

Chem@Nano '21

Abstract Book



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Invited Talks

A Brain-Inspired Intelligent Device

Prof. G. U. Kulkarni

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Nanostructured electrocatalysts for HER and OER

Prof. Ashok K. Ganguli

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Reduction of Graphene Oxide: Intermediates and Product

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Graphene based materials have gathered immense research interest, particularly for energy storage devices. Here, we have explored top-down approach to chemically synthesize graphene with some residual functional groups, commonly referred reduced graphene oxide where we start with cheap and abundant graphite flakes to produce gram-scale end product. Graphite was first oxidized to graphene oxide (GO) by modified Hummer's method followed by subsequent reduction to reduced graphene oxide (rGO). We have employed, for the first time, transition metal salts as mild and unconventional reducing agents for the reduction of GO producing two- and three-dimensional rGOs. The isolated rGOs exhibited superior supercapacitor performance compared to rGOs synthesized via conventional reducing agents. As for the intermediates of GO to rGO reduction, we could isolate various crystalline solids whereby rGO was found to be chemically integrated with exotic low-dimensional magnetic systems.

Manipulation of Lattice Strain at Atomic scale to Generate Materials for Fuel Cell, Water Splitting and CO₂ reduction

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Enhancement in electrochemical activity can be achieved by the generation of strain in the system which modulates the electronic structure and hence, the interaction of intermediates with the catalyst surface. Strain effect can be generated by lattice mismatch, which alters the adsorption energy along with modulation of the d-band centre. In alloys/solid solutions or substitution strain is generated due to the incorporation of a second element into the lattice of solvent elements which can be closely associated with structural defectiveness like grain boundary, defects thereby having a direct effect on the adsorption strength of the reaction intermediates. In case of tensile strain wherein a metal with smaller lattice parameter is inserted into the lattice of a metal with higher lattice parameter resulting in modulating the d-band centre. Since, generation of strain leads to variation in adsorption energy of the reaction intermediates it can be correlated to coordination number (CN) which is defined as the number of nearest neighbours for a specific site and local structure variations in the crystal structures. We have exploited this concept in a variety of materials. In my talk I will provide a brief information of different systems developed by lattice strain tuning. The examples are: the concept of inverse strain effect by generating tensile strain with Cu substitution in Pd lattice of Pd₁₇Se₁₅. The inverse strain effect modulated the electronic structure such that free energy of hydrogen adsorption was lowered with an optimal value that is close to zero thereby, augmenting the HER activity. The compressive strain induced in the Pd lattice upon alloying with Bi resulted in PdBi alloy exhibiting ORR activity at-par with state-of-the-art catalyst Pt/C. Reduction in particle size led to generation of strain in metal carbides (MoC and WC) leading to alteration in the relative binding energy of the intermediates thereby, affecting the current density in HER.

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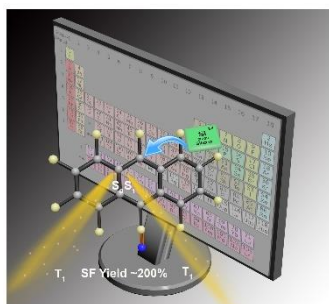
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Singlet Fission in Organic Chromophoric Aggregates: A Tool to Expand the Limit of Solar cells

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Singlet Fission (SF) is a multi-exciton generation (MEG) pathway where in a pair of triplet exciton is formed between two neighbouring chromophores starting from a singlet excitation on a molecule. This *spin allowed* SF process opens a new avenue for increasing the solar energy conversion efficiency for solar cells. Production of two correlated triplet states from one single exciton attracts significant attention due to its ability to harness the higher energy photons into a photovoltaic cell rather than losing this excess energy for low band gap semiconductors. Though there are several experimental reports in polyaromatic hydrocarbons (PAH) for SF, a rational design for choice of the molecular systems still remains at infancy. This lecture would address the theoretical challenges in this area namely (a) Choice of molecules which satisfy the three thermodynamic conditions of SF (b) Crystal engineering of molecular forces in aggregates of chromophores for maximizing the SF yield and (c) Current state-of-the-art in the understanding the mechanism and role of charge-transfer (CT) states. We present few studies from our laboratory on logical design of singlet fission (SF) in aggregates.



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Enhanced Atomic Ordering Leads to Ultra-High Thermoelectric Performance

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With about 2/3 of all utilized energy is being lost as heat. Thermoelectric materials can convert waste heat to electrical energy, and it will have significant role in future energy management. High thermoelectric performance is generally achieved either by electronic structure modulations or through phonon scattering enhancements, which often counteract each other. A leap in performance requires innovative strategies that simultaneously optimize electronic and phonon transports. We demonstrate high thermoelectric performance with a near room-temperature figure of merit, $zT \sim 1.5$ and a maximum $zT \sim 2.6$ at 573 K by optimizing atomic disorder in Cd doped polycrystalline AgSbTe_2 .¹ Cadmium doping in AgSbTe_2 enhances cationic ordering, which simultaneously improves electronic properties by tuning disorder-induced localization of electronic states and reduces lattice thermal conductivity via spontaneous formation of nanoscale ($\sim 2\text{-}4$ nm) superstructures and coupling of soft vibrations localized within ~ 1 nm around Cd sites with local strain modulation. The strategy is applicable to most of other thermoelectric materials which exhibit inherent atomic disorder.

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Colloidal 2D Nanocrystals: Tuning the Emission Spectrum across the Visible and Near Infrared Spectral Range

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Two-dimensional (2D) colloidal semiconductor nanocrystals, also known as nanoplatelets (NPLs), represent a special class of materials where excitons share the benefits of strong confinement in the one direction and weakly bound motion in the other two dimensions, yielding an enhanced band-edge oscillator strength and associated emission rate. The thicknesses of 2D NPLs can be controlled with atomic precision from just a few to several atomic layers, so no inhomogeneous photoluminescence line broadening is observed at room temperature. Thus along with the advantages of colloidal quantum dots, for instance solution processability, widely tunable light absorption and emission with high quantum yield, NPLs exhibited additional unique spectroscopic properties, such as high extinction coefficients, sharp band-edge transitions, ultranarrow emission bandwidths, fast exciton recombination rates, exceptionally large exciton and biexciton binding energies and suppressed Auger recombination. Consequently, rational design of 2D NPLs has attracted a lot of interest recently to engineer their optoelectronic properties for advanced photonic and electronic applications. In this talk, I will discuss our recent results of CdSe-based 2D nanocrystals, featuring thickness controlled CdSe NPLs suitable as phosphors for lasing or light emitting devices, as well as doped CdSe:Ag NPLs and CdSe/CdS/CdTe heterostructured NPLs which exhibit fluorescence that is strongly Stokes shifted and has a lifetime beyond 100 ns, in the latter case the CdS barrier yields emission from CdSe and CdTe direct transitions along with the Type-II emission. This flexibility to design NPL heterostructures has led to a wide range of applications from luminescent solar concentrators to ultrafast scintillators and fluorescence upconversion. To further tune the emission spectrum we introduced 2D PbS NPLs using a single-source precursor approach. NIR emitting 2D PbS NPLs are promising building blocks for future solution processed photonic and optoelectronic applications.

Ultrafast Charge Carrier Dynamics of 2D-Transition Metal Chalcogenides

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Black Nano Gold for Hot Electron Mediated Photo-Catalysis

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Climate change due to excessive carbon dioxide (CO₂) is the Most Serious Problem Mankind Has Ever Faced. Capture and then conversion of CO₂ to useful materials and fuels using solar energy are the best ways to tackle these challenges. Recently we have reported range of nanomaterials/ nanocatalysts such as DFNS¹, Black Gold², Defective Nanosilica³, Solid Acids⁴, Lithium Silicate Nanosheets,⁵ and Magnesium,⁶ to capture CO₂ and then convert to fuels and chemicals using solar energy. In this talk, I will discuss the tuning of catalytic behavior of dendritic plasmonic colloidosomes (DPCs) by plasmonic hotspots.² A cycle-by-cycle solution-phase synthetic protocol yielded high-surface-area DPCs by controlled nucleation-growth of gold nanoparticles. These DPCs, which had varying interparticle distances and particle-size distributions, absorb light over the entire visible region as well as in the near-infrared region of the solar spectrum, transforming golden colored gold into black gold. They produced intense hotspots of localized electric fields as well as heat, which were quantified and visualized by Raman thermometry and electron energy loss spectroscopy plasmon mapping. These DPCs can be effectively utilized for the oxidation reaction of cinnamyl alcohol using pure oxygen as the oxidant, hydrosilylation of aldehydes as well as for temperature jump assisted protein unfolding and purification of seawater to drinkable water via steam generation. Black gold DPCs also converts CO₂ to methane (fuel) at atmospheric pressure and temperature, using solar energy.²

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1,4-Conjugate Addition Reaction Assisted Synthesis of Functional and Durable Bio-inspired Interfaces

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The nature-inspired wettabilities are with immense potential for various prospective applications including oil/water separation, anti-corrosion, underwater robotics, protein crystallization, drug delivery, open microfluidics, water harvesting etc. In common practice, essential chemistry and appropriate topography that conferred the special liquid wettability were mostly achieved by associating delicate chemistries. Eventually, the synthesized materials suffered from poor durability challenge. To develop durable and functional bioinspired wettability, recently, we have extended 1,4 conjugate addition reaction between amine and acrylates at ambient condition. Further, porous and chemically reactive interfaces were prepared for tailoring various important and functional liquid wettability. Even a strategic associating of crosslinker can provide highly tolerant and hard superhydrophobic coating on geometrically complex and soft materials. Such simple chemical approach also allowed to reveal important fundamental aspects related to different bio-inspired wettability. Taking advantage of the durable bio-inspired wettability, synthesized nature inspired interfaces were successfully applied to demonstrate some practically relevant outdoor applications— including oil/water separation, water harvesting etc.

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Designing Functional Polymers and Supramolecular Materials for Sensors, Optoelectronics and Healthcare Applications

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New functional luminescent dyes, including conjugated polymers and oligomers based on the principle of aggregation-induced emission (AIE) have been designed and developed.¹⁻⁷ They have been utilized for chemosensors,^{1,2} biosensors,³ bioimaging,³⁻⁶ optoelectronic devices⁵⁻¹³ and latent finger printing applications. By introducing specific functional groups aggregation caused quenching (ACQ) molecules were converted to bright AIE/AIEE dyes which were utilized as excellent platforms in solution as well solid phase for the detection of important analytes of relevance to environment, cancer therapeutics, anti-amyloid activity as well as wash-free bioimaging applications. These organic dyes and functional materials displayed strong self-assembling nature in water, in crystalline and amorphous forms on desired surfaces, in physiological environment allowing them to be applied as sensors, healthcare probes and optoelectronic devices.¹⁻¹³ This lecture will present the design principles that were utilized to develop several advanced materials and their remarkable applications by introducing functional group engineering.

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Highly Efficient Ambipolar Charge Transport in Semiconducting Discotic Liquid Crystals

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The hunt for condign ambipolar charge transport materials remains a significant challenge over the past few years. To achieve such demand, intensive efforts are being made using organic semiconductors that carries high electrical performance as well as can be easily processed using different solution processing techniques. However, the crucial challenge is to find a subtle balance between the mobility and processability of these materials. For example, single crystals, known for high mobilities, suffer from inherent fragility and flexibility, which limit their usability in devices. Similarly, in polymeric systems, inadequate solubility, low purity, and structural and energetic disorder have curbed their charge transport properties. To overcome these challenges, recent research has focused on organic small molecules, which offer solution-processed, defect-free films along with high chemical purity. In this context, discotic liquid crystals (DLCs) comprising a central rigid aromatic core substituted with a mantle offer flexible alkyl chains, are currently in the spotlight of material scientists. This talk will unmask a unique ability of Heterocoronene¹ based DLCs and others²⁻⁵ to serve as highly efficient ambipolar charge carrier transporting organic semiconductor when used in Space Charge Limited Current (SCLC) devices. These bipolar transport materials would be highly cost-effective due to incorporation of a single layer of organic materials in device architecture. Our results are comparable with the best amorphous as well as polycrystalline organic semiconductors reported till date.

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Student Presentations

Unravelling a graphene-exfoliation technique analogy in the making of ultrathin nickel-iron oxyhydroxides@nickel foam to promote OER

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One of the major objectives of using the improved hummer's method was to exfoliate the graphene layers by oxidising and thereafter reducing them to obtain highly conductive reduced graphene layers, which can be used in the construction of electronic devices or as a part of catalyst composites in energy conversion reactions. Herein, we have employed a similar idea to exfoliate the layered double hydroxide (LDH), which is proposed as a promising material for OER electrocatalysis.^{1,2} Usually, the efficiency of this material is largely restricted due to its sheet-like morphology which is susceptible to stacking.³ In this work, NiFe-LDH sheets were fabricated on nickel foam in one step co-precipitation technique and their ultrathin nanosheets (~2 nm) are obtained by *in-situ* oxygen plasma controlled exfoliation. In addition, the oxygen vacancies in exfoliated sheets were generated by a chemical reduction method that further improved the electronic conductivity and overall electrocatalytic performance of the catalyst. The approach assists to enhance the shortcomings like poor conductivity and low stability of NiFe-layered hydroxides to be an efficient electrocatalyst. It is also observed that catalyst having 60 s of O-plasma exposure after chemical reduction i.e. NiFe-OOH_{OV} outperformed remaining electrocatalysts and exhibited superior OER activity with a low overpotential of 330 mV to achieve a high current density of 50 mA cm⁻². The catalyst also displays an impressive OER overpotential of 288 mV at 10 mA cm⁻² of current density when normalized with ECSA and excellent long-term stability in alkaline electrolytes. Remarkably, ultrathin defect-rich catalyst continuously produces O₂ resulting in high faradaic efficiency of 97.6% for the OER.

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Metal Oxide Solid Solutions for Photocatalytic Hydrogen Evolution Reaction

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Hydrogen generation by solar water splitting has been considered as a promising green energy technique as the solar energy is an abundant natural resource and does not contribute to carbon footprints.¹ This also offers one of the best method to solve the energy crisis without causing any environmental issue that result from the burning of fossil fuels.² Recently, several kinds of oxide based semiconductors have been developed as photocatalysts for production of H₂ from water. To improve the photocatalytic hydrogen performance, various strategies such as morphology control, defect engineering, and band engineering have been developed. Among these methods, defect engineering is considered as one of the effective way to modulate the electronic band structure, charge carrier transfer and surface-active sites construction of photocatalysts.³ The synthesis of solid solutions is also the prime approach for band engineering, aiming at improving the light absorption and facilitating the photogenerated e-h pair separation. Here, the impact of oxygen vacancies and ZnO segregated phase on the photocatalytic activity has been discussed. In this work, we have synthesized ZnFe_{2-x}Ga_xO₄ solid solutions via citrate-gel method and studied the water splitting activity for hydrogen generation in the presence of sacrificial agent. It has been found that the hydrogen production rate systematically increases from ZnFe₂O₄ (3089 μmolh⁻¹g⁻¹) to ZnGa₂O₄ (3989 μmolh⁻¹g⁻¹) in the series. Formation of additional ZnO phase with incorporation of Ga³⁺ in the ZnFe₂O₄ structure improves the hydrogen evolution activity. This study suggests that the spinel-ZnO composites phases to be promising catalyst for photocatalytic hydrogen evolution.

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Impact of different nanocarbon-based hybrid materials in energy storage applications

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Designing and fabrication of energy storage systems with high energy and power density as well as long cycling life are highly required to avoid the electrical fluctuations in the renewable power sources for the sustained power delivery. Supercapacitors with excellent power density and rechargeable batteries with high energy density are currently both considered to be novel, environmentally friendly and high-performance energy storage devices. For the development of cost effective, accessible, high efficiency and long term durability, porous carbonaceous materials are currently the most promising candidate for energy storage materials. Herein, interconnected porous graphene have been explored as supercapacitive material as well as current collector in developing metal-free interdigitated microsupercapacitor (IMSC) due to its superior conductivity and porosity. Electrochemical followed by laser-irradiation (LI) method gives advancement in prototyping conductive graphene-based robust MSC device with large working voltage window of 1.2 V in aqueous solid electrolyte.¹ The resulting LIG MSC delivers long-term stability with 100% retention of initial capacitance in an on-chip energy device. The hybrid structure of commercial solar cell and modularized metal free supercapacitor with 10.8 V working voltage was designed to facilitate progress toward a self-sustainable energy future. In the next attempt, we demonstrate electrodeposited porous Ni₃P superstructures on activated carbon cloth (CC*) as a robust cathode material towards enhanced Ni-Zn aqueous battery technology. The unique porous structure of Ni₃P electrode offers remarkable specific capacity of 258 mAh g⁻¹ along with tremendous high-rate capability (maintains 81% at 11 A g⁻¹). Moreover, the Ni₃P@CC*/Zn@CC* battery is capable of showing a record-high specific capacity of 322 mA h g⁻¹, power density 17.5 kW kg⁻¹ and imposing energy density of 661.98 Wh kg⁻¹ towards affordable and practical energy storage. Furthermore, the combination of the SCs and battery system results a hybrid energy storage device will yield fast charging rate and the high energy density of battery, which is highly desirable for the forthcoming electrical technology.

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Ultrafast Plasmon Dynamics in Near-Infrared Active Non-Stoichiometric Semiconductor Cu_{2-x}E (E=S, Se) Nanocrystals

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Infrared (IR) light is an untapped energy source that accounts for nearly half of all solar energy. Non-stoichiometric plasmonic semiconductor nanocrystals (NCs) exhibit localized surface plasmon resonance from visible to IR region, which can be utilized for different application. Despite numerous examples, hot hole-driven procedures for Cu_{2-x}E (E=S, Se) NCs remain elusive. In present investigation, we have demonstrated ultrafast hot hole dynamics in Cu_{2-x}S and Cu_{2-x}Se NCs in presence of molecular adsorbate methylene blue (MB) with the aid of femtosecond transient broadband (Visible-IR) pump-probe spectroscopy. Ultrafast plasmon dynamics of Cu_{2-x}Se NCs have been monitored with changing the chemical composition and estimated hole-phonon relaxation time constant found to be in the range of 240-440 fs after 400 and 800 nm excitation. Hole-phonon coupling constant (G) has been determine and found to be in the range of $(1.6-2.7) \times 10^{10} \text{ J K}^{-1}\text{s}^{-1}\text{cm}^{-3}$ for Cu_{2-x}S NCs, which is one order lower as compared to metallic system. However, hole-hole, hole-phonon and phonon-phonon scattering are faster in presence of MB for Cu_{2-x}Se NCs system. Further, we have investigated conductivity measurements for Cu_{2-x}Se and $\text{Cu}_{2-x}\text{Se@MB}$ thin film and found drastic improvements in conductivity for $\text{Cu}_{2-x}\text{Se@MB}$ NCs system. We propose that our results will guide to design and development of new semiconductor based plasmonic NCs for efficient photo-detector and photo-transistor application.

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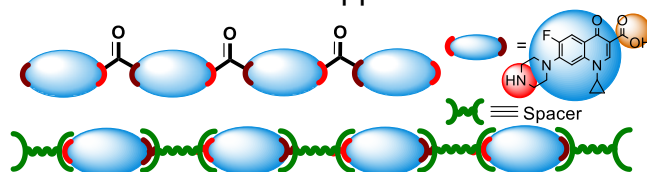
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Unraveling the effect of non-drug spacers on a true drug-polymer: Comparative study of their antimicrobial activity

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Infections by pathogenic microorganisms are of serious concern in the fields of drugs, drug resistance, medical devices, hospital surfaces, dental procedure, surgical equipment, health care products, and other hygienic applications (e.g., water purification systems, food packaging and storage, textiles, and domestic appliances, etc.). Antimicrobial polymers (AMP) are the materials that can kill/inhibit the growth of microorganisms on their surface or in the surrounding environment *via* different mechanisms. To prevent health hazards, AMP has received significant attention from academic and industrial research and is often found to perform better than their monomer analogues in terms of enhanced antimicrobial activity, reduced toxicity, minimized environmental hazards, sustained-release activity, and resistance, etc. Hence, significant efforts have been put to polymerize the monomers or modify the existing polymers using spacers or other polymer backbones to achieve materials with efficient antimicrobial activity.^{1,2} However, the self-polymerization of such drug units without using any spacers has not been explored to understand the importance of the spacer effect in drug polymers. Herein, we envisaged that it is possible to self-polymerize 1-cyclopropyl-6-fluoro-4-oxo-7-piperazine-1-ylquinoline-3-carboxylic acid (ciprofloxacin, **1**), a second-generation broad-spectrum drug in the class of fluoroquinolones, *via* a simple synthetic approach leading to form drug-polymer **C₀P₁** having no spacing unit. For comparison, polymers with varying spacing units involving alkyl chains of C₂ (**C₂P₂**) and C₁₀ (**C₁₀P₃**) have been realized. The trend for minimum inhibitory concentration study in solution against *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) was observed as **1**>**C₀P₁**>**C₂P₂**>**C₁₀P₃**. Further, the trend for the antibacterial activity for polymer-coated nylon sutures was observed as **C₀P₁**>**1**>**C₂P₂**>**3**>**C₁₀P₃**>**2** and **C₀P₁**>**C₂P₂**>**1**>**3**>**C₁₀P₃**>**2** for *E. coli* and *S. aureus*, respectively. In this talk, I will be discussing these results in detail. In the end, stating that the bioefficacy of a drug-polymer can be retained and enhanced by not having non-bioactive spacer units in it and self-polymerization of capable drug moieties may open a vast area of research with various applications.



Schematic representation of polymers with and without spacers.

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Nanostructured metal decorated metal oxides for energy related applications

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Metal oxides have been exploited widely for the photoelectrochemical applications owing to their tunable band edges, inexpensiveness, high abundance and stability.¹ To enhance the catalytic activity of metal oxides for organic conversion, surface decoration has been done with metal to tune the band edge positions.² Here, a process for the synthesis of black gold (BG) using a citrate-assisted chemical route and m-ZrO₂ by a hydrothermal method at 200 °C has been developed. Further, different concentrations of black gold are being used to decorate the surface of zirconia by exploitation of surface potential of zirconia and gold surfaces. The catalyst having 6 mol % concentration of black gold shows excellent electrocatalytic activity for ethanol oxidation with low oxidation peak potential (1.17 V) and high peak current density (8.54 mA cm⁻²). The current density ratio (j_f/j_b) is also high (2.54) for this catalyst indicating its high tolerance toward poisoning by intermediate species generated during the catalytic cycle. The enhanced electrocatalytic activity can be attributed to the high tolerance of gold toward CO poisoning and high stability of the ZrO₂ support. The black gold decorated zirconia catalyst showed enhanced activity during photoelectrochemical studies when the entire spectrum of light falls on the catalyst. Ultrafast transient studies demonstrated plasmonic excitation of metallic free electrons and subsequent charge separation in the black gold-ZrO₂ heterointerface as the key factor for enhanced photoelectrocatalytic activity.³

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Solar-H₂O₂ production over metal-free photocatalytic systems: A greener approach

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Solar-H₂O₂ production integrated with water oxidation or biomass valorization presents exceptional advantages of Eco-friendly and sustainability over commercial Anthraquinone oxidation process (AOP), which accounts for >95 % global H₂O₂ production. In our first study, solar-H₂O₂ production along with biomass valorization to value added chemicals achieved under sunlight over a metal-free polymeric oxygen allied carbon nitride (CNO), affording 34 $\mu\text{mol/g}$ of H₂O₂ along with 51 % of Diformylfuran (DFF) after 8.5 h under natural sunlight. In our next study, solar-H₂O₂ produced from pure water over a metal-free Heptazine-porphyrin (HMP-PPR), affording 151 $\mu\text{mol/g}$ of H₂O₂ from water after 4 h under natural sunlight. Therefore, sunlight-driven H₂O₂ production integrated with water oxidation or biomass valorization could take the future H₂O₂ production to sustainable routes.

Iodo-Functionalized Salicylideneimine-Boron Complexes as Photosensitization Agents for Water Purification and Anti-microbial Activity

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Organoboron compounds are typically one of the most extensively employed class of reagents in organic chemistry and catalysis. Boron has emerged as a key element for luminescent organic compounds over the last decade leading to interesting photophysical properties and finding applications ranging from solar cells and optoelectronics to sensing and cell imaging.¹ The delocalization of the π -electrons of organic chelates to the vacant p -orbitals of boron rigidifies the boron-containing organic compounds and thus stabilizes the π -conjugated skeleton thereby intensifying the associated emission. The type of the ligands and the nature of the substituted groups on either the ligands or boron can alter the photophysical properties of these compounds to a great extent. Schiff base based boranils are extensively reported with interesting luminescent properties but their photosensitization ability are hardly explored in detail. The ease of synthesis and good reaction yields with intriguing photophysics, motivated us to employ these category of compounds as photosensitizers.

We have prepared a series of small organic molecules and polymers containing iodo-functionalized salicylideneimine-boron complexes from commercially available starting materials.² Owing to the heavy atom effect leading to enhanced spin orbit coupling, the iodo-functionalized derivatives were observed to aid in the photosensitized generation of singlet oxygen with a remarkable singlet oxygen yield of more than 90%. Thin films incorporating these molecules were prepared using a polymer as a supporting matrix or through the layer-by-layer assembly, and were demonstrated to be capable of serving as a medium for the photosensitized degradation of organic water pollutants and as anti-microbial coatings.

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Ultrafast Processes in Nanoscale System for Light Harvesting: Watching Excitons Move

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Conjugated polymer-based nanostructures have been explored extensively from energy harvesting to healthcare applications due to their unique photophysical properties. Formation of conjugated polymer nanoparticles (PNPs) from pristine polymer lead to changes in excitonic absorption bands, photoluminescence (PL) bands, and relaxation kinetics as compared to respective pristine polymer due to the inter-chain interactions between the chromophoric sub-units. We have probed the formation of PNPs and their collapsing mechanism from extended form using ultrafast spectroscopic analysis and time resolved anisotropy. Further, we have shown the formation of the low-lying delocalized collective state from global and target analysis of the spectroscopic data. Other aspects of ultrafast photoinduced processes of the PNPs, namely exciton generation and diffusion, carrier transfer and population transfer from excited states are also highlighted from global and target analysis of transient absorption spectra. After obtaining knowledge about fundamental photophysics of conjugated polymer nanoparticles, we designed hybrid light-harvesting systems based on polymer nanoparticles. They showed promising light-harvesting nature such as photocatalysis, photovoltaics; where significant charge separation occurs due to photoinduced population transfer. These fundamental understandings of the charge transfer dynamics open up new possibilities to design efficient light-harvesting system based on inorganic-organic hybrid system.

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Structuring Liquid Droplets and Controlling Molecular Diffusion using Supramolecular Constructs

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Pillar[5]arene (P[5]A), an emerging class of macrocycle, is a promising candidate for stabilizing the liquid-liquid interface and the 2D assembly of P[5]A at the interface can promote self-assembly into well-defined architectures. Herein, pillar[5]arene carboxylic acid derivative (P[5]AA) was synthesized to study the pH-responsive self-assembly at oil-water interface mediated by hydrogen bonding interaction. The assembly was reversibly modulated via a jamming to unjamming transition thus reversibly shaping the P[5]AA stabilized pendant droplets. Furthermore, the interfacial jamming of P[5]AA aggregates enabled pH-switchable molecular diffusion of encapsulants through liquid-liquid interface.

Development of DNA origami based nanogap-engineerable plasmonic nanoantennas for single molecule sensing

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Single molecule spectroscopy is a fascinating optical tool that allows observing the static and dynamic events at single molecule level, necessary for a range of applications.¹ However, poor signal to noise ratio limited the wide applicability of single molecule detection methods for commercial applications. Plasmonic nanoantennas consisting of metal nanoparticles can overcome this constraint as they have the ability to concentrate light into nanoscale volumes, leading to dramatic enhancement in the electromagnetic field.²⁻³ The motivation of the present study is to design plasmonic nanoantennas comprising of anisotropic nanostructures with a control over interparticle gap and orientation using DNA origami technique.⁴ The designed bimetallic Au@Ag nanostructures is utilized for enhancing Raman signal of a single fluorophore and biologically relevant thrombin protein molecule positioned in the junction of the dimeric nanostructures.⁵ Further, label-free SERS based detection of a bacterial biomarker, pyocyanin at ultralow concentration is demonstrated using the dimer Au@Ag structures.⁶ Next, single biocompatible quantum dot (QD) is immobilized at the center of DNA origami monomer. The single QD in the plasmonic hotspot of designed plasmonic nanoantennas will be further used for single molecule spectroscopic analysis.

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Non-porous Interpenetrating Co-*bpe* MOF for Colorimetric iodide sensing

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MOF with their accessible voids/ channels has been explored immensely for sensing due to their exclusive host-guest chemistry. However, unavailability of pores/voids in interpenetrating non-porous MOFs limits their applications in sensing. We herein report for the first time, hitherto, a non-porous MOF with interpenetrating ladder structure for iodide sensing. Co-*bpe* MOF was synthesized by hydrothermal reaction among Cobalt nitrate and 1,2-bis(4-pyridyl)ethylene (*bpe*) in methanol and tested against colorimetric sensing of halides. The supramolecular structure of the Co-*bpe* MOF was stabilized through strong hydrogen bonding. We propose double substitution reaction mechanism for iodide detection which is one of its own kind. While Co-*bpe* showed a significant color change from dark maroon to dark green in presence of iodide, the rest of the halides did not display any pronounced colorimetric effect. The limit of detection (LOD) of this material was found to be 2.7×10^{-7} M. This work focuses on the equal competency of non-porous MOF material with the porous MOFs in sensing applications.

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Sr-Ti-O based structures for Photocatalytic Hydrogen Evolution Reaction

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With the ongoing growth in the world population and depletion of non-renewable energy resources, the development of renewable energy is becoming one of the most important challenges in the world ¹. The utilization of solar energy to generate hydrogen, a clean and green source of energy can quench the world's energy thirst. Recently, photocatalytic water splitting ² has emerged as an effective technique to solve the energy crises by using semiconducting material as photocatalyst. Morphology, size, crystallinity, and crystal structure are few important parameters that play a major role in tuning the photocatalytic properties of the materials ³. Here, we discuss two important parameters wherein in one of the studies, the collective impact of morphology, size, and exposed facets on photocatalytic activity has been discussed. In the second study, the impact of crystal structure on photocatalytic activity has been discussed.

The first impact has been showcased⁴ by tuning the morphology, size, and nature of exposed facets of SrTiO₃ using various polyols (water (no polyol), ethylene glycol (EG), and polyethylene glycol (PEG-300 and PEG-400)). We found that the size of the nanostructures increased with a decrease in the dielectric constant of the solvent. The morphology varied from nanocubes to flower-like assembly, truncated nanocuboids, and nano-cuboids with a decrease in the dielectric constant of the solvent. The top exposed facet was observed to be [001] for all the samples. Along with [001] facet, [011̄] facet for the sample was synthesized using ethylene glycol (EG) and polyethylene glycol, PEG-300 as the solvent. We observed that with a decrease in the dielectric constant of polyols, the photocatalytic hydrogen evolution decreased.

In the second study, three structures from Sr_nTi_{n+1}O_{3n+1} series for (n = ∞, 1, 2) viz. SrTiO₃, Sr₂TiO₄, and Sr₃Ti₂O₇ were synthesized through the modified hydrothermal method. Cubes of size ~80 nm were obtained for perovskite SrTiO₃ whereas layered sheet-like structures were obtained for Ruddlesden-popper phase, Sr₂TiO₄, and Sr₃Ti₂O₇. We observed that hydrogen evolution varied with the increasing number of SrO layers in the unit cell and followed the order Sr₃Ti₂O₇ > Sr₂TiO₄ > SrTiO₃.

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