Biological Center (ECBC) and U.S. Defense Threat Reduction Agency (DTRA) for its potential application towards the detection, identification and characterization of biological (bio) agents. Specifically, spectroscopic measurements conducted on biological materials and agents have produced spectral features within the THz frequency regime (i.e., ~ 300 GHz to 1000 GHz) that appear to be representative of the internal structure and characteristics of the biological samples that have been considered – e.g., DNA, RNA and bacterial spores. However, the THz spectroscopic approach is problematic in that the spectral features observed from bulk samples of the biological materials tends to be very weak (i.e., ~ 1-5% local variation in spectral absorption) and of limited number within the band (i.e., < 50-100 spectral features). One fundamental approach for avoiding the previously cited limitations is to prescribe novel techniques whereby the THz-frequency absorption signatures could be collected from individual biological molecules at the nanoscale. To this end, ARO, ECBC and DTRA have launched numerous research efforts that seek to develop new devices and architectures that will be effective in extracting THz signatures from target bio-molecules. This presentation will overview a number of multidisciplinary research projects focused the engineering demonstration of novel devices and architectures that have promise for THz-frequency sensing and imaging at the nanoscale.

Keywords: Devices, Architectures, Terahertz Sensing, Molecular, Nanoscale