ABSTRACTS
(INVITED SPEAKERS)

Tuning of Band Off-sets at the interface of Coupled Quantum Dots through Band Gap Variation-Prospects for Photovoltaics

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Coupled quantum dots (CQDs) are often referred to as artificial molecules because their electronic properties are dictated by the mutual interaction of two constituent blocks [1]. Unlike the electronic property tuning by varying the size or shape of a mono-component quantum dot (QDs), CQDs rely on controlling energy states via band-offset engineering at the material interface. Type-II CQDs offers a spatially indirect band gap resulting in a transition energy gap smaller than the band gaps of either of the constituting QDs [2]. The band off-set is determined by the band gaps of the constituent QDs which largely depends on the sizes or shapes of the QDs. Hence, by varying the size of one constituent component while retaining the other size fixed, the band off-sets at the material interface can be tuned in a controlled way. Such complex nanostructures will allow spontaneous charge carrier separation at the interface driven by the band off-set. Additionally, CQDs offer a wide photon absorption range in comparison to the mono-component QDs. Both these features simultaneously are suitable for photovoltaic applications. We demonestrate the usefulness of above mentioned features by designing component size modulated type-II CQDs composed of a fixed sized ZnSe QD and size-tuned CdS QDs. Selective tuning of band off-sets allows natural separation of photoexcited charge carriers which facilitates photovoltaic features in contrary to the limited photon-to-current conversion efficiencies of mono-component quantum dots.

References:

1. S. Sengupta, N. Ganguly, I. Dasgupta, D. D. Sarma, S. Acharya *Adv. Mater*. **2011**, *23*, 1998–2003.
2. S. A. Ivanov, A. Piryatinski, J. Nanda, S. Tretiak, K. R. Zavadil, W. O. Wallace, D. Werder, V. Klimov *J. Am. Chem. Soc.* **2007**, *129*, 11708–11719.

Rose Petals and Lotus Leaves: Nanotechnology Lessons from Nature

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Though the modern concept of Nanotechnology is usually credited to Richard Feynman, many of the relevant ideas and applications pre-date him by several centuries. Perhaps more surprisingly and unnoticed by us till recently, Nature herself has been perfecting – over millennia – many nanotechnology-based concepts. Such concepts have led to applications in areas that range from nano-photonics to reversible adhesives to super-hydrophobic surfaces. In this talk, I will focus on one such lesson in nanotechnology that we are learning from nature.

Many naturally occurring surfaces (feathers of a duck, feet of a lizard, lotus leaf) are super-hydrophobic, *i.e.*, the contact angle for water is very high (>140°). However, some natural super-hydrophobic surfaces show an additional property. Both rose petals and lotus leaves show a high contact angle. But, while a water drop quickly rolls off a lotus leaf, it sticks to a rose petal so well that it does not fall off even on inverting the petal! It is now known that whether a hydrophobic surface is 'slippery' (lotus leaf) or 'sticky' (rose petal) depends on the complexity of the surface microstructure. I will describe how the hierarchical nature of the surface – structured at both the micro and the nano scale – can give rise to a whole range of surface properties that we can now replicate in the lab [1] using clustered metal nanorod arrays as the building block [2] for a complex (hierarchical) surface. This is an excellent example of a nanostructure assembly showing 'emergent' behavior [3].

References:

1. I Chakraborty, N Singh, S Gohil, S Ghosh, P Ayyub *Soft Matter.* **2013**, *9*, 11513-11520
2. P Bhattacharya, S Gohil, J Mazher, S Ghosh, P Ayyub *Nanotechnology* **2008**, *19*, 075709
3. P Ayyub *J. Cluster Sci.* **2009**, *20*, 429-451

Nanoscale Magnonics: A New Paradigm towards All-Magnetic Computation

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Spin waves are known for many decades while magnonics is an emerging topic with both fundamental interest and application potential. Magnons with frequencies between GHz and sub-THz have wavelengths in the deep nanoscale due to their smaller velocities and magnonics fits perfectly with nanotechnology. It promises a new era of all-magnetic computation encircling on-chip information communication, processing and logic operations in addition to storage and memory. For magnonics to become a viable and sustainable technology it is essential to build a knowledge base of excitation, manipulation and detection of spin waves in various 1-D and 2-D periodic magnetic structures.

Here, we present manipulation of spin waves in optically excited and detected spin dynamics in two-dimensional ferromagnetic nanodots and nanoantidots lattices. Femtosecond laser pulses are used to create hot electrons in metallic thin films and nanostructures followed by thermalization of electron and spin populations yielding a sub-picosecond demagnetization. This is followed a two-step relaxation process and excitation of spin waves and its damping, which are detected with a sub-100 fs temporal and sub-μm spatial resolutions by a home-built time-resolved magneto-optical Kerr microscope.[1] Various aspects of the dynamics as a function of the lattice constant, lattice symmetry, and bias field strength and orientation have been investigated and new observations such as magnonic mode splitting, bandgap formation, tunability of bandgaps, dynamic dephasing and transition from collective to non collective dynamics are discussed based upon the experimental data and numerical simulations.[2-4] We further discuss the possibility of using coupled nanodots for all-magnetic transistor operations.[5]

References:

1. A. Barman, A. Haldar *Solid State Phys.* **2014**, *65*, 1-108.
2. B. Rana et al. *ACS Nano* **2011**, *5*, 9559.
3. R. Mandal et al. *ACS Nano* **2012**, *6*, 3397.
4. S. Saha et al. *Adv. Funct. Mater.* **2013**, *23*, 2378.
5. D. Kumar et al. *Sci. Rep.* **2014**, *4*, 4108.

Activation of Graphenic Carbon by Tuning Conjugation and Magnetic Order: A Computational Study

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Onsite Coulomb repulsion and conjugation are two major competing interactions in graphene that determine physical and chemical properties of 3coordinated sp2 carbon networks in general. Chemical functionalization such as substitutional doping by nor ptype dopants, and physical functionalization such as application of electric fields through gates, are found to be capable of nontrivially altering the balance between the two interactions, leading to exotic functionalities. Firstprinciples studies suggest a new paradigm of activation of graphenic carbon upon doping by boron or nitrogen in experimentally observed configurations. Results are in conformity with the electrocatalytic functionality of boron and nitrogen doped graphene and carbon nanotubes towards oxygen reduction reactions reported extensively in recent years. Regarding physical functionalization, charge density variation due to electric field applied through experimentally plausible gates, is found to be capable of inducing spin separation in armchair edged nanoribbons which are known to have nonmagnetic ground state. A systematic variety of magnetic ground states allowing spin polarized transport in zigzag as well as armchair edged nanoribbons are accesible through application of patterned electric field possible by gates of different shapes and sizes. The interplay of conjugation and the nearestneighbour antiferromagnetic ordering inherent to graphene is central to both the topics.

Atomic Layer Deposition in Nanoelectronics and Photovoltaics

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Atomic layer deposition (ALD) is a thin film deposition technology which is used to fabricate ultrathin, highly uniform and conformal material layers on complex, three dimensional objects with atomic precision. ALD uses alternating, self-limiting surface controlled chemical reactions between gaseous precursors and a surface to deposit material in an atomic layer-by-layer fashion. The virtue of the ALD technique is that the deposition is controlled at the atomic level by self-limiting surface reactions by alternate exposure of the substrate surface to different gas-phase precursors. Each surface reaction occurs between a gas phase reactant (precursor) and a surface functional group creating a product molecule and a new surface functional group that is not reactive with the precursor. After pumping away the first precursor and the reaction products, a second precursor is introduced, which deposits a second element through reaction with the new surface functional group and then restores the initial surface functional group. This set of reactions form one ALD-cycle resulting in less than one atomic layer of film growth, typically 0.5–1.0Å per cycle. The cycle can be repeated until the desired film thickness is reached. ALD has recently been adopted in production by the mainstream semiconductor industry to answer the needs of downscaling and is the method of choice for depositing high quality films with ultimate growth control and with excellent step coverage on very demanding high aspect ratio features. Recently it has been recognized that this method has also applications in many other areas relying on thin films including the area of photovoltaics.

ALD is extensively used for deposition of high-k dielectric like HfO_2 by thermal as well as plasma method using TEMAH (tetrakis ethyl methyl amido hafnium) and H_2O as precursors. Hafnium oxide layers deposited by atomic layer deposition (ALD) are of great interest as ultra-thin high-*j* MOS gate dielectrics. On silicon they are perceived as a suitable replacement for traditional thermally grown SiO_2 gates and on germanium, where thermal oxidation is not an option, they offer the prospect of a high-quality deposited dielectric. The ALD reactor was standardized by extensively finding out the variation deposition rate of HfO_2 with TEMAH and H_2O pulse times, TEMAH and H_2O pump out times, precursors oven temperatures and precursors line temperatures. These data helped optimize the deposition of thickest film in least number of cycles. Deposited film thicknesses were measured by ellipsometry and TEM. Stoichiometry of HfO_2 was determined by Auger spectroscopy. The uniformity of deposited layer over a 100 cm diameter wafer was excellent. C-V and I-V measurements were done to find k value of and leakage current through the dielectric layer. The highest value of K for HfO_2 was found to be 18 and highest breakdown voltage was 3.5 MV/cm.

Minimizing losses in solar cells, thereby improving their efficiency is a key focus of any organization involved in photovoltaic (PV) research. Although ALD has been adopted in production by the mainstream semiconductor industry to answer the needs of downscaling, ALD has applications in solar photovoltaics (PV) also. ALD has been researched for use in several solar cell applications dating from the early nineties to the present day. These applications include absorber films, buffer layers, interface layers, transparent front contacts, photoanodes and surface passivation of crystalline silicon (c-Si) solar cells. Among all the application of ALD passivation layers in c-Si solar cells and ALD buffer layers in CIGS solar cells are considered the most promising for the PV industry in the coming years. It is expected that these two applications can compete with established technologies and therefore have a significant market potential.

Chemical Reaction Involving Surface Ions of Colloidal Quantum Dots

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Synthesis and post-synthetic modification of colloidal quantum dots (Qdots) have received great attention, owing to their application potential, based on the optical properties of the as-prepared or as-modified Qdots. However, we propose that the surface cations of the nanocrystals could be chemically reactive, leading to changes in their optical properties and even to the formation of new species. We have pursued three kinds of reactions.

In the first case, the number of surface cations in the Mn^{2+}-doped ZnS Qdots could be engineered by treatment with with cation exchange resins.[1] The result was an increase in quantum yield due to dopant emission at 600 nm. The result could be explained based on the removal of clusters of cations present on the surface of the Qdots Further removal of cations led to loss of luminescence.

Secondly, the emission at 600 nm, due to Mn^{2+} ions ($^4T_1$ - $^6A_1$) in Mn^{2+}-doped ZnS Qdots gets reduced in the presence of an oxidizing agent – potassium peroxodisulphate (KPS).[2] Treatment with $NaBH_4$ led to the recovery of the lost emission. Interestingly, as-prepared non-luminescent Cu^{2+}-doped ZnS nanocrstals emit at 540 nm, only when reacted with a reducing agent.[3] The emission is lost gradually due to aerial oxidation or fast in the presence of an oxidizing agent. Thus the oxidation state of the emitting species is critical to the emission of doped Qdots. Importantly, when Cu^{2+} and Mn^{2+} doubly doped ZnS is treated with a reducing agent not only does the emission due to Cu^+ appears but also that due to Mn^{2+} increases, as the quencher (Cu^{2+}) concentration is reduced simultaneously.[4]

In the third work, we pursue reaction of Qdots with organic molecular species (ligands) leading to the formation of inorganic complexes on their surfaces. This results in the formation of a new species involving Qdot and inorganic complex; we define it as quantum dot complex (QDC).[5,6] The optical properties and enhancement of thermal stability of the complex in QDC and the retention of property of the Qdot provide a new way of chemistry involving Qdots.

Reference:

1. R. Begum, S. Bhandari, A. Chattopadhyay. *Langmuir* (**2012**, *28*, 9722–9728.
2. R. Begum, A. Chattopadhyay *Langmuir* **2011**, *27*, 6433-6439.
3. R. Begum, A. K. Sahoo, S. S. Ghosh, A. Chattopadhyay *Nanoscale*, **2014**, 6, 953-961.
4. R. Begum, A. Chattopadhyay *J. Phys. Chem. Lett.* **2014**, 5, 126–130.
5. S. Bhandari, S. Roy, S. Pramanik, A. Chattopadhyay *Langmuir* **201**), *30*, 10760-10765.
6. S. Bhandari, S. Roy, S. Pramanik, A. Chattopadhyay *Langmuir* **2015.**
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Controlling Magnetism in and on Carbon Materials: A Tale of Two Stories

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In this work, we will discuss magnetism of adatom on bilayer graphene [1,2] and the edge magnetism in small sized graphene nano-flakes [3,4].

In the first part we will report first-principles investigation of the electronic and magnetic properties of adatom on bilayer graphene. In particular, we study the influence of an applied gate-voltage. Our study carried out for a choice of three different adatoms, Na, Cu and Fe, shows that the nature of adatom-graphene bonding evolves from ionic to covalent, in moving from alkali metal, Na to transition metal, Cu or Fe. This leads to the formation of magnetic moments in the latter cases (Cu, Fe) and its absence in the former (Na). Application of an external electric field to bilayer graphene, completely changes the scenario, switching on a magnetic moment for Na adatom, and switching off the magnetic moments for Cu, and Fe adatoms. We also investigate the magnetic interaction and its manipulation between two Fe adatoms.[2]

In the second part, we will discuss the manipulation of magnetism in small sized hexagonal graphene nanoflakes. We explore possible ways to manipulate the intrinsic edge magnetism in hexagonal graphene nanoflake with zigzag edges, using density functional theory supplemented with on-site Coulomb interaction. The effect of carrier doping, chemical modification at the edge, and finite temperature on the edge magnetism has been studied. The magnetic phase diagram with varied carrier doping, and on-site Coulomb interaction is found to be complex. In addition to the intrinsic antiferromagnetic solution, as predicted for charge neutral hexagonal nanoflake, fully polarized ferromagnetic, and mixed phase solutions are obtained depending on the doped carrier concentration, and on-site Coulomb interaction. The complexity arises due to the competing nature of local Coulomb interaction and carrier doping, favoring antiferromagnetic and ferromagnetic coupling, respectively. Chemical modification of the edge atoms by hydrogen leads to partial quenching of local moments, giving rise to a richer phase diagram consisting of antiferromagnetic, ferromagnetic, mixed, and nonmagnetic phases. We further report the influence of temperature on the long-range magnetic ordering at the edge using ab initio molecular dynamics. In agreement with the recent experimental observations, we find that temperature can also alter the magnetic state of neutral nanoflake, which is otherwise antiferromagnetic at zero temperature. These findings will have important implications in controlling magnetism in graphene based low dimensional structures for technological purpose, and in understanding varied experimental reports.[3] We also study the small sized nanographene within the framework of extended Hubbard model and find good agreement with general findings obtained based on density functional theory.

Work carried out in collaboration with Dhani Nafday, Mukul Kabir, Sajeev Chacko and Dilip Kanhere.

Reference:

1. D. Nafday, T. Saha-Dasgupta *Phys. Rev. B* **2013**, *88*, 205422.
2. D. Nafday, T. Saha-Dasgupta under preparation.
3. M. Kabir, T. Saha-Dasgupta *Phys. Rev. B* **2014**, *90*, 035403.
4. S. Chacko, D. Nafday, D. G. Kanhere, T. Saha-Dasgupta, *Phys. Rev. B* **2014**, *90*, 155433.

Probing Phase Transitions in Nanoscale Correlated Systems Showing MIT and CDW Physics Using Nanomechanics

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Elastic properties and strain state of materials provide an avenue to study phase transitions. The resonant frequency of a doubly beam allows measurements of the elastic properties as function of temperature along with other parameters. In this talk I will discuss experiments using nanoscale electromechanical devices to study metal insulator transition (MIT) in VO2 and charge density wave (CDW) physics in NbSe3. Simultaneous resistance and resonance measurements for VO2 [1] indicate M1-M2 phase transition in the insulating state with a drop in resonant frequency concomitant with an increase in resistance. The resonant frequency increases by 7~MHz with the growth of metallic domain (M2-R transition) due to the development of tensile strain in the nanobeam. Our approach to dynamically track strain coupled with simultaneous resistance and resonance measurements using electromechanical resonators enables the study of lattice-involved interactions more precisely than static strain measurements. The elastic response of suspended NbSe3 nanowires [2] is studied across the charge density wave phase transition. The nanoscale dimensions of the resonator lead to a large resonant frequency (~10–100 MHz), bringing the excited phonon frequency in close proximity of the plasmon mode of the electronic condensate—a parameter window not accessible in bulk systems. The interaction between the phonon and plasmon modes strongly modifies the elastic properties at high frequencies. This is manifested in the nanomechanics of the system as a sharp peak in the temperature dependence of the elastic modulus in the charge density wave phase. Funding support from Government of India is gratefully acknowledged.

Reference:

1. Parekh et al. *Nano Lett.* **2013**, *13*, 4685.
2. Sengupta et al. *Phys. Rev. Lett.* **2013**, *110*, 166403.

Design of Nanostructures for Efficient Light Harvesting

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An outstanding challenge in the realm of attacking environmental concerns through photocatalysis is the development of nanomaterials functional in the visible region. Tunability of electronic and optical properties of materials through appropriate design of semiconductor nanostructures has been an important subject in nanotechnology[1]. Our work involves the design of core/shell nanostructures and composites manifesting exciton transport through interfaces and junctions resulting in an appreciable photocatalytic activity. Using core/shell geometry and the appropriate sensitizer, we have tuned the absorption of ZnO, TiO_2 and $NaNbO_3$ nanostructures from the UV to the visible region. These wide band gap semiconductors with narrow band gap sensitizer make core/shell nanostructures with the expanded light harvesting range usful for the destructive oxidation of noxious organic pollutants with the goal to ameliorate the environment. An efficient charge separation owing to core/shell geometry and resulting type-II band alignment between core and the sensitizer shell, creates a step-like radial potential favoring the localization of one of the carriers in the core and the other in the shell[2,3].

We have also investigated interfacial ultrafast exciton transfer and separation which results in fast photodegradation of organic pollutants using CdS-graphene composites where around 400 nm CdS supraparticles (QD cluster) have been conjugated uniformly with few micron multi-layer graphene sheets. Charge delocalization in cluster QDs, ultrafast electron transfer (<150fs) to graphene sheet and separation of exciton which leads to slower exciton recombination in CdS supraparticles composites with graphene, have been observed using ultrafast transient absorption spectroscopic technique[4].

References:

1. A. K. Ganguli, S. Vaidya, A. Ganguly, *Chem. Soc. Rev*. **2010,** *39*, 474-485.
2. S. Kumar, S. Khanchandani, M. Thirumal, A. K. Ganguli, *ACS Appl. Mater. Interfaces* **2014**, *6*, 13221−13233.
3. S. Khanchandani, P. K Srivastava, S. Kumar, S. Ghosh, A. K. Ganguli *Inorg. Chem*. **2014**, *53*, 8902−8912.
4. K. Ojha, T. Debnath, P. Maity, M. Makkar, P. K Chowdhury, H. N. Ghosh, A. K Ganguli; *Chem. Commun.* 2014. (Communicated)

Understanding the Physics and Chemistry of Nano-materials Using Density Functional Theory

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Ab initio density functional theory (DFT) is an important tool not only to understand the chemical bonding and microscopic couplings that are essential to specific property of nano materials but also to design new materials with desired properties or modify existing materials with new properties. In this talk I will discuss one example from each of the above cases.

In the first part of my talk I will show how DFT can be used to predict properties of graphene on a Ni and Co substrates. Our calculations show that there is an induced ferrimagnetism on a graphene sheet supported on ferromagnetic substrates. The Dirac cone is destroyed and there is a slight opening up of band gap in the graphene sheet at the K-point of the Brillouin zone. Further we predict how the spin alignment (as well as the band gap) can be tuned from ferri to ferromagnetic (semi metal to insulating) by adsorbing hydrogen on the supported graphene sheet. Finally I will also show how we can decouple the interaction between the graphene sheet and the substrate by intercalating oxygen atoms between the two.

In the second part I will show how DFT helps in understanding experimental observations. Some recent measurements of the absorption and photoluminescence properties of cadmium sulphide nanotubes with overall size beyond the quantum confinement regime show that while the absorption spectra are unaffected by the change in size there is an anamolous red shift in the photoluminescence spectra with increase in size. Our DFT calculations have identified that the shift in the emission peak of the photoluminescence spectra is a result of the interplay between Cd vacancies on the surface of these nanotubes and the crystalline strain, which was incorporated in these nanotubes during their growth process. Most importantly our results show that rather than the defect concentration, it is the nature of the defect that plays a crucial role in determining the optical properties of these nanotubes. For this particular case of CdS nanotubes we find that though S interstitials are the most abundant ones, however it is the Cd vacancies with second lowest formation energies, which significantly affect the photoluminesence spectra.

Cell-Nanoparticle Interaction: Effect of Nanoparticle Multivalency

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Nanoparticles have wide range of application in biomedical science and variety of nanoboconjugate is required for such application. One important aspect of nanobioconjugate is their multivalency and associated cooperative binding that significantly dictates their interaction with biological interface. Multivalency of nanobioconjugate arises due to the presence of multiple numbers of affinity biomolecule attached on the nanoparticle surface and this number subsequently determines their application performance. The limitation of currently available nanobioconjugates is the uncontrolled number of affinity biomolecules present on the nanoparticle surface that leads to variety of unwanted phenomena and limits the application performance. We are synthesizing nanobioconjugate with varied average number of biomolecules between 1-100 and investigating their performance as cellular and sub-cellular imaging probe. This talk will focus on our effort in making nanobioconjugate with controlled number of biomolecule and effect of nanoparticle multivalency on cellular uptake mechanism.

Surface Functionalization of Transition Metal Oxide Nanoparticles

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In the present paper we report that ferrite and other transition metal oxide nanoparticles can be functionalized with suitable ligands to get biocompatible and water soluble nanoparticles with enhanced and novel multifunctional properties. We observed that $CoFe_2O_4$ nanoparticles (NPs) functionalized with surfactants having π-acceptor/π-donor head group along with different chain-length show much higher coercivity compared to bare particles due to NP-ligand interaction which modifies the splitting of d-orbital energy levels as well as spin motion of surface Co^{+2} ions. Intrinsic multicolour fluorescence in $MnFe_2O_4$ nanoparticles from blue, cyan, and green to red is observed upon functionalization with a small organic ligand such as Na-tartrate because of ligand-to-metal charge transfer from tartrate ligand to lowest unoccupied energy level of $Mn^{2+/3+}$or Fe^{3+} of the NPs and Jahn−Teller distorted d−d transitions centered over Mn^{3+} ions in the NPs [2, 3].

Reference:

1. R. Rakshit, M. Mandal, M. Pal, K. Mandal *Appl. Phys. Lett.* **2014**, *104*, 092412.
2. M. Pal, R. Rakshit, K. Mandal *Appl. Phys. Lett.* **2014**, *104*, 233110.
3. M. Pal, R. Rakshit, K. Mandal *ACS Appl. Mater. Interfaces* **2014**, *6*, 4903.

Magnetically Doped ITO Nanocrystals Exhibit Plasmonics, Electrical Conductivity, and Carrier-Mediated Magnetic Coupling

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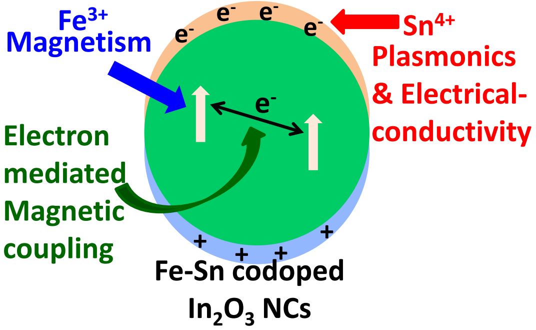

I will talk about a unique category of material that simultaneously exhibit (i) strong localized surface plasmon resonance (LSPR) in near to mid infrared region, (ii) weak ferromagnetism at room temperature, and (iii) high electrical conductivity (~10 S/cm). All these properties are obtained by lattice doping of transition metal ions in a transparent conducting oxide nanocrystal, for example, codoping of Sn and Fe in In_2O_3 nanocrystals. Sn^{4+} provides free electrons for LSPR and electrical conductivity, whereas, Fe^{3+} provides magnetic spin. More importantly, interaction between free electron and magnetic spin leads to carrier mediated magnetic coupling, useful for spin-based applications. In addition to the above mentioned properties, the nanocrystals are solution processed and transparent to visible light. Many other different combinations of dopants and hosts are now being explored for optimization of different properties.

References:

1. B. Tandon, G. S. Shanker, A. Nag *J. Phys. Chem. Lett.* **2014**, *5*, 2306.
2. G. S. Shanker, B. Tandon, T. Shibata, S. Chattopadhyay, A. Nag. *Chem. Mater. (in press).*

Giant Electronic Effect with Weak Interaction: 2-Dimensional Atomic Scale Materials on Insulators

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In this talk we will present the role of substrates on the electronic and phononic structure of atomic scale 2-dimensional materials such as graphene, MoS_2 as well as topological insulators like Bi_2Se_3. For example, using Green's function based screened coulomb method it is observed that, quasi particle gap of graphene nanoribbon on weakly interacting boron nitride substrate is renormalized substantially (band gap changes up to 1 eV), and such renormalization is highly sensitive to the type of insulating substrates. The results are discussed in terms of modification of self energy of electrons that arises due to dielectric screening at the atomic scale and the findings are compared with recent experiments. Implications of such results to nanoscale devices including that on silicon on insulator at the atomic scale (SOI-A) will be discussed.

Pauli Blocking Dynamics in Optically Excited Quantum Dots

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Quantum dots (QDs) have atom-like discrete energy levels owing to their three-dimensional quantum confinement. Carrier relaxation through these discrete energy levels in QDs is expected to be influenced by the Pauli's exclusion principle. We have investigated the Pauli blocking dynamics of carriers in self-assembled InAs/GaAs QDs using excitation correlation (EC) spectroscopy which is a variant of a pump-probe technique [1]. The EC signal is define as $EC(\hbar\omega,\tau) = PL_{12}(\hbar\omega,\tau) - PL_{12}(\hbar\omega,\tau=0)$, where $PL_{12}(\hbar\omega,\tau)$ is the steady-state PL signal measured at an energy $\hbar\omega$ at a delay τ between two pulses. The EC signal provides a quantitative measure of the nonlinear effects associated with the redistribution and recombination of carriers which should be influenced by the Pauli's exclusion principle.

We measure spectrally-resolved EC signal at different delay τ. The time evolution of the EC signal measured at two different excitation fluences (I) for the first three QD states (denoted by G, X1, and X2, respectively) is shown in Fig. 1. It is seen that near zero delay, the signal from the state G is snubbed while that from the X1 state can either be smaller or larger than the observed signal at longer delays, depending on the excitation fluence. The results can be understood in terms of Pauli blocking in QDs. A minimal theoretical model, which combines carrier loss kinetics with principle of detailed balance and Pauli's exclusion principle, quantitatively reproduces (solid lines in Fig. 1) the observations.

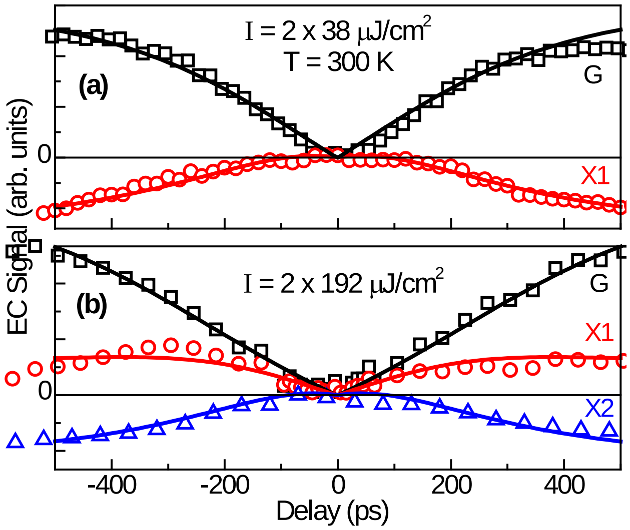

Fig. 1: Delay dependence of the EC signal measured two different excitation fluences for the first three QD states, G, X1, and X2, respectively. The solid lines are fits to the data by our model calculation.

Reference:

1. R. Mondal, B. Bansal, A. Mandal, S. Chakrabarti, B. Pal *Phys. Rev. B* **2013**, *87*, 115317.

Nano Keno: Why Nano?

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Nanoscience/Nanotechnology is creating a wealth of new materials and manufacturing possibilities, which in turn will profoundly impact our economy, our environment, and our society. In the proposed presentation an overview on our nano-activity in the application driven basic research will be highlighted. Our continuous strive for the development of low-cost solar light harvesting material, toxic metal sensing material and materials for affordable healthcare in the diagnosis and treatment of diseases will also be highlighted.

References:

http://www.bose.res.in/~skpal/pub.htm

Metal and Metal Oxide Particles in the Nanoregime

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Coinage metals exhibit rich plasmon band in the visible.Hence the three metals, copper, silver and gold in the nanoregime find useful application in Raman scattering studies. That eventually become surface enhanced Raman scattering (SERS) for single molecule detection involving all the three coinage metal substrates. Unprecedented fluorescence property has recently been observed taking the coinage metal nanoparticles to sub-nanometer size range. Thus fluorescence and Raman scattering find a common coinage metal platform for spectroscopic studies.

Catalysis is a never ending endeavor but useful event in science especially in chemical science. This field is also enormously enriched with coinage metal and coinage metal-incorporated nanocomposites of transition metal oxides.

Finally, band gap energy quantitatively guarantees the activation of these materials for light driven photocatalysis. Keeping the solar light spectrum in mind band gap tuning is needed often times to activate a material which bears an inherent large band gap value.Thus doping a suitable material has now been a common practice. Then photo produced hole-electron generation becomes facile. Another problem crops up there. That is hole and electron recombination. The problem has been solved by metal or metal ion support.We have tackled the problem by the implementation of the concept of high index faced material or bringing hetero-junction or porous architecture out of a suitable composite. Low cost material for catalysis synthesis and applications would be focused.

References:

1. S. Dutta, S. Sarkar, C. Ray, A. Roy, R. Sahoo, T. Pal. *ACS Appl. Mater. Interfaces*, **2014**, *6*, 9134–9143.
2. S. Dutta, C. Ray, S. Sarkar, M. Pradhan, Y. Negishi, T. Pal. *ACS Appl. Mater. Interfaces*, **2013**, *5*, 8724–8732.
3. M. Ganguly, J. Pal, S. Das, C. Mondal, A. Pal, Y. Negishi, T. Pal. *Langmuir* **2013**, *29*, 10945–10958.
4. R. Sahoo, A. Roy, C. Ray, C. Mondal, Y. Negishi, S. M. Yusuf, A. Pal, T. Pal. *J. Phys. Chem. C* **2014**, *118*, 11485–11494.
5. J. Pal, M. Ganguly, C. Mondal, A. Roy, Y. Negishi, T. Pal. *J. Phys. Chem. C* **2013**, *117*, 24640–24653
6. J. Pal, M. Ganguly, C. Mondal, Y. Negishi, T. Pal *Nanoscale*, **2014**. (Accepted)

Chemistry with Bigger Atoms

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Solids that utilize semiconductor nanocrystal quantum dots as building units have been demonstrated to exist, however the inter-particle forces in such materials are decidedly not chemical. We demonstrate the formation of charge transfer states in a binary quantum dot mixture. Charge resides in quantum confined states of one of the participating quantum dots. Coulomb forces that arise from charge transfer lead to the precipitation of a stoichiometric, ionic quantum dot solid. These solids are shown to behave in the same manner as compounds, with quantum dots taking on the role of atoms. We will examine the many peculiar ramifications of working with big atoms.

New Challenges of Luminescent Nanomaterials

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Luminescent nanomaterials can be classified into five classes; doped nanomaterials, semiconductor-type quantum dots (Q-dots), carbon dots (C-dots), metal nanoclusters and semiconducting polymer nanoparticles.[1-9] Core-shell nanostructures materials are found to be efficient for various applications. The study of nanoscale matter-radiation interactions offers numerous opportunities for both fundamental research and technological applications in photonics and biophotonics. The understanding of excited state dynamics of photo excited quantum dots is essential for technological applications such as efficient solar energy conversion, light emitting diodes, photovoltaic cells and so on. Here, our emphasis is directed to describe the influence of size, shape and composition of quantum dot on their different relaxation processes, i.e. radiative relaxation rate, nonradiative relaxation rate and number of trap states. We will discuss about the photophysical properties of new generation luminescent nanoparticles i.e. metal cluster and carbon dots Finally, we will discuss dye/porphyrin doped semiconducting polymer nanoparticles for future applications.

References:

1. S. Sadhu, A. Patra *J. Phys. Chem. C* **2012**, *116*, 15167.
2. T. Sen, A. Patra *J. Phys. Chem. C* **2012**, *116*, 17307.
3. S. Sadhu, A. Patra *J. Phys. Chem. C* **2011**, *115*, 16867.
4. A. Kar, A. Patra *Nanoscale* **2012**, *4*, 3608.
5. S. Sadhu, A. Patra *ChemPhysChem*. **2013**, *14*, 2641.
6. S. Kundu, S. Sadhu, R. Bera, B. Pramanik, A. Patra *J. Phys. Chem. C*, **2013**,*117*, 23987-23995.
7. S. Bhattacharyya, A. Patra *J. Photochem. Photobiol. C: Photochemistry* **2014**, *20*, 51–70.
8. A. Kar, A. Patra *J. Mater. Chem. C.* **2014**, *2*, 6706-6722.
9. A Kar, S. Kundu, A. Patra *ChemPhysChem* **2014** (accepted).

Some Interesting Chemistry in Designing Semiconductor Nano Heterostructures in Reaction Flask

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Designing nanostructures in reaction flask and monitoring the progress of the crystal growth remain always exciting for the chemist. In some cases the reactions are planned and one gets the structures as per the design; but in major cases the new nanostructures appear surprisingly. In either case, one has to wait with excitement to see the images in microscope and those sometimes give pleasure and sometimes generate frustration. Keeping these views in mind of a chemist, the talk would present the solution phase architect of some peculiar hetero-structures with combination of binary and multinary semiconductors where the growth of one part is planned before loading the chemicals in reaction flask and other part appeared surprisingly. This would include the formation of Sb_2S_3-$AgSbS_2$, Sb_2Se_3-$CuSbSe_2$ and some other hetero-structures involving group II-VI semiconductors. In addition, some new concepts in understanding the fundamental aspects of crystal growths like super ion conductor catalytic growth, diffusion controlled kinetics in shape architect, nucleation density controlled crystal growth mechanism, sheet rapping mechanism for tube and rod formation etc would be discussed.

New Synthetic Approaches for the Preparation of Metal Nanoparticle Dispersions and Assemblies in Different Solvent Media

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The stability of the nanoparticles in different solvent media is crucially governed by the type of capping agent used. Realization of some of the potential applications of nanoscale particles requires them to be as monodisperse as possible. Another interesting aspect of the nanomaterials is the dependency of their properties on the shapes. Thus it becomes very clear that there is lot of interest in controlling the shape and sizes of these nanoparticles and there are many studies towards achieving these goals. In this talk we will present some of our efforts towards controlling the size and shape of nanoparticles by using the chemical molecules as tools for such purposes. More specifically, we have been working on “digestive ripening” process in which a colloidal suspension in a solvent is refluxed at or above the solvent boiling temperature in the presence of the surface active agent resulting in the conversion of a highly polydisperse colloid into a highly monodisperse one ($\sigma < 5\%$). Another important issue concerning the nanoparticle synthesis is their dispersion in different solvent media. The stability of the nanoparticles in different solvent media is crucially governed by the type of capping agent used . Water dispersibility is an essential criterion to realize bio-applications of nanoparticles. Apart from the traditional protocols involving charge imparting reducing/ stabilizing agents, many reducing agents in combination with water dispersible polymers, surfactants and capping agents have been used to accomplish this important stipulation. In this context we have been working on developing various methods to prepare stable and water dispersible metal nanoparticles. The metals studied were Au, Ag and magnetic Co and Ni. Several strategies have been adapted to achieve water dispersity. Recently we have made significant progress in the synthesis of sophorolipids (a dimeric glucose –sophorose- attached to the $\boxed{-1}$ carbon of a fatty acid). These sophorolipids (SLs) have been the centre of interest for their documented antimicrobial, antifungal and antiviral activities. We have shown that these could be employed as good capping agents as well as reducing/capping agents. Utilization of SLs as capping and reducing agents also enabled us to make nanoparticle dispersions by continuous flow methods. The details of the above results will be presented during the talk.

Intriguing Structure and Transport Behaviour of Ultrathin Single Crystalline Gold Nanowires

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Growing anisotropic nanostructures of high symmetry materials is a challenging task owing to the symmetry breaking that is required. We have developed a simple wet chemical method by which ultrathin (< 2 nm diameter) Au nanowires could be grown in the solution phase. In the first part of the talk, I will discuss the details of the mechanism of these wires using electron microscopy as the principal supporting tool.

In the second part, I will discuss methods to grow these wires on substrates and directly between pre-patterned contact pads. This enables the direct measurement of electrical transport through these wires for the first time. We find an unexpected insulating behaviour in these wires with the resistivity decreasing as a function of the temperature of measurement. The implications of this observation will be discussed. In the third part, I will present some intriguing results on the atomic structure of these nanowires where we find modulations of atomic planes normal to the growth directions. Finally I will present some interesting applications of these ultrathin metal nanowires in sensing and catalysis.

Reference:

1. A. Roy, T. Pandey, N. Ravishankar, A. Singh, *J. Phys. Chem. C.* **2014**, *118*, 18676-682.
2. A. Roy, S. Kundu, K. Müller, A. Rosenauer, S. Singh, P. Pant, M. P. Gururajan, P. Kumar, J. Weissmüller, A. K. Singh, N. Ravishankar *Nano Lett.* **2014**, *14*, 4859-66.
3. A. Leelavathi, G. Madras, N. Ravishankar *J. Am. Chem. Soc.* **2014**, *136*, 14445-455.
4. S. Kundu, A. Leelavathi, G. Madras, N. Ravishankar *Langmuir* **2014**, *30*, 12690-695.
5. P. Kundu, S. Turner, S. V. Aert, N. Ravishankar, G. V. Tendeloo *ACS Nano* **2014**, *8*, 499-506.
6. A. Roy, T. Pandey, N. Ravishankar, A. K. Singh *AIP Advances* **2013**, *3*, 032131-032131-7.
7. U. Chandni, P. Kundu, S. Kundu, N. Ravishankar, A. Ghosh *Adv. Mater.* **2013**, *25*, 2486-89.
8. P. Kundu, U. Chandni, A. Ghosh, N. Ravishankar *Nanoscale* **2012**, *4* 433-437.
9. U. Chandni, P. Kundu, A. K. Singh, N. Ravishankar, A. Ghosh *ACS Nano* **2011**, *5*, 8398-8403.
10. P. Kundu, A. Halder, B. Viswanath, D. Kundu, G. Ramanath, N. Ravishankar, *J. Am. Chem. Soc.* **2010**, *132*, 20-21.
11. A. Halder, N. Ravishankar *Adv. Mater.* **2007**, *19*, 1854-1858.

Optical Properties of Two Dimensional Materials for Photonic Devices

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Graphene oxide (GO) shows insulating behavior but controlling the oxygen density during the oxidation of graphite, results in a semiconducting characteristics with an optical bandgap (~1.7 eV). The modification of individual oxygen functional groups and the resultant optical properties of graphene oxide suspension were investigated using controlled photothermal reduction by infrared irradiation. The yellow-red emission (~ 610 nm) originated from the defect assisted localized states in GO due to epoxy/hydroxyl (C-O/-OH) functional groups and that of blue one (~ 500 nm) was ascribed to the carbonyl (C=O) assisted localized electronic states. With increase in reduction time and IR power density, the intensity of yellow-red emission was found to decrease, with the blue emission being the prominent one. We have studied graphene oxide (GO) based p-n heterojunction on n-Si. The device on illumination shows a broadband (300 nm-1100 nm) spectral response with a characteristic peak at ~700 nm, in agreement with the photoluminescence emission from GO. Very high photo-to-dark current ratio (> 10^5) is observed upon illumination of UV light. On the other hand, transition metal dichalcogenides (TMD), an emerging class of two dimensional materials are interesting due to the presence of a finite and direct energy gap in low dimensions, with a wide range electronic and optical attributes. We have demonstrated the ability to gradually tailoring of the optical properties of MoS_2 naonocrystals in terms of PL response and optical absorption, making them attractive for future photonic devices.

Single Nanowire Devices: Techniques and Physics Issues

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Generally experiments on nanomaterials are done on an ensemble of nanomaterials. Thanks to recent progress on nanolithography using Focused Ion beam (FIB) as well as e-beam lithography (EBL), it is now possible to make single nanowire level electrical as well as opto-electrical experiments. These nanowires can be a single functional unit that can be a metal or a semiconductor (elemental or compound). This allows one to do solid state physics at a different length where one can individually address a nanowire electrically and optically without the problem of size dispersion or averaging over an ensemble with a large number of them.

The talk will briefly discuss the motivation of such experiments, the tools and techniques for such experiments. This will be followed by certain results that we have obtained in such single nanowire measurements.

The results that will be discussed will include:
(a) Single nanowire photo detectors of length $\leq 1\mu$m, showing ultra large responsivity, (b) Single nanowires that show resistive state switching with possibility of fabricating RRAM at single nanowire level and (c) Noise and fluctuations measured on single nanowires/nanotubes.

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Charge Separation and Extraction from Colloidally Synthesized Nanostructures

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Semiconductor nanomaterials or quantum dots (QD) as they are popularly known have found a widespread use in luminescence applications including light emitting device and biological tags. Also, they are gaining importance for QD sensitized photovoltaic materials. The challenge is to understand how their properties can be influenced.

In this lecture, I will discuss a few possibilities for charge separation and extraction as well. Inorganic complexes aid in charge separation. Even enzymes can lead to charge extraction depending on their structure. An example of a nanoheterostructure will be discussed where simultaneous emission from both Type I and Type II junctions can be obtained. Another example would be the use of metal-semiconductor interface in order to extract charges and use for photocatalysis.

Wave-function Collapse and Strain Tuning as Distinct Tools to Engineer Photoluminescence

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One of the most spectacular aspects of semiconductor nanocrystals has been their photoluminescence properties, offering wide-ranging tunability of the emitted light and a high degree of quantum efficiency, not usually achievable with corresponding bulk materials; this has led to an intense interest in such materials, both in terms of fundamental science and technological possibilities. There are primarily two distinct classes of light-emitting nanocrystal materials. One class makes use of the band-gap emission, thereby achieving a high degree of tunability as a function of the nanocrystal size via the quantum confinement effect. However, this class of photoluminescence tends to be more easily affected by surface degradation and is seriously limited in its usefulness due to severe self-absorption problems. The other route makes use of deexcitation through atomic-like levels of a dopant ion via energy transfer between the host nanocrystal and the dopant site, thereby obviating any problem of self-absorption and achieving a greater stability of the luminescence, but forgoing the tunability with the nanocrystal size. In my presentation, I shall discuss how one may go beyond these expected limitations of each case, making the band-gap emission intrinsically stable (by devising ways to collapse the active wave-functions) and dopant emission tunable (by strain engineering at the dopant site), through understanding the fundamental processes involved in each case, that require shifting away from some of the dominant dogmas in the field.

Raman Spectroscopy: A Non-destructive Tool for Detection at Single Molecule Level

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Detection of single-molecule is the ultimate sensitivity required in chemical analysis, trace detection and biosensing.[1,2] Surface Enhanced Raman Scattering (SERS) is a powerful nondestructive tool for acquisition of characteristic fingerprint at single-molecule level. Compared to normal Raman signals, SERS signals are ideally amplified 10^{13} to 10^{15} times when the probe molecules reside in the nanogaps (known as "*hot-spots*") between metal nanoparticles.[3-5] The practical applications of SERS demand Raman signals to be reproducible and stable, and the substrate to be synthesized facilely. Recently, biomolecules have drawn huge research attentions for their templating capacities to realize stable metal nanoclusters (NCs) with uniform interior nanogap.

In my talk I will show a simple and inexpensive method for the fabrication of highly stable wirelike silver-NCs with an inter-particle gap of 1.7 ± 0.2 nm using DNA as a template. An uniform and reproducible SERS signals have been observed upto a picomolar (pM) concentration of dye molecules. The enhancement factor we have achieved is sufficient to detect single molecules[6]. Moreover, the SERS signal is not highly dependent on the polarization of the excitation laser, as confirmed from both the experimental and theoretical simulation results.[6]

* work done in collaboration with D. Majumdar, P. K. Mondal, S. Kundu

References:

1. X. S. Xie, J. K. Trautman *Annu. Rev. Phys. Chem.* **1998**, *49*, 441−480.
2. F. Kulzer, M. Orrit *Annu. Rev. Phys. Chem.* **2004**, *55*, 585−611.
3. S. Nie, S. R. Emory *Science* **1997**, *275*, 1102−1106.
4. Q. Li, Y. Jiang, R. Han, X. Zhong, S. Liu, Z. Y. Li, Y. Sha, D. Xu *Small* **2013**, *9*, 927−932.
5. D. K. Lim, K. -S. Jeon, J. -H. Hwang, H. Kim, H. Kwon, Y. D. Suh, J. -M. Nam, *Nat. Nanotechnol*. **2011**, *6*, 452−460.
6. D. Majumdar, A. Singha, P. K. Mondal, S. Kundu *ACS Appl. Mater. Interfaces* **2013**, *5*, 7798-7807.

Diffusion in Nanocrystal Doping: A Boon or a Bane

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Doping in semiconductor quantum dots has been shown to have distinct advantages for applications compared to their undoped counterparts [1]. However, so far, the efficient synthesis of these uniformly doped nanocrystals has been the bottleneck for their implementation in devices. Diffusion of dopants or impurities in host nanocrystals out of the host have posed a serious threat to the efficient synthesis of doped nanocrystals [2]. This problem has been extensively studied and some techniques like nucleation doping [1], or dopant insertion at growth stage [3] or optimal use of temperature to retain the dopant [4], interplay between the thermodynamic versus kinetic control [5] have evolved over a period of time with reasonable success. However, so far, these techniques have not been helpful specifically in avoiding clustering or phase separation leading to non-uniform doping of the nanocrystals. Uniform doping, specifically for magnetic impurities is crucial and is predicted to show room temperature ferromagnetism [6]. In this talk, I will discuss the constructive use of diffusion of dopants out of the nanocrystal to obtain a uniformly doped nanocrystal using CdS as a model system. I will also show that this novel strategy can also be applied to a wide range of dopants like Mn, Fe, Co and Ni to obtain promising magnetic, optical and magneto-optical responses compared to earlier materials.

References:

1. N. Pradhan, X. Peng *J. Am. Chem. Soc.* **2007**, *129*, 3339.
2. G. M. Dalpian, J. R. Chelikowsky *Phys. Rev. Lett.* **2006**, *96*, 226802.
3. N. Pradhan, D. Goorskey, J. Thessing, S. Peng *J. Am. Chem. Soc.* **2005**, *127*, 17586.
4. D. Chen, R. Viswanatha, G. L. Ong, R. Xie, M. Balasubramaninan, X. Peng, *J. Am. Chem. Soc.* **2009**, *131*, 9333.
5. V. A. Vlaskin, C. J. Barrows, C. S. Erickson, D. R. Gamelin *J. Am. Chem. Soc.* **2013**, *135*, 14380.
6. S. -J. Han, J. W. Song, C.-H. Yang, S. H. Park, J.-H. Park, Y. H. Jeong, K. W. Rhie *Appl. Phys. Lett.* **2002**, *81*, 4212.

ABSTRACTS
(POSTERS)

Effect of anisotropic Fe-nanorod addition to magnetite-based MR suspensions: a dynamic magnetorheological study

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Uniform magnetite nanospheres (~300 nm) were synthesized by solvothermal method in presence iron (III) acetylacetonate, polyacrylic acid in ethylene glycol at elevated temperature. Iron nanorods of approximately 700 nm in length were prepared by same method in presence of iron (III) nitrate, hydrazine and cetyl trimethylammonium bromide in ethylene glycol for 6h at 190^0C. Three magnetorheological fluids (MRF) were prepared by dispersing suitable amount of magnetite and iron nanorod in silicone oil. We report enhanced stability and yielding behavior for bidisperse MRFs containing magnetite nanoparticles and Fe-nanorods, compared to MRF containing only spherical magnetite nanoparticles. A parallel plate rotational rheometer with magnetic field attachment was used for Magnetorheological characterization. It was observed that the magnitude of field-dependent yielding behavior as a function of time increase with the increase in amount of Fe-nanorods. This can be attributed to the asymmetric shape of the Fe-nanorods. Furthermore, sedimentation stability was enhanced for the fluids with increasing iron nanorod substitution.

Electrical unipolar resistive state switching in a single nanowire of CuTCNQ

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Metal-TCNQ charge transfer complexes are widely researched as a strong candidate for Resistive Random Access Memory (ReRAM) for their bipolar resistive state switching property. We report here a new type of *unipolar* resistive state switching in *a single strand* of a nanowire of Cu:TCNQ with symmetric (Pt/Cu:TCNQ/Pt) and asymmetric (Cu/Cu:TCNQ/Pt-Au) electrodes configuration, a phenomena that have not been reported till date. The devices show resistive state switching with high on-off resistance ratio at low threshold voltage (< 4V). A numerical calculation based on a phenomenological model was used to explain the observed phenomena. It is proposed that the applied bias leads to a Cu filament formation near the top or bottom contacts. These filaments mediate the charge transfers from electrode to Cu:TCNQ. Thus, CuTCNQ single nanowire switch will be a promising material rewritable ReRAM and nanoscale switching devices.

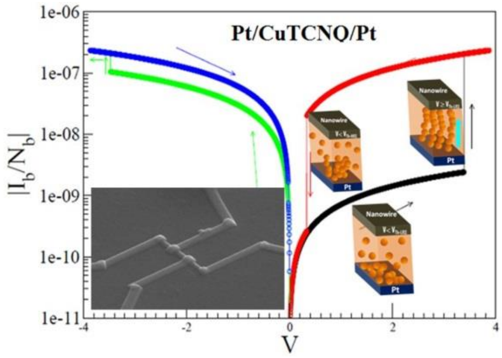

Figure: Log |*I*|-*V* curves of a single nanowire of CuTCNQ connected with FEB deposited Pt in Pt\CuTCNQ\Pt configuration. *Inset:* SEM image of device under test

Low temperature electrical transport and 1/f Noise Spectroscopy in heavily doped Single Germanium Nanowires

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In recent years device scaling has led to a revival in the study of Germanium due to higher value of carrier mobility as compared to Silicon which is the dominating material in microelectronics due to easy availability, processing and formation of native oxide. Germanium nanowires show a promising application in FET, photodetectors and very recently in Lithium Ion battery anodes. To understand the basic transport properties in doped germanium nanowires with diameter below 100nm, we have studied the low temperature electrical transport including Impedance Spectroscopy and low frequency noise spectroscopy in a single strand of a Ge nanowire of diameter 60 nm. The nanowires were grown by vapor phase using Au nanoparticles as catalysts. The Ge nanowires that have been used are heavily doped and are close to the insulator-metal boundary. The temperature dependence of the resistivity shows weak localization behavior with the resistivity saturating to finite residual value for low temperature. The Au/Cr contact pads on the Ge nanowires make Schottky type junctions. The barrier height, the frequency dependence impedance as well as the 1/f noise, (flicker noise) were studied to understand some of the basic issues of electrical transport in these nanowires.

Nonlinear alternating current conductance in nano-crystalline La_2NiMnO_6 for identifying Griffiths-like phase with significant electro-magnetic correlation.

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Double perovskites have the general formula: A_2BCO_6 (A = La, Ba, Sr, Nd ; B= Ni, Ru, Mo, and C = Mn, Ti, Mg). The mixed–valent double perovskites A_2BCO_6 have received particular interest because of their intriguing structural, magnetic and magneto transport properties [1]. In this report, the signature of Griffiths like phase is inferred from the electrical transport measurement of the real part of ac conductance $\Sigma(T,f)$ of nano-crystalline double perovskite La_2NiMnO_6. The system exhibits a paramagnetic insulating phase (PMI) in the temperature range 225K to 300K, a ferromagnetic insulating phase (FMI) between 125K to 185K; and the intermediate region shows Griffiths like phase. At a fixed temperature T, $\Sigma(T,f)$ remains almost constant to the value Σ_o up to a certain frequency, known as the onset frequency fc and increases from Σ_o as frequency is increased from fc. Scaled appropriately, the data for $\Sigma(T,f)$ at different T fall on the same universal curve indicating the existence of a general scaling formalism for the ac conductance. f_c scales with Σ_o as $f_c = \Sigma_0^{x}f$,where x_f is the nonlinearity exponent characterising the onset [2]. Log-log plot f as a function of Σ_o exhibits structure over the range of temperature measured. The slopes are 1.03±0.007 and 0.49±0.025 in the temperature range from 125K to 185K (Ferromagnetic Curie temperature) and 225K (Paramagnetic Curie temperature) to 300K respectively. The gradual crossover in slope occurs in the intermediate temperature range from 185K to 225K signifies the existence of Griffiths phase [3,4]. A simple phenomenological R-RC model consistent with the microstructural conduction mechanism in PMI and FMI phases is developed to reproduce the nonlinear character of ac conductance, the onset frequency f and the nonlinearity exponent. Scaling theories with reliable models are used to analyze the results of ac conduction and the nonlinearity exponent both in ferro- and paramagnetic phases in this polycrystalline double perovskite.

Reference

[1]. Dass R.I., Yan J.Q., Goodenough J.B. Phy. Rev. B. 2004; **69:** 014401-014409 and Kobayashi K.I., Kimura T., Sawada H., Terakuwa K., Tokura Y. Nature. 1998; **395:** 677-680.

[2]. Ghosh T.N., Nandi U.N., Jana D., Dey K., Giri S. J. Appl. Phys. 2014; 116:129902-129910.

[3]. Nair H.S., Swain D., Hariharan N., Adiga S., Narayana C., Elizabeth S. J . Appl. Phys. 2011; 110: 123919-123925.

[4]. Masud M.G., Ghosh A., Sannigrahi J., Chaudhuri B.K. J. Phys: Condens. Matter. 2012; 24: 295902-295909.

p-i-n Heterojuctions with BiFeO$_3$ Perovskite Nanoparticles and *p*- and *n*-Type Oxides: Photovoltaic Properties

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We report the fabrication of *p-i-n* heterojunctions based on a thin film of perovskite BiFeO$_3$ nanoparticles. In this all inorganic oxide based *p-i-n* device structure, the *p*-type and the *n*-type oxide semiconductor plays the role of hole- and electron-collecting layer, respectively. Whereas the perovskite, sandwiched between the collecting layers, acts as an intrinsic semiconductor. We have characterized the perovskite and the carrier collecting materials, From the spectrum of the density of states, obtained from scanning tunneling microscopy, we could locate the band edges to infer the nature of the active semiconductor materials. The energy level diagram of *p-i-n* heterojunctions showed that type-II band alignment formed at the *p-i* and *i-n* interfaces, favoring carrier separation at both of them. We have compared the photovoltaic properties of the perovskite in *p-i-n* heterojunctions and also in *p-i* and *i-n* junctions. From current-voltage characteristics and impedance spectroscopy, we have observed that two depletion regions were formed at the *p-i* and *i*-n interfaces of a *p-i-n* heterojunction. The two depletion regions operative at a *p-i-n* heterojunction have yielded better photovoltaic properties as compared to devices having one depletion region in the *p-i* or the *i-n* junction. The results evidenced photovoltaic devices based on all-inorganic oxide, nontoxic, and perovskite materials.

Ultrafast Dynamics of Solvation and Charge Migration in a DNA-based Biomaterial

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Charge migration along DNA molecules is key factor for the DNA-based devices in optoelectronics and biotechnology. Association of significant amount of water molecules in the DNA-based materials for the intactness of DNA structure and their dynamical role in the charge transfer (CT) dynamics is less attendent in the contemporary literature. In the present study, we have used genomic DNA-cetyltrimethyl ammonium chloride (CTMA) complex, a technological important biomaterial and Hoechest 33258 (H258) well-known DNA minor groove binder as fluorogenic probe for the dynamical solvation studies. The CT dynamics of CdSe/ZnS quantum dots (QDs; 5.2 nm) embedded in the as-prepared and swelled biomaterial have also been studied and correlated with that of the time scale of solvation. We have extended our studies on the temperature dependent CT dynamics QDs in a nano-environment of an anionic, sodium bis (2-ethylhexyl) sulfosuccinate reverse micelle (AOT-RMs), where number of water molecules and their dynamics can be tuned in a controlled manner. A direct correlation of the dynamics of solvation and that of the CT in the nano-environments clearly suggests that the hydration barrier within Arrhenius framework essentially dictates the charge transfer dynamics.

A model for the direct to indirect band gap transition in monolayer $MoSe_2$

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A monolayer of $MoSe_2$ is found to be a direct band gap semiconductor. We show, within ab-initioelectronic structure calculations, that a modest biaxial tensile strain of 3 % is able to drive it into an indirect band gap semiconductor with the valence band maximum (VBM) shifting from K point to Γ point. An analysis of the charge density reveals that while Mo-Mo interactions contribute to the VBM at 0 % strain, Mo-Se interactions contribute to the highest occupied band at Γ point. A scaling of the hopping interaction strengths within an appropriate tight binding model is able to capture the transition

Effect of Coulomb Interaction in Aggregation of Charged Colloids

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Accessible geometries of colloidal aggregates, formed by a few number of particles, depend on the range of the interaction within the system. It is shown by some other group that, for six-particle aggregates in the presence of short-range depletion interaction, the polytetrahedral configuration is 24 times more likely than the octahedral form. We investigated the occurrence probability of these two aggregate configurations using a Monte-Carlo technique, where the charged aggregates are kept dispersed into some monovalent ionic solution, and thus the system constituents interact mutually by long-range coulomb forces. For different values of aggregate charges and salt concentrations, though the polytetrahedral configuration is found to be more probable than the octahedral configuration at T=300K, the discrimination between these two configurations is reduced because of the presence of long-range coulomb interaction.

Synthesis of Hybrid Nanocomposites as an Adsorbent for CO_2 Capture and Catalyst for Reduction Reactions

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Inorganic-organic hybrid nanocomposites have received a special attention not only due to their outstanding properties, such as high mechanical strength, thermal stability, high refractive index and low coefficient of thermal expansion, but also their potential application as an adsorbent, catalyst, nanoreactor, and for the controlled release of drug or bio-molecules. We have developed a nanocomposite through the selective modification of the outer surface of the halloysite nanotubes (HNTs) with an organosilane which produces a novel solid adsorbent to capture CO_2 from ambient air. The synthesized adsorbent was characterized by different physical methods which ensure the grafting of aminosilane onto the outer surfaces of the halloysite nanotubes. The adsorption kinetics of the different abundant isotopes of CO_2 on functionalized halloysite nanotubes at standard ambient temperature and pressure have been studied by laser-based high-precision carbon dioxide isotope analyzer exploiting integrated cavity output spectroscopy technique. We have demonstrated the regenerability and recyclability of the adsorbent for CO_2 capture and the adsorption of CO_2 from the ambient air by HNTs follows fractional-order kinetic model. Further, HNTs/metal nanocomposites have been synthesized based on the immobilization of metal precursors followed by reduction or by direct loading of preformed metal nanoparticles over the surface of modified HNTs. The as-synthesized HNTs/metal nanocomposites have been exploited as heterogeneous catalysts for the reduction of nitro aromatics.

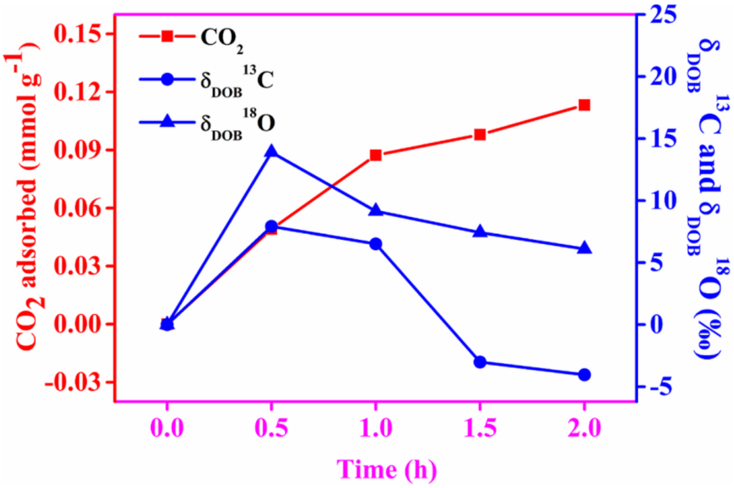

Figure. Adsorption kinetics of major abundant isotopes of CO_2 present in ambient air. The adsorption of $^{13}CO_2$ and ^{18}O of CO_2 are expressed as $\delta_{DOB}{}^{13}C$‰ and $\delta_{DOB}{}^{18}O$‰.

Synthesis and characterization of nanomaterials.

Preferential growth of Au on CdSe quantum dots using Langmuir-Blodgett technique [1]

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Oleyl amine capped CdSe quantum dots (QDs) were synthesised by hot injection technique. These QDs formed a self assembled monolayer on aqueous subphase of Langmuir-Blodgett (LB) trough as evidenced from surface pressure-area (Π-A) isotherm. When these QDs exposed to $HAuCl_4$ at reasonable good surface pressure (so that movement of the particles was restricted) the metal tip formed was exclusively at one side of the QDs. This is simple but very efficient route to form metal (Au)-QD hybrid nanostructure via LB technique. Due to the restricted movement of QD, only a small fraction of it was unveiled to $HAuCl_4$ which confirmed that the metal counterpart of hybrid nanostructure could be deposited exclusively on one side of QDs. This method also differs from other methods of metal tip formation as most of these methods are associated with the multiple island formation initially which migrates towards the end of anisotropic materials whereas this method is associated with the single tip formation at one side which grows with time to a certain extent.

Reference:

1. S. Das, B. Satpati, H. Chauhan, S. Deka, C. S. Gopinath and T. Bala, *RSC Adv.*, 2014, **4**, 64535

Synthesis and physical property study on a single nanowire based device of optimally doped Manganite

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The complex oxide systems recently have gained enormous interests from basic physics as well as from possibilities to technological applications due to the notable advancement in the fabrication of devices using single nanowire (NW). Nanowires of functional oxide materials, because of their unique one-dimensional structural characteristic and size effects, exhibit many physical properties that are different from their bulk counterpart. Our motivation in the present investigation is to what extent they retain their functionality and the modification in the physical properties on size reduction. We report here the synthesis and physical properties of functional oxide NW of optimally doped manganite $La_{0.7}Ca_{0.3}MnO_3$ (LCMO) fabricated by hydrothermal method. Spatially resolved techniques like, Transmission electron microscope (TEM) based Electron energy loss spectroscopy (EELS) was used to characterize the nanowires in a single NW level. Structural simulation was done on the diffraction pattern obtained from TEM data taken on a single NW LCMO by using JEMS software. The simulated result yield information on structural modifications due to size reduction and also the information on growth direction of the NW. A single NW with d ~ 65 nm based device was made by using Cr/Au contact pads by inter-connectors made of Pt using a dual beam system FEI-HELIOS 600. The temperature dependent electrical resistivity measurement exhibits metallic nature of the single NW of LCMO as obtained in bulk. For better understanding the transport mechanism, low frequency a.c resistance fluctuation (noise) spectroscopy study was done on the single NW based device of optimally doped Manganite system.

Reference:

1. Subarna Datta *et al*, *Journal of Nanomaterials*, **2013**, Volume 2013, 162315, 6pages.
2. Subarna Datta *et al*, *Appl. Phys. Lett.* **2014**, 105, 073117.

Optical Transition in Mn Doped Binary Semiconductors

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Mn doping in semiconductors is a scenario where transition metal is found to interact strongly with the host materials. Despite this one finds that a transition between Mn levels is invariant of the host material, suggestive of a strongly atomic character of the transition. Considering the case of Mn doping in binary semiconductors CdS, CdSe, ZnS and ZnSe we have been able to capture this effect theoretically. This is shown to result from a re-normalization of the hopping interaction strength and the crystal field splitting inspite of the host semiconductor being changed which leads to very similar transition energies.

Electronic Structure, Phase Stability and Resistivity of Hybrid Hexagonal $C_x(BN)_{1-x}$ Two-dimensional Nanomaterial: A First-principles Study

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We use density functional theory based first-principles method to investigate the bandstructure and phase stability in the laterally grown hexagonal $C_x(BN)_{1-x}$, two-dimensional Graphene and h-BN hybrid nanomaterials, which were synthesized by experimental groups recently (Liu et al, Nature Nanotech, 8, 119 (2013)). Our detail electronic structure calculations on such materials, with both armchair and zigzag interfaces between the Graphene and h-BN domains, indicate that the band-gap decreases non-monotonically with the concentration of Carbon. The calculated bandstructure shows the onset of Dirac cone like features near the band-gap at high Carbon concentration (x ~ 0:8). From the calculated energy of formation, the phase stability of $C_x(BN)_{1-x}$ was studied using a regular solution model and the system was found to be in the ordered phase below a few thousand Kelvin. Furthermore, using the Boltzmann transport theory we calculate the electrical resistivity from the bandstructure of $C_x(BN)_{1-x}$ at different temperature (T), which shows a linear behavior when plotted in the logarithmic scale against T^{-1}, as observed experimentally.

Enchanced structural and optical properties of Li doped $Zn_{0.98-x}Mn_{0.02}Li_xO$

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In present work, nanocrystalline $Zn_{0.98-x}Mn_{0.02}Li_xO$ powders were successfully prepared from the citrate modified $Zn(NO_3)_2.6H_2O$ solution. Structural characterization of samples was performed by an X-ray diffractometer which shows all the samples are single phase with hexagonal wurtzite structure (JCPDS file no.:36-1451). Variation in lattice parameters a and c shows that c/a ratio and u parameter (which is a measure of the amount by which each atom is displaced with respect to the next along the c-axis). changes due which The bond length along the c-axis is longer than the other three bonds because the ZnO_4 tetrahedra are distorted along the c-axis, which results in a dipole moment.[1] The absorption peak shows all sample show blue shift as compared to pure ZnO and then shows red shift with higher Li-concentration as compared to 1% Li doping. The room temperature PL measurements shows an emission peak at around 376 nm viz. near band edge emission (NBE) as it corresponds to the energy of the band gap of the samples, violet emission related to oxygen vacancies, the violet-blue and blue emissions may be attributed to the defect related positively charged Zn vacancies, The blue-green band emission is possibly due to surface defects.

REFERENCE

1. S. S. Gaikwad, *J. Mater. Chem. C, 2, 7264 (2014)*

Photoluminescence and photocatalytic activity of monodispersed colloidal "ligand free Ln^{3+}-doped $PbMoO_4$ nanocrystals"

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Recently, there has been an increasing interest towards developing water dispersible[1] Ln^{3+}-doped nanocrystals (NCs) due to their interesting scope for application in bioimaging, sensor, catalysis, etc. Different organic capping ligands are generally used to disperse NCs in various solvents. While the property of an individual nanocrystal is mainly governed by the core, its interaction with the surrounding environment depends on the capping ligand.[2] In photocatalytic applications, the capping ligands sometimes act as an inhibitor by reducing the chances of electron and hole transfers from the catalyst to oxygen or substrate. In this work, we have synthesized ligand-free colloidal Eu^{3+}-doped $PbMoO_4$ NCs that form a stable dispersion in polar solvents. The surface of the NCs is designed to have excess residual ions (Pb^{2+} or MoO_4^{2-}) compared to the counter-ionic species, thereby providing a partially charged nanocrystal surface.[2] These charged nanocrystal surfaces cause electrostatic repulsion, providing a colloidal stability in polar solvents.[2] Microscopic measurements suggest the formation of spherical shaped nanoparticles with an average size of 10 nm. Upon UV excitation, the Eu^{3+}-doped $PbMoO_4$ NCs display intense red emission characteristic of Eu^{3+} ions. These NCs exhibit strong photocatalytic activity in the UV region, which is verified from the degradation of Rhodamine B dye by ~70% within 3h at pH 5.5. The strong luminescence efficiency and photocatalytic activity make the water dispersible Ln^{3+}-doped $PbMoO_4$ NCs a potential material for dual applications like luminescent and photocatalyst.

References:

1. A. Dash, S. Sarkar, V. N. K. B. Adusumalli and V. Mahalingam, *Langmuir* 2014, **30**, 1401-1409.
2. K. P. Kadlag, M. J. Rao and A. Nag, *J. Phys. Chem. Lett.* 2013, **4**, 1676-1681.

Flexible Thin Film Transistor (TFT) made on Kapton® with ON/OFF ratio $\geq 10^7$ with nanostructured ZnO film channel and Electric Double Layer Gate

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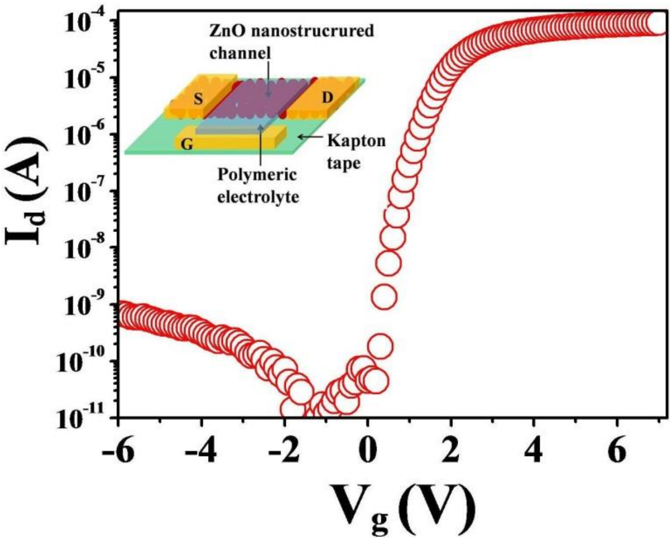
Flexible electronics which are stretchable, light weight and cost effective have attracted increasing attention. We report here fabrication of a Thin film Transistor (TFT) on flexible Kapton® substrate by using polymeric electrolyte (PEO/$LiClO_4$) as a gate dielectric. The TFT uses a strongly textured nanostructured ZnO film grown on a Kapton® tape by pulse laser deposition. The TFT shows a high current ON/OFF ratio $\geq 10^7$ at a very low threshold voltage in the range $\approx$ 1V to 2V. The enabling physics that allows such a high switching ratio is the high mobility oriented nanostructured film that can achieve a field effect mobility in excess of $20 cm^2/Vsec$, that are generally obtained in epitaxial films of ZnO. The other two important effects that give rise to a large ON/OFF ratio are (a) the all-around-gate structure that forms during the solidification process of the polymeric gate and (b) the electric double layer (EDL) that forms due to the electrolyte gate dielectric. The observed gate capacitance $C_{int} \approx 2 \mu F/cm^2$. The field effect, due to large C_{int}, induces a surface charge of $(\Delta Q) \approx 10^{13} /cm^2$ by 1V gate bias. Accumulation of such a large induced surface charge brings down the threshold voltage of the TFT to a range that it can be operated even by a single Li ion battery.



Transfer characteristic of ZnO- TFT. Inset shows the schematic diagram of the TFT.

Atomically Thin Semiconductor Nanosheets for Optoelectronic Applications

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The challenging properties of II-VI semiconductor nanostructure materials, originating from size and shape dependent carrier confinement, are for new generation of modern sensors and devices. The lateral confinement of carriers in two dimensional (2D) nanostructures leading to the observation of massless electrons, high mobility, low electron-phonon scattering, giant oscillator strength and high proclaiming capability etc. are emerging research interests for designing of advance nano-optoelectronic devices. To understand the behaviour of the 2D nanomaterials, atomically-thin cadmium selenide (CdSe) nanosheets (NS) of nearly 3 nm thickness have been synthesized using lamellar soft template mediated growth technique. Small angle x-ray scattering and transmission electron microscopic studies affirm the presence of hexagonal CdSe layer NS. The strong and well determined optical absorption peaks revealed the uniformity in the NS within the strong quantum confinement regime. As observed from photoluminescence (PL) and its decay analysis, the CdSe NS exhibit strong band edge blue PL, with a recombination rate, 3.9 ns.

K**eywords:** semiconductor; nanosheet; SAXS; photoluminescence

Site Selective Adsorption of Atomic Hydrogen on Hexagonal Boron Nitride Monolayer: Effect of Hydrogen Coverage and Substrate

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Using plane-wave based density functional theory we have studied the adsorption of atomic H on a hexagonal boron nitride (h-BN) sheet supported on Ni(111) surface as a function of H coverage, namely, the clean sheet (0 ML), 0.125 ML, 0.25 ML and 0.5 ML of H atoms. From our calculations we show that the otherwise insulating and non-magnetic h-BN becomes conducting and ferromagnetic (with small net moment of -0.01 μB) when deposited on Ni(111) . For 0.125 ML coverage the B site is favorable, while for 0.25 ML coverage H prefers to adsorb on adjacent B and N sites. These observations agree well with an earlier experimental report [2], where they find that the B site is the most favorable one for adsorption of H atoms at very low H coverages on h-BN supported on Ni(111) surface, and a theoretical study by Weck et al.[3] on BN(0001) surface. However for 0.5 ML H coverage we find the N site is more favorable for the supported h-BN sheet, while for the freestanding one, the B site is the more preferred one.

Ligand-Free Metal Sulfide Nanocrystals for Luminescence and Solar Cells

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Colloidal inorganic nanocrystals (NCs) are generally capped with organic ligands. While the property of the individual NC is determined by the inorganic core, its interaction with surroundings is governed by the capping ligands. These organic capping ligands are typically insulating in nature, and thus, organic capped inorganic NCs are not suitable for integration in electronic and optoelectronic devices. We prepared ligand-free colloidal semiconductor NCs of undoped and Mn-doped $Zn_xCd_{1-x}S$, and $AgInS_2$.[2,3] These Ligand-free NCs have excess sulfide ions on the surface, resulting in a negatively charged NC surface. Negatively charged NCs repel each other providing colloidal stability in a polar solvent. Mn-doped samples exhibit strong Mn related luminescence. Unlike organic capped NCs, preliminary results suggest that the ligand-free NCs are electronically coupled to each other in their close packed film. Steady-state and excited state photophysical properties of $AgInS_2$ NCs suggest defect-induced light absorption and emission. $AgInS_2$ NC sensitized solar cell shows power conversion efficiency close to 1%, with open circuit voltage of ~0.45 V.

References:

1. Kadlag, K. P.; Rao, M. J.; Nag**, A.** *J. Phys. Chem. Lett.* **2013**, *4*, 1676.
2. Kadlag, K. P.; Patil, P.; M. Rao, M. J.; Datta, S.; Nag**, A.** *CrystEnggComm*, 2014, **16**, 3605.

Impact of Metal Ions in Porphyrin-Based Applied Materials for Visible-Light Photocatalysis: Key Information from Ultrafast Electronic Spectroscopy

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Protoporphyrin IX-zinc oxide (PP-ZnO) nanohybrid have been synthesized for applications in photocatalytic devices. High-resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD), and steady-state infrared, absorption, and emission spectroscopies have been used to analyze the structural details and optical properties of these nanohybrids. Time-resolved fluorescence and transient absorption techniques have been applied to study the ultrafast dynamic events that are key to photocatalytic activities. The photocatalytic efficiency under visible-light irradiation in the presence of naturally abundant iron(III) and copper(II) ions has been found to be significantly retarded in the former case, but enhanced in the latter case. More importantly, Femtosecond (fs) transient absorption data have clearly demonstrated that the residence of photo excited electrons from the sensitizer PP in the centrally located iron moiety hinders ground-state bleach recovery of the sensitizer, affecting the overall photocatalytic rate of the nanohybrid. The presence of copper(II) ions, on the other hand, offers additional stability against photobleaching and eventually enhances the efficiency of photocatalysis. In addition, we have also explored the role of UV light in the efficiency of photocatalysis and have rationalized our observations from femtosecond- to picosecond- resolved studies.

Bilirubin Stabilised Gold Nanoparticle: a Bio-conjugated Material with Catalytic Activity

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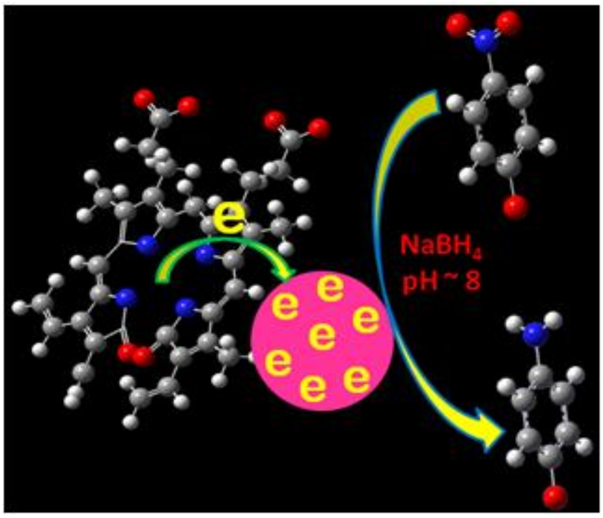
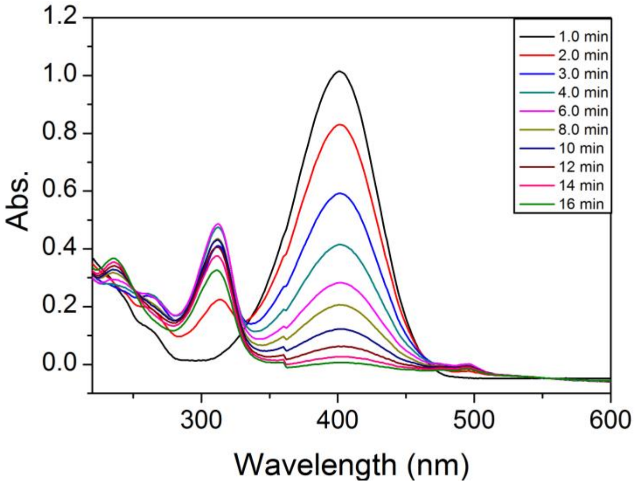
Nanoscale gold particles have been extensively modified with polymers, dendrimers, short-chain organic molecules, and inorganic materials to enhance stability and other properties (e.g., catalytic, photonic, and optical) for various applications including delivery vehicles, catalytic systems, optical devices, and biomedical materials. Currently we have demonstrated the production of mono-dispersed and spherical gold nanoparticles in a ‘green’ process using bilirubin (BR) which acts as reducing agent as well as capping agent to provide it unique stability. Optical behaviour and stability of bilirubin coated gold nanoparticles (AuBR) was illustrated. FT-IR and steady state fluorescence measurements were performed to illustrate the binding interaction of BR with Au (III) ion and the nanoparticles. BR showed a strong affinity towards Au (III) and the measured binding constant was ~4.3×10^5 M^{-1}. It caused reduction of Au (III) ion and rendered the formation of cubic face centered AuBR nanoparticles which was ~20 nm in diameter as confirmed by transmission electron microscopy imaging. The existence of bilirubin moiety on the gold surface was confirmed by FT-IR measurement.[1] Further we have focused on its catalytic activity of p-nitro phenol (PNP) reduction. It shows excellent catalytic activity on PNP reduction.





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[1] Maity, M. Das, S. Maiti, N.C. Stability and binding interaction of bilirubin on a gold nano-surface: steady state fluorescence and FT-IR investigation, ***Phys. Chem. Chem. Phys.***, 2014, DOI: 10.1039/C4CP02649G

Magnetite (Fe_3O_4) Hollow Spheres synthesis and a Study on Magnetic Properties for Hyperthermia Application

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Here we have proposed how micelles act as template to evolve hollow–nanospheres of magnetite by solvo-thermal technique. We have seen that oleylamine plays an important role to generate hollow-sphere like particles and magnetic properties of these particles will be suitable for hyperthermic application of these kinds of particles. Structural analysis was done by XRD measurement and morphological measurements like SEM and TEM was performed to confirm the shape and size of hollow sphere particles. Being hollow in structure and magnetic in nature such materials will also be useful in other application fields like in drug delivery, arsenic and heavy metal removal by adsorption technique, magnetic separation etc.

Methyl oleate-capped upconverting nanocrystals: A simple and general ligand exchange strategy to render nanocrystals dispersible in aqueous and organic medium

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Lanthanide (Ln^{3+})-doped nanomaterials receive huge research interest due to their unique characteristics such as long luminescence lifetime, wide spectral tunability and narrow band width etc. In addition, interest in these materials is further enhanced due to their ability to convert low energy photons into high energy photons via non linear multipoton process known as upconversion. In this article we report a simple and general ligand exchange strategy to functionalize the nanocrystals both with hydrophobic and hydrophilic ligands. This is achieved by first capping the Er/Yb-doped $NaYF_4$ nanocrystals with a weak binding ligand such as methyl oleate and subsequently ligand exchanged with various organic ligands. The method involves only a simple stirring or sonication of the nanocrystals dispersion with the ligands of interest. Dicarboxylic acids such as adipic acid, succinic acid and malonic acid functionalized nanocrystals which are difficult to achieve via thermal decomposition method were easily prepared by this method. In addition, low boiling point ligands like hexanoic acid is easily coated over the surface of the Er/Yb-doped $NaYF_4$ nanocrystals. Both size and shape of the nanocrystals are preserved after ligand exchange process. The methyl oleate capped Er/Yb-doped $NaYF_4$ nanocrystals display strong upconversion emission after ligand exchanged with hydrophobic and hydrophilic ligands.

References:

1) Auzel, F. *Chem. Rev*. **2004**, *104*, 139.

2) Sarkar, S.; Meesaragandla, B.; Hazra, C.; Mahalingam, V. *Adv. Mater*. **2013**, *25*, 856.

3. Meesaragandla, B.; Sarkar, S.; Hazra, C.; Mahalingam, V. *Chempluschem.* **2013**, *78*, 1338.

Synthesis and Optoelectronic/thermoelectric Applications of Branched Semiconductor Nanocrystals and 1-D nanowires

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While conventional spherical colloidal nanocrystals have shown promise in these fields due to their ease of fabrication, processibility and salient optical properties, it may be envisaged that more applications may emerge if nanocrystals can be synthesized in shapes of higher complexity and therefore increased functionality. Here we will presents a systematic, surfactant-driven hot injection method to synthesize CdSe seeded CdS nanoheterostructures with very high yield. This was extended to other systems such as CdSe/CdTe and CdTe/CdS or PbSe/PbS and Ag_2Se/Ag_2S via cation exchange techniques. In order to elucidate the reactivity of the facets at the tips of such branched structures as a function of the shape of the arms, we exposed the structures of various arm dimensions to controlled amounts of metal precursors and discovered conditions in which the metal nanoparticle can be deposited precisely at the tip of one of four arms with symmetric reactivity. In next, we will showcase the utility of such branched heterostructures in applications such as light emitting diodes, photodetectors and solar cells. At the end we will display thermoelectric power conversion based on semiconductor nanowires.

Ag_2S Magic-Sized Nanocrystals Exhibiting Sharp NIR Excitonic Absorption and Luminescence

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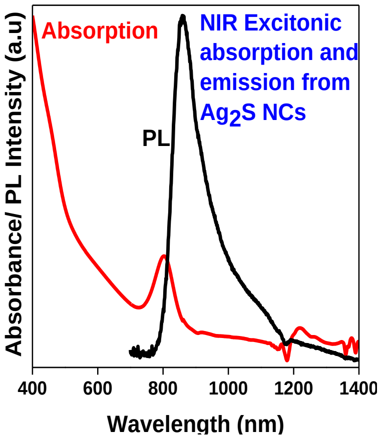

Colloidal Ag_2S nanocrystals typically exhibit broad absorption spectrum without showing excitonic peaks. In order to rule out the possibility of wide size distribution of synthesized nanocrystals that might broaden the absorption spectra, we employed a reversible cation exchange strategy, CdS ↔ Ag_2S, where CdS nanocrystals exhibit sharp excitonic peaks whereas, Ag_2S nanocrystals with same size-distribution exhibit broad absorption spectrum. So the size dispersity is not the cause of broad absorption spectrum of Ag_2S nanocrystals, instead, the small Bohr excitonic radius of Ag_2S might be the probable cause. Therefore, we prepared ~2 nm magic-sized Ag_2S nanocrystals with narrow size-distribution. The small size ensures quantum confinement of charge carriers in our nanocrystals, therefore the nanocrystals exhibit sharp excitonic absorption and emission in the near-infrared (NIR) 802 nm and 860 nm respectively, which are significantly blue-sifted compared with bulk band gap of 1130 nm. The observed radiative photoluminescence (PL) lifetime is 8 ns, which is the fastest lifetime reported so far for Ag_2S nanocrystals. The fast PL decay can be attributed to enhanced overlap of electron and hole wavefunctions in the small magic-sized nanocrystals. While the NIR PL is useful for biological labelling, the band gap is also suitable for photovoltaic applications. We are exploring the possibility of quantum dot sensitized solar cells using the non-toxic Ag_2S nanocrystals.

Synthesis of $Ag_{1.92}Mo_3O_{10}.H_2O$ Nanowire from $AgNO_3$ Assisted Etching of Ammonium Phosphomolybdate: A Material with High Adsorption Capacity

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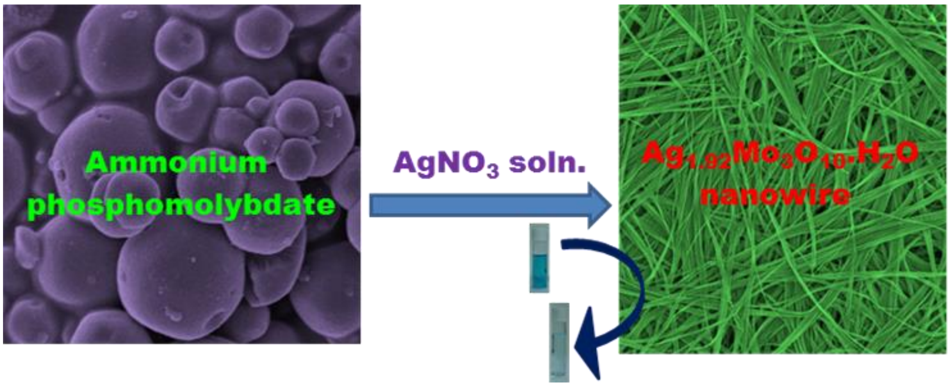
Ultralong $Ag_{1.92}Mo_3O_{10}.H_2O$ nanowires have been obtained due to selective etching of ammonium phosphomolybdate (APM) only by Ag^+ ion in water under stirring condition. The spherical yellow APM particle upon etching by Ag^+ ion expels PO_4^{3-} and generates hollow sphere. These etching and hollowing disrupt robust APM structure. Concentration of etching agent and reaction time are crucial for the formation of $Ag_{1.92}Mo_3O_{10}.H_2O$ nanowire. The growth of nanowires occurs probably due to etching followed by Ostwald ripening, oriented attachment and splitting process. Finally, the as-synthesized nanowire exhibits high capacity to adsorb cationic dyes on its surface. It shows superb adsorption properties, with maximum adsorption capacity of 110 mg g^{-1}, 175 mg g^{-1}, 160 mg g^{-1} for methylene blue, methyl green, crystal violet, respectively. This would find immense importance in the industries.



Growth And Structural Study Of TiO_2 Nanorods Grown By Hydrothermal Method

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Titania (TiO_2) nanorods have shown promise for applicability in dye sensitized solar cells (DSSC) and may present a cost effective solution for the fabrication of efficient and affordable solar power generation. In contrast to traditional silicon solar cell fabrication, the fabrication of DSSCs does not require expensive high energy, vacuum, and temperature processes. Titania nanorods have the potential to increase the electron transport rate in DSSCs by forming a direct electrical pathway, thus improving the performance. We report here the growth array of aligned TiO_2 nanorod by hydrothermal method on a FTO coated glass substrate at 150^oC in an autoclave. The nanorods were characterized using XRD, FESEM and HRTEM. X- Ray result confirms the phase purity and rutile structure of ensemble of nanorods with preferred orientation along (002). FESEM microstructure shows that the ensemble of nanorods were grown with an average length of 8-10µm and diameter ranging between 100-400nm. Lattice spacing of a single nanorod (~0.34 nm) from SAD pattern as well as HRTEM image confirms that the single nanorod is (001) oriented. Energy Filtered Mapping of a single nanorod confirms the homogeneous distribution of Ti and O. EELS spectrum shows the presence of single valence state of Ti and O. Structural simulation was done on TiO_2 ensemble as well as single nanorod using JEMS software. From simulation the growth direction of a single nanorod was found to be along (001) and the mean bond length was ~1.9 Å. Correlation of the simulated data with the obtained experimental data has been done on a single nanorod level.

References:

[1] B. Liu, and S. Aydil J. AM. CHEM. SOC. 2009, *131*, 3985–3990

[2] Xinjian Feng et. al *Nano Lett.,* Vol. 8, No. 11, 2008

Cu Doping in Ligand Free CdS Nanocrystals: Conductivity and Electronic Structure Study

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Ligand free Cu doped CdS nanocrystals (NCs) have been synthesized to elucidate their surface electronic structure. The Cu doped ligand free NCs unlike their undoped counterparts are shown to be luminescent. We used this Cu related emission as a probe to study the nature of the surface trap states that results in negligible luminescence in the undoped NCs. The concentration of the sulfide ligands is shown to play a crucial role in the surface passivation of the NCs. Electrical conductivity of these NCs was also studied and they were shown to exhibit significant conductivity of $\sim 10^{-4}$ S cm^{-1}. Further we have shown that the electrical conductivity is closely correlated to the surface charge and hence the trap states of the individual NCs that has far-reaching consequences in the device optimization.

Surface Modification of Co-Based Nanostructures to Develop Intrinsic Fluorescence and Catalytic Activity

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Herein we report the molecular functionalization of promising transition metal oxide nanostructures, like Co_3O_4 nanocubes, using nontoxic and biocompatible organic ligand sodium tartrate. The electronic structural modification of the nanocubes imparted through functionalization and subsequent water solubilization reveals multiple absorption bands in the UV-vis region. Further surface modification of the solubilized nanocubes, leads to the emergence of intrinsic multi-color fluorescence (from blue, cyan, green to red region of the spectrum), upon excitation at proper wavelengths, where the respective excitation wavelengths have a direct correlation with the observed UV-vis absorption bands. Using a multitude of spectroscopic tools we have investigated the mechanistic insight behind the origin of different UV-vis absorption bands and emergence of multicolor photoluminescence from the functionalized nanocubes. Magnetic study reveals that, antiferromagnetic nature of Co_3O_4 nanocubes changes to ferromagnetic behavior upon functionalization, however, the overall magnetic response was very weak. To combine strong magnetism with this novel optical property, we followed the same surface modification strategy in case of $CoFe_2O_4$ nanoparticles, which reveals that irrespective of size and shape, all Co-based oxides can develop intrinsic multicolor fluorescence upon facile functionalization with sodium tartrate ligands. Surface modified Co-based oxide nanostructures also show excellent catalytic activity in degradation of biologically and environmentally harmful dyes. We hope that, our developed facile functionalization strategy of Co-based oxides will open up new opportunities in the field of biomedical applications such as bio-imaging and targeted drug delivery.

References:

1. Pal, M., Kumar Singh, A., Rakshit, R., Mandal, K. Surface Chemistry Modulated Introduction of Multifunctionality within Co_3O_4 Nanocubes , *communicated..*
2. Pal, M., Kundu, A., Rakshit, R., Mandal, K. Development of Intrinsic Magneto-Fluorescent $CoFe_2O_4$ Nanoparticles and their Application in Catalysis, *communicated..*

Gold over layer assisted oxidation control of zinc foil in open air to generate ZnO tetrapod: Excellent photocatalyst and ethanol sensor

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Stimulated by profound morphological dependence of nanomaterials features and applications recent era witnesses exuberance in designing of shape and dimension tailored material at nanoscale. Amongst them, ZnO with diverse nanoforms possessing unique features, recognize as the ideal candidate for foreseeable electronic and optoelectronic devices. From the broad range of ZnO nanoforms, tetrapods are of special significance as they possess distinct 3D tetrahedral geometry and have unique propitious as building blocks for novel material via growth of branch points on top of their existing geometry. Additionally they show credential in diverse fields like electron emission, gas sensing, photocatalyst etc. Realizing its potential, novel tetrapod synthesis protocol is highly desirable as previous reports require stringent experimental criteria and complex process control. Here we present a facile and economical synthesis approach for ZnO tetrapods via gold over layer aided controlled oxidation of zinc foil in open air which is free from the bottlenecks related to other protocols. Simplicity and high scalability is hall mark of this protocol. Not restricted to structural realization only, environmental remediation ability of these tetrapod was inspected through the photocatalytic degradation study of hazardous Rhodamine B dye. Further these tetrapods are also employed to design ethanol sensor.

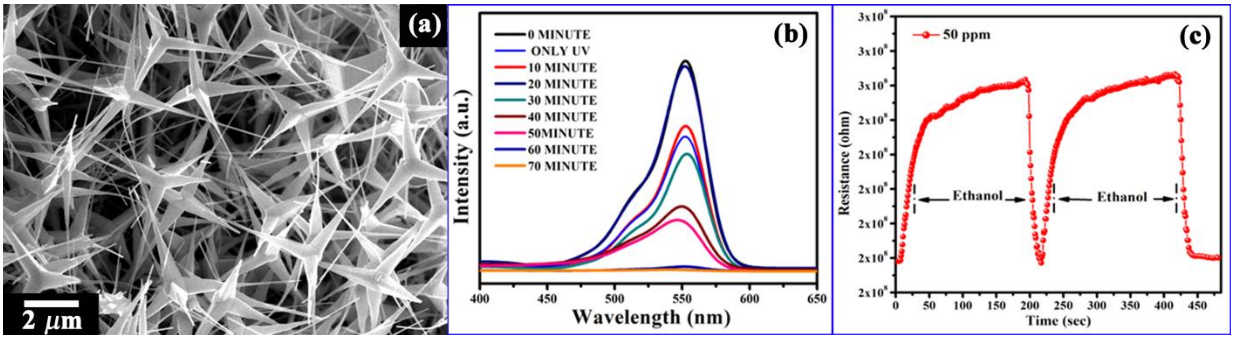

Figure: (a) FESEM image of synthesized ZnO tetrapods, (b) Temporal evolution of UV-vis absorption spectra corresponding to Rhodamine B, (c) two cycles response–recovery characteristics of ethanol sensing.

New Emergence of Interfacial properties of different 2-D materials

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Affiliation: TIFR Centre for Interdiciplinary Research

Graphene as 2-D materials rise an huge interest in materials science as well as fundamental science. This atomically thin layer gives huge conductance, mechanical strengths etc. People tried to mimic 2-D materials as well through synthesizing Transition Metal Dichalcogenides, h-BN etc. These materials have own characteristic features unlike graphene. But in solution of two different 2- D materials produces new aggregrated materials with finite band-gap which can be controlled with concentration ratio of these individuals materilas. This points that the aggregated structure is not random due to paricular band-gap and absorption peak. We are in search of fundamental parameter which controls these self-assembly of definite structure. Later the question comes as can we control the parameter or probe the interaction at the interface and make new functional materilas or devices ? Our approach is based on electrochemistry, mechanical analysis, spectrocopy etc.

Ultrafast FRET at Fiber Tips: Potential Applications in Sensitive Remote Sensing of Molecular Interaction

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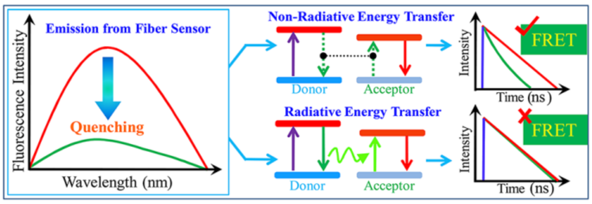
Förster resonance energy transfer (FRET) strategy is well adopted in fiber-optics for efficient sensor design. However, resonance type energy transfer from one molecule (donor) to other (acceptor) should meet few key properties including donor to acceptor energy migration in non-radiative way, which is hard to conclude from simply emission quenching of the donor, rather needs careful investigation of excited state lifetime of the donor molecule. In the present study, we have shown that the evanescent field of an optical fiber can be coupled to covalently attached donor (dansyl) molecules at the fiber tip. By using picosecond resolved time correlated single photon counting (TCSPC) we have demonstrated that dansyl at the fiber tip transfers energy to a DNA-intercalating dye ethidium upon surface adsorption of DNA at the fiber tip. Our ultrafast detection scheme selectively distinguishes the probe (dansyl) emission from the intrinsic emission of the fiber. It allows us to estimate the distance between the probe and the surface adsorbed DNA. We have remotely sensed the dielectric constant (polarity) of an environment as the excited state lifetime of the probe dansyl heavily depends on the polarity of the immediate host environment. The reusability of the fiber tip has also been demonstrated.



Evaluation of Semi-metallic Fe_3O_4 Nanocavities using Terahertz Waves

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Variable sized magnetite (Fe_3O_4) nanoparticles (NPs) and nano hollow spheres (NHSs) were prepared by template free solvothermal process. The terahertz (THz) absorption spectra of these nanostructures suggest that the NPs are optically transparent to THz electromagnetic radiation whereas its hollow configuration (NHS) performs as an excellent opaque object in the frequency of 0.4 - 2.0 THz. Detailed study indicates that the multiple resonance peaks in the absorption spectra are due to low frequency acoustic vibrational phonon modes of Fe_3O_4 nanostructures. Moreover, the THz absorption is found to increase with increasing shell thickness of the NHS. The invariance of frequency dependent magnetic permeability points out that the absorption is basically due to dielectric loss instead of magnetic loss. The THz conductivity study reveals that Fe_3O_4 NHSs exhibit enhanced THz conductivity in comparison to the NPs due to thermally activated polaronic hopping which is found to increase with increasing THz absorption. Finally, the size dependent THz conductivity of NHSs suggests that the magnitude of conductivity increases with increasing average crystallite size of the nanostructure.

Synthesis of Mesoporous Co_3O_4 Nanostructures via Soft templating route: An Excellent Visible light Photocatalyst

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Transition metal oxides are less-costly alternatives to gold based catalyst. Specially mesoporous Co_3O_4 with varied morphologies is important because of its appropriate pore size that can be utilised as heterogeneous catalyst, sensors etc. In the present work, we have synthesised Co_3O_4 via soft templating route using different cationic templates at 75°C, followed by calcination of the metal oxalates at 300°C. All the precursors used are aqueous based like cobalt nitrate, oxalic acid, phosphoric acid, cetyltrimethylammonium bromide (CTAB), 1-butyl-3-methylimidazolium bromide (IMB) and pyridinium bromide (PYB). The amount of these cationic templates are varied comprising $Co(NO_3)_2.6H_2O$: oxalic acid: cationic templates ratio of 1:0.6:x, where x=0.2, 0.3, 0.4. The synthesized powders are characterized by DTA/TG, XRD, FTIR, Raman, FESEM, TEM and N_2 adsorption-desorption studies. The prepared Co_3O_4 are utilised as visible light photocatalyst to degrade carcinogenic azo group containing dye, Chicago sky blue 6B (CSB). In this study we found Co_3O_4 catalyst synthesised using pyridinium bromide of 0.3 millimolar ratio as template is catalytically most active among the other Co_3O_4 catalyst, showing rate constant of 0.1431 min^{-1}. The microstructure of the particles obtained using (a) CTAB (b) IMB (c) PYB templates (0.2, 0.3, 0.4 millimolar ratio, used) are shown in Fig. 1A, and Fig 1B depicts the catalytic efficiency (Rate constant) of the corresponding samples

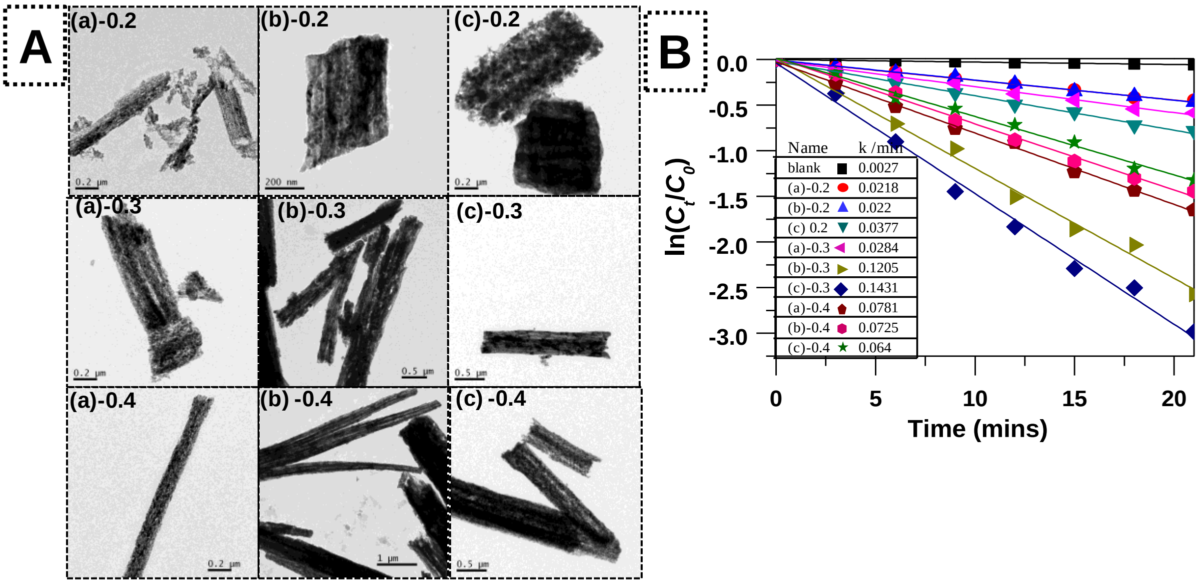

Fig. 1: (A) Microstructure from TEM (B) Plot for determination of rate constant regarding photodegradation of Chicago sky blue 6B (CSB) dye without any catalyst (blank) and in presence of Co_3O_4 catalyst prepared using cationic templates (a) CTAB (b) IMB (c) PYB of 0.2, 0.3, 0.4 millimolar ratio.

Acknowledgement: The authors like to thank Director of CSIR-CGCRI, DST-SERB Project, Government of India (no. GAP 0616) for funding. M.Roy and S. Ghosh thank CSIR for their fellowships.

Uniform Doping of Magnetic Ions in Semiconductor Quantum Dots from Inside Out

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Over the last few decades, there have been a lot of research devoted towards the exploration of materials which combine properties of ferromagnets and semiconductors. Transition metal doped semiconductors or diluted magnetic semiconductors[1,2] (DMS) have come out as an emerging class of materials which shows room temperature ferromagnetism. These DMS materials can have potential use in spintronics, magnetic memory devices and other spin based information technologies.

It was predicted that semiconducting system having magnetic impurity, uniformly doped inside, shows room temperature ferromagnetism. But during synthesis, clustering or phase separation has made this job challenging. We have developed a novel strategy to synthesize highly crystalline, single domain diluted magnetic semiconductor[2] (DMS) system starting from a small magnetic core and allowing it to diffuse uniformly inside a thick CdS semiconductor shell and achieve DMS quantum dots (QDs). We have chosen magnetic Fe_3O_4 core as a model system for our study. X-ray absorption spectroscopy (XAS) was used to probe the local environment and the analysis shows a clear evolution form core shell structure to a homogeneous distribution of magnetic impurities inside the semiconductor QDs. This uniformity in dopant distribution allows this material to show room temperature ferromagnetism and higher saturation magnetization when compared to earlier studies.

(1) Dietl, T.; Ohno, H.; Matsukura, F.; Cibert, J.; Ferrand, D. *Science* **2000**, *287*, 1019.

(2) Dietl, T. *Nature Mater.* **2010**, *9*, 965.

MSubmerged Iron Nanoparticle for Evolution of Fe_3O_4 Based Photoactive and Adsorbent Materials

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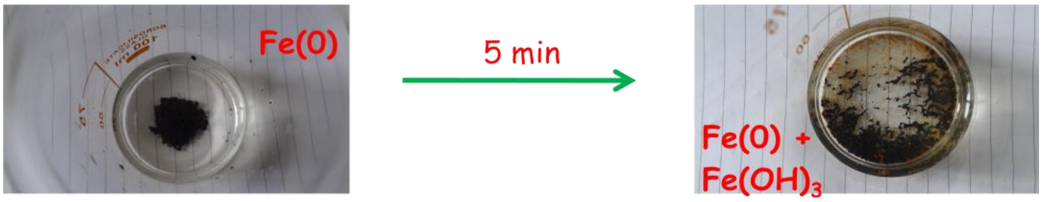
A ternary Pd@CdS@Fe_3O_4 hybrid material and a binary hierarchical Fe_3O_4-MnO_2 composite have been synthesized from Fe(0) as the precursor material. Fresh Fe(0) nanoparticles were prepared from air free hot water without any surface oxidation and reserved under submerged condition in water using a door magnet. For the ternary hybrid material first Fe_3O_4 has been prepared from Fe(0) at 180˚C using our laboratory developed modified hydrothermal (MHT) technique. Then CdS was decorated over cubic Fe_3O_4 and finally Pd(0) was loaded over CdS. Decoration of this ternary composite was carried out without functionalizing the surface. Pd(0) loading has been done out of in situ reduction of Pd^{2+} and interestingly the excess S^{2-} ion from CdS caused Pd^{2+} reduction i.e. no external reducing agent was used. On the other hand for the preparation of binary composite, Fe_3O_4-MnO_2 was done as a result of oxidation of submerged Fe(0) by $KMnO_4$ solution at MHT under 180˚C temperature. Both the as-synthesized materials were used for the water purification purpose, where the ternary Pd@CdS@Fe_3O_4 hybrid behaved as the photocatalyst and the flower like Fe_3O_4-MnO_2 was used as the adsorbent. Due to the presence of Fe_3O_4, both materials were ferromagnetic in nature. Thus both the materials are recyclable which is very important for the industrial application.



With magnet

Without magnet

One pot synthesis of tin oxide decorated boron doped graphene material

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Alternative Energy and Nanotechnology Laboratory (AENL),
Indian Institute of Technology Madras, Department of Physics, Chennai, Tamil Nadu, India

We report a simple, cost effective, one pot synthesis of SnO_x decorated boron doped graphene (*B*-G) using non- hazardous boric acid as the boron precursor via hydrogen induced reduction technique. The synthesized material, SnO_x/B-G, was characterized by X ray diffraction (XRD), X-ray photoelectron and Raman spectroscopy. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images show a uniform decoration of SnO_x nanoparticles over layered *B*-G support. SnO_x/B-G shows potential function as anode material for Li ion battery application.

A facile method for synthesis of Co-core Au-shell nanohybrid

Debasmita Sardar and **Tanushree Bala ***

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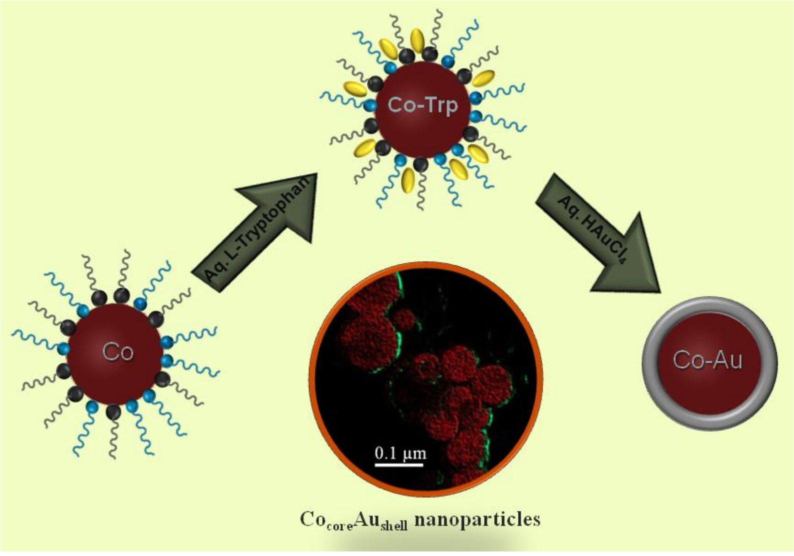
& CRNN, University of Calcutta, JD 2, Sector III, Salt Lake, Kolkata: 700098, India.

The synthesis of nanomaterials is of prime importance in the field of nanoscience and nanotechnology. Unification of multiple properties of different materials into a single stuff to form hybrid nanostructure is a significant progress in this field. Encapsulating magnetic nanoparticle in a well defined envelop of noble metal to form a core-shell hybrid nanostructure can enhance both the biocompatibility and stability of the material.

Here we have demonstrated simple water based method where heterostructured Co-Au core-shell nanoparticles have been synthesized by reducing $AuCl_4^-$ ion on Cobalt nanoparticles after a minor but effective modification on cobalt-surface by an amino acid. The core shell morphology is emphatically confirmed by the thorough investigation using UV-Vis spectroscopy, X-ray Photoelectron Spectroscopy (XPS), Transmission Electron Microscopic Analysis (TEM). Detailed Fourier Transform Infrared Spectroscopy (FTIR) proves the surface modification of Co nanoparticle. The magnetic characteristics of the hybrid nanoparticle have been studied thoroughly using Vibrating Sample Magnetometer (VSM) which confirms the material to be superparamagnetic in nature. The above mentioned characterizations will be discussed during presentation. The synthetic strategy mentioned here, is purely water based and does not involve costly and/or toxic chemicals at any stage of the process and thus can evoke potential applications including biological systems.



Reference:

A facile method for synthesis of Co-core Au-shell nanohybrid,

Debasmita Sardar,[a] S. K. Neogi, S. Bandyopadhyay, B. Satpati, R. Jain, C. S. Gopinath and T. Bala[a*] (*New J. Chem.*, 2014, **38**, 4107.)

Topic: Synthesis and characterization of nanomaterials Ultrafast Photoinduced Dynamics in Biologically Important Porphyrin Sensitized Semiconductor Nanostructures

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In recent times, significant achievements in the use of zinc oxide (ZnO) nanoparticles (NPs) as delivery vehicles of cancer drugs have been made. The present study is an attempt to explore the key photoinduced dynamics in ZnO NPs upon complexation with a model cancer drug protoporphyrin IX (PP). The nanohybrid has been characterized by FTIR, Raman scattering and UV-Vis absorption spectroscopy. Picosecond-resolved Förster resonance energy transfer (FRET) from the defect mediated emission of ZnO NPs to PP has been used to study the formation of the nanohybrid at the molecular level. Picosecond-resolved fluorescence studies of PP−ZnO nanohybrids reveal efficient electron migration from photoexcited PP to ZnO, eventually enhancing the ROS activity. The dichlorofluorescin (DCFH) oxidation and no oxidation of luminol in PP/PP-ZnO nanohybrids upon green light illumination indicate that the nature of ROS is essentially singlet oxygen rather superoxide anions. Direct evidence of the role of electron transfer as a key player for enhanced ROS generation from the nanohybrid is also clear from the photocurrent measurement studies. We have also used the nanohybrid in a model photodynamic therapy application in a light sensitized bacteriological culture experiment.

References:

1. S. Sardar, S. Chaudhuri, P. Kar, S. Sarkar, P. Lemmens and S. K. Pal “Direct Observation of Key Photoinduced Dynamics in a Potential Nano-delivery Vehicle of Cancer Drugs”, Phys. Chem. Chem. Phys. 17 (2015) 166.
2. S. Sardar, S. Sarkar, M. T. Z. Myint, S. Al-Harthi, J. Dutta and S. K. Pal “Role of Central Metal Ion in Hematoporphyrin-Functionalized Titania in Solar Energy Conversion Dynamics”, Phys. Chem. Chem. Phys. 15 (2013) 18562.

Enhanced Visible Light Photo-electrochemical and Photo-switching Activities of TiO_2/ZnO Core/Shell Nano-heterostructure Array

Ayan Sarkar[1], Asutosh K. Singh[2], Gobinda Gopal Khan[1], Debasish Sarkar[3] and Kalyan Mandal[2]

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[3]Solid State and Structural Chemistry Unit, Indian Institute of Science, C.V. Raman Ave, Bengaluru 560012, India.

Here we report a simplistic method for preparing vertically aligned 1D arrays of type II n–n TiO_2/ZnO core/shell nano-heterostructures by growing the nano-shell of ZnO on the electrochemically synthesized TiO_2 nanotubes core for visible light driven photo-electrochemical applications. The strong interfacial interaction at the type II heterojunction leads to an effective interfacial charge separation and charge transport. The presence of various defects such as surface states, interface states and other defects in the nano heterostructure enable it for improved visible light photo-electrochemical performance. The presence of such defects has also been confirmed by the UV-Vis. absorption, cathodoluminescence and crystallographic studies. The TiO_2/ZnO core/shell nano-heterostructures exhibit strong green luminescence due to the defect transitions. The TiO_2/ZnO core/shell nano-heterostructures photo-electrode show significant enhancement of visible light absorption and it provides a photocurrent density of 0.7 mA/cm^2 at 1 V vs. Ag/AgCl, which is almost 2.7 times that of the TiO_2/ZnO core/shell nano-heterostructures under dark conditions. The EIS results demonstrate that the substantially improved photo-electrochemical and photo-switching performance of the nano-heterostructures photo-anode is because of the enhancement of interfacial charge transfer and the increase in the charge carrier density, caused by the incorporation of the ZnO nano-shell on TiO_2 nanotube core.

Engineering of high performance supercapacitor electrodes based on metal/metal-oxide core/shell nano-heterostructures

Ashutosh Kumar Singh[*] **and Kalyan Mandal**

Department of Condensed Matter Physics and Material Sciences, S. N. Bose National Centre
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This study demonstrates the fabrication technique of novel nano-heterostructures (NHs) and their comparative study of electrochemical performance as supercapacitor electrodes. The fabricated Co-Ni/Co_3O_4-NiO core/shell nano-heterostructures supercapacitor electrodes offer the desired properties of macroporosity to allow facile electrolyte flow, thereby reducing device resistance and nanoporosity with large surface area to allow faster reaction kinetics. In three electrode configuration, Co-Ni/Co_3O_4-NiO core/shell nano-heterostructures supercapacitor electrodes exhibited specific capacitance values (2013 F g^{-1} at a constant current density of 2.5 A g^{-1}), high energy (44.7 Wh kg^{-1}), power density (7.5 kW kg^{-1}), good capacitance retention and long cyclicality. The remarkable electrochemical property of the large surface area nano-heterostructures is demonstrated based on the effective nano-architectural design of the electrode with the coexistence of the highly redox active materials at the surface supported by highly conducting metal channel at the core for faster charge transport.

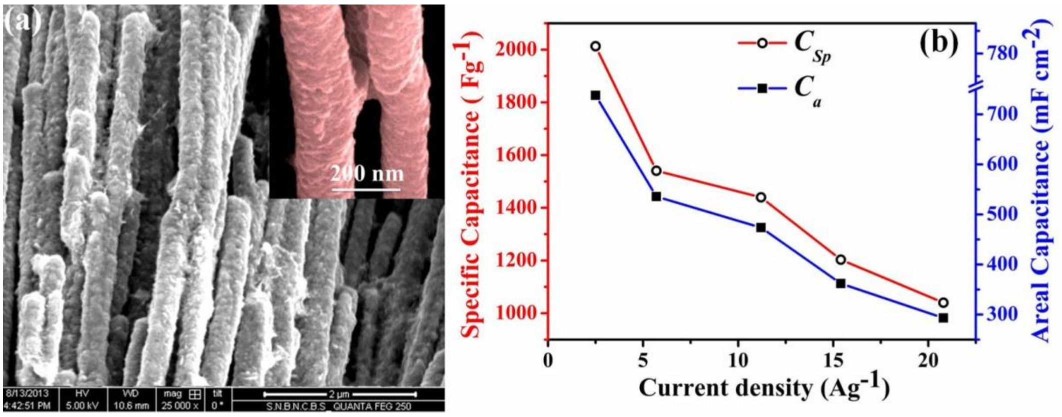

Figure: (a) EFTEM micrographs and **(b)** variation of areal (Ca) capacitance and specific capacitance (Csp) as a function of current density for Co-Ni/Co_3O_4-NiO core/shell NHs,.

Strain and morphology of graphene membranes on responsive microhydrogel patterns

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We study the configuration of atomically-thin graphene membranes on tunable microhydrogel patterns. The polyethylene oxide microhydrogel structures patterned by electron-beam lithography show increase in height, with a persistent swelling ratio up to ~10, upon exposure to vapors of an organic solvent. We demonstrate that modifying the height fluctuations of the microhydrogel affects the strain and morphology of ultrathin graphene membrane over-layer. Raman spectroscopic investigations indicate that small lattice strains can be switched on in mechanically exfoliated few-layer graphene membranes that span these microhydrogel structures. In case of chemical-vapor deposited single-layer graphene, we observe Raman signatures of local depinning of the membranes upon swelling of microhydrogel pillars. We attribute this depinning transition to the competition between membrane-substrate adhesion energy and membrane strain energy, where the latter is tuned by hydrogel swelling.

This work is published in Applied Physics letters journal in November 2014

Reference: P. R. Shaina and M. Jaiswal, Appl. Phys. Lett. 105, 193103 (2014)

Synthesis of Zn^{2+} doped MgO nanoparticles using layered Mg-Zn hydroxide precursors and studies on their optical properties

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Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee 247667, India

Doped metal oxide nanoparticles are useful in a wide variety of applications such as optoelectronics, catalysis, luminescent devices, etc. The present study is devoted to doping of Zn^{2+} in MgO nanoparticles. Zn^{2+} doped MgO can be synthesized by various methods and new methods are often explored for its synthesis. In the present study, layered Mg-Zn hydroxide precursors with different Zn^{2+} concentrations were synthesized by sol-gel method and they were heated at 500 °C to 1000 °C to get Zn^{2+} doped MgO nanoparticles. X-ray diffraction studies showed a single set of peaks due to cubic MgO and the peaks were shifted towards lower 2θ because of the larger size of Zn^{2+} (0.74 Å) compared to Mg^{2+} (0.70 Å). Small nanoparticles in the doped samples were observed by scanning electron microscopy and TEM analysis (size = 25 to 40 nm). Pure MgO is optically transparent in 200-800 nm while in the diffuse reflectance spectra of Zn^{2+} doped MgO nanoparticles, absorption near 250 nm was observed. In the photoluminescence spectra, emission bands at about 367 nm and 470 nm attributed to oxygen vacancies were observed. The Zn^{2+} doped MgO nanoparticles may be explored for applications in photovoltaics and antibacterial materials.

Demonstration of Electronic Grade and Flexible Semiconductor Film Employing Sintering of Colloidal Ligand-Free PbS and PbSe Nanocrystals at Room Temperature

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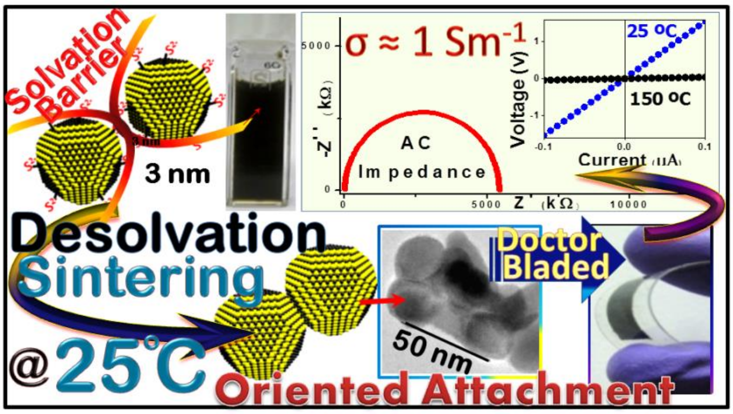

Electronic grade semiconductor films have been achieved via sintering of solution processed ligand-free PbS and PbSe nanocrystals at room temperature. Prior attempts for similar films required sintering of nanocrystals at >350 ^{o}C inhibiting processing of films on flexible polymer substrate, and also expensive. We reduced the sintering temperature via employing two strategies: (i) use of ligand-free nanocrystals, and (ii) oriented attachment of nanocrystals. Ligand-free PbS and PbSe nanocrystals were synthesized at 70 ^{O}C. However, these nanocrystals agglomerate with time in formamide and upon removal of solvation energy, nanocrystals undergo oriented attachment forming larger elongated crystals. The crystallite size of nanocrystals in the precipitate is about an order of magnitude larger compared to that of the colloidal NCs obtained by UV-vis-NIR spectrum.

Room temperature processed PbS and PbSe nanocrystal films on glass exhibit DC conductivity 1.1 S/m and 137 S/m respectively; upon mild annealing at 150 ^{o}C. AC impedance distinguished the contributions of grain and grain boundary in charge transport mechanism. Transport properties retain similar after repeated bending of films on flexible polyethylene terephthalate (PET) substrate. Developed strategy can be extended to a variety of NC systems including doped and heterostructured NCs, achieving electronic grade and flexible films of functional SC.

First principles study of stability and electronic properties of monolayer and bilayers of Germanium

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First principles studies have shown that a monolayer of Germanium (germanene) have low-buckled, honeycomb structures. Similar to graphene and silicene the charge carriers behave like massless Dirac fermion as their π and π* bands cross linearly at the Fermi level. Here we have investigated the possibility of formation of bilayers of germanene and their electronic possibilities. We find that the bilayers can stack in several forms of AA and AB stacking which are energetically similar. Among these the planar AA one is the most stable one with a cohesive energy of -3.38eV/Ge atom. The phonon dispersion of this system do not exhibit any instabilities throughout the Brillouin zone suggesting that this strucutre is also dynamically stable. However the electronic strucutre shows that unlike the monolayer, the bilayers are metallic. Further the Dirac cone is shifted to 1.135 eV below Fermi energy.

References:

(1)S.Cahangirov et al., PRL 102,236804(2009)
(2)H.Sahin et al.,PRB 88,045434(2013)