
Nanoscience in India: a perspective

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India has emerged as a leading player in the field of nanoscience and nanotechnology over the last decade. The Indian nano-endavor got its initial push through the Nano Science and Nano Technology (NS&NT) initiative (now the Nano Mission) of the Department of Science and Technology (DST), Government of India in 2002 and has accelerated very fast since then. This article is intended to sketch a brief picture of the recent nanoscience and technology activities in India with special emphasis on synthesis of nanomaterials and emergence of new properties in them. Application of nanomaterials into the very basic needs of India like water purification and energy creation along with the recent developments at the bio-nano interface will be discussed. State of nanoscience education at educational institutions in India and nanoscience based industrial initiatives will be touched upon.

1 Introduction

Nanoscience in India is vivid, diverse and expanding as in other parts of the world. The variety and diversity of the area resemble that of India itself and therefore, precisely capturing this panoramic view in the limited space is nearly impossible. Although one can trace back the creation of nanoscale matter in India to the *Vedic* period (1700–1100 BC) as evidenced from the presence of nanoparticles in several *Ayurvedic* preparations,¹ systematic efforts to understand such materials science of the past are rare. Recent investigations into the metallurgical processing prevalent in India showed the existence of nanoscale matter in a few weaponry of 300 BC which was attributed to the extraordinary strength of these materials.^{2,3} These practices, whether in Indian medicine or in metal processing, continue to exist in several parts of the country, but there have been very limited systematic and scientific efforts to correlate the properties with the nanoscale constituents.

This article is intended to present a broad overview of the recent and emerging trends in the Indian landscape of nanoscience. Although matter at the nanoscale, called ultrafine particles then, were probed extensively in 1980's and 90's with emphasis on material science, catalysis, quasicrystals and related disciplines, a sea change in the exploration of nanoscale matter happened due to the Nano Science and Nano Technology (NS&NT) initiative of the Department of Science and Technology (DST) in 2002 (now the Nano Mission, <http://nanomission.gov.in>). Although the investment was modest in the initial years (US\$12 million for first 5 years *i.e.* 2001–2006⁴) and continued to remain small (US\$200 million during 2007–2012⁵) in comparison to other adjacent countries (*e.g.* US\$760 million in China, US\$689 million in Taiwan, US\$35 million in Malaysia, *etc.*⁵), the

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outcome has been phenomenal. Indian publications in nanoscience increased from 1412 to 3616 during 2006–2011 in comparison to 355 to 971 during 2001–2005.⁶ Large part of the investment in nanoscience went to create infrastructure necessary for the exploration of nanoscale matter. As a result, a number of Units on Nanoscience (UNS) and Centres of Nanoscience (CNS) (20 in all) got created across the length and breadth of the country. As a result, it was not necessary to wait for months together for a high resolution transmission electron micrograph or carry samples discretely on your trip abroad for a quick measurement. Several other funding agencies supported the growth of nanoscience research in India. Department of biotechnology (DBT) provides support for nanotechnology related to life sciences. Council of Scientific and Industrial Research (CSIR) and Science and Engineering Research Council (SERC) of the DST also support research projects in diverse areas of nanoscience covering both basic and applied sciences. Although there are several other agencies such as Ministry of Information Technology (MIT), Defence Research and Development Organisation (DRDO), Indian Council of Medical Research (ICMR), University Grants Commission (UGC), Board of Research in Nuclear Studies (BRNS) of the Department of Atomic Energy, Indian Space Research Organization (ISRO) and Indian Council of Agricultural Research (ICAR)) have been funding research programs in the area, the efforts of DST have been the largest in fostering basic research in the country. Over 270 research projects have been funded over the period 2002–2011,⁷ producing about 670 Ph.Ds and over 4000 research papers in this window of time.⁸ Besides publications, 120 Indian and 38 foreign patents were filed in the five year term of Nano Mission of which 24 Indian and 11 foreign patents were granted.⁸ Figure 1 summarizes this rapid expansion of the science at the nanoscale in India. While this continues to fascinate scientists, it is merely 5% in the global umbrella of nanoscience and technology related activities, judged from the fraction of publications.⁶

The Indian nano endeavor continues largely in the plethora of nano-materials synthetic chemistry can unravel. As a result, chemists continue to

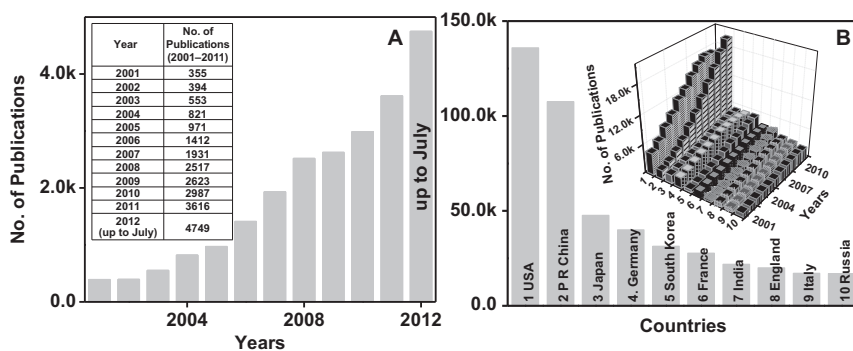


Fig. 1 (A) Increase in number of publications over the years (2001–July, 2012) in India in nanoscience and technology. Number of publications per year is shown in the inset. (B) Total number of publications in nanoscience and technology in the top 10 countries over the time span of 2001–2011. Year-wise increase in number of publications in those countries is shown in the inset.⁶

be more active in the area; chemical physics and biology complement the chemical efforts. Very few applications and devices have come about as in other parts of the world. Despite this, the early example of commercial success of nano has come from India touching upon the basic needs of India such as water.^{9,10} As a result of the close link with society, social scientists have been fascinated by the emerging implications of the area.¹¹ It has got into newspaper and public media¹² and even popular science books in regional languages.¹³

In the following, we present the recent excitements captured in materials, applications, biology and industry. Past efforts of various groups in diverse areas of their activity are collected in reviews and books. Chemistry of nanomaterials,¹⁴ carbon nanotubes,¹⁵ graphenic materials,^{16,17} nanofluids,¹⁸ nanoparticle assemblies,^{19,20} self organized structures,^{21,22} organic nanomaterials²³ polymer nanowires,²⁴ *etc.* are covered in excellent monographs and reviews. For a complete and up-to-date understanding of the nanoscience endeavor in India, it is important to consult these as well. Education in this discipline and implications to the largely young India (50% of Indian population are under the age of 25, from 2011 census) will be touched upon. We are aware that only representative work of several authors have been captured here and we are silent about the work of several others. In both these instances, the readers may consult the cited reviews.

2 Nanoscience research in India

2.1 Different nanomaterials-synthesis and new properties

2.1.1 Noble metal nanomaterials. Nanoparticles have become important materials these days not only due to their excellent structural features but also by their unusual functional attributes. Due to this reason, a considerable amount of attention has been paid to discover new ways to reduce the size of the constituent particles of every material to the nanometer length scale. Following Faraday's breakthrough of the synthesis of colloidal gold,²⁵ several new nanostructured materials and synthetic protocols were developed. Based on the confinement of electronic motion along specific axes, nanomaterials are mainly divided into two categories isotropic and anisotropic particles. Synthesis of such materials involves a wide variety of strategies as careful tuning of shape and size of the particles at this length scale can result in alteration of their physiochemical and optoelectronic properties. Simple chemical reduction of metal precursors using carefully controlled variation of synthetic parameters can yield nanoparticles of varying size, shape and composition in high yield with monodispersity. Microemulsion based synthesis is another effective way for the synthesis of various nanoparticles which Ganguli *et al.* has discussed in detail elsewhere.²⁶ Anisotropic materials such as nanorods,^{27,28} nanowires, triangles,^{29,30} nanoribbons,³¹ nanoprisms,³² flowers,^{33,34} *etc.*, have been widely studied and synthetic routes such as seed-mediated synthesis, biological synthesis, polyol synthesis, galvanic displacement methods, template-mediated synthesis *etc.* have been explored.³⁵

Among the multitude of anisotropic noble metal nanomaterials synthesized, an exciting addition from the Indian context is the work by Murali

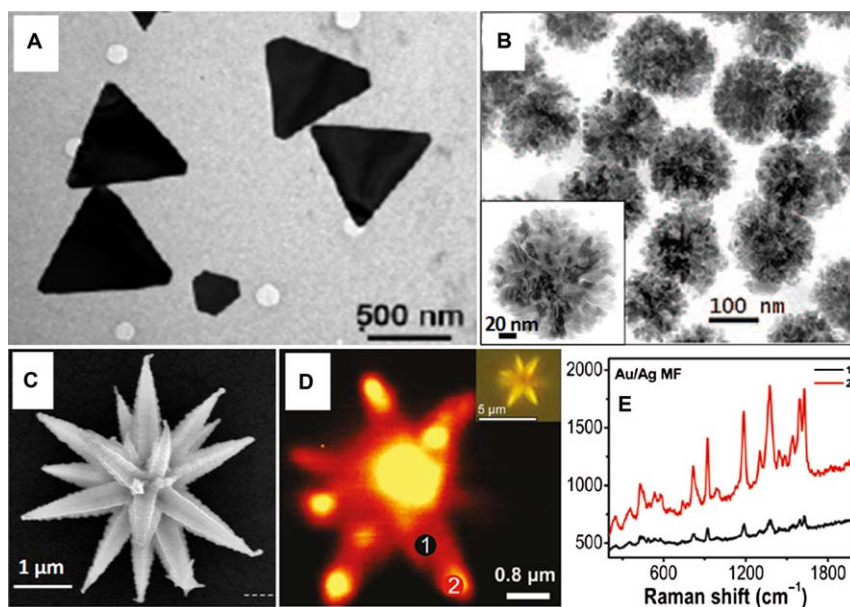


Fig. 2 (A) TEM image of gold nanotriangles synthesized by the biological reduction of HAuCl_4 solution with lemon grass extract (adapted from Ref. 32). (B) TEM image of nanostructured Au nanoparticles with marigold like morphology (nMG). Inset shows a single nMG (adapted from Ref. 33). (C) FESEM image of a gold mesoflower (adapted from Ref. 34). (D) Raman image of a single bimetallic Ag-Au mesoflower (adapted from Ref. 46). (E) Raman spectra of adsorbed crystal violet molecules on different regions of bimetallic Ag-Au mesoflower (marked in D).

Sastry *et al.* using biological templates/reducing agents. They developed a new synthetic strategy for making nanomaterials of various sizes and shapes by following biological routes.³⁶ In their pioneering work, they used the fungus, *Fusarium oxysporum*, to make gold nanoparticles.³⁷ Subsequently they made thin, flat, and single crystalline gold nanoprisms (Fig. 2A) using lemongrass (*Cymbopogon flexuosus*) extract.³² This method had a great impact in the area of anisotropic nanomaterials synthesis as it was difficult to make gold nanotriangles by a simple method in a highly reproducible manner. The method was 'green' as the reduction of Au^{3+} is induced by the reducing sugar (aldoses) present in the plant extract which resulted in a visible color change from pale yellow to ruby red during the reaction. Moreover, the possibilities of such bio-friendly nanotriangles in view of many bio-related applications received great attention all around the world. The other advantage of this method is that, the size of nanoprisms and thereby its longitudinal SPR band in the NIR region can be tuned by simple variation of the concentration of lemongrass extract in the reaction medium.³⁸ Several other biological systems such as tea leaves,³⁹ tamarind leaf,⁴⁰ neem seed extract,⁴¹ *Vitis vinefera* (grapes),⁴² clove buds (*Syzygium aromaticum*),⁴³ bacteria such as lactobacillus,⁴⁴ *etc.* have also been reported to make nanoparticles of noble metals.

Apart from biological synthesis, various synthetic protocols were widely used to make nanomaterials of unusual properties and applications. Jana has demonstrated that gram scale synthesis of various monodisperse

anisotropic materials of gold and silver such as nanorods, nanospheroids, platelets and cubes with controllable aspect ratios can be achieved by modified surfactant-based seed-mediated method.²⁷ Pramod and George Thomas investigated plasmon coupling in gold nanorods as a function of long-axis orientation.⁴⁵ Aligned arrays of uniform equilateral nanotriangles with NIR absorbing and SERS properties were demonstrated by Pradeep and Sajanlal, using an electric field assisted seed mediated approach.²⁹ Here, the gold seed nanoparticles (of 4 nm diameter) attached to the conducting glass surface were grown at low temperature into gold nanotriangles by applying an electric potential. Also, a highly anisotropic mesostructured material of gold, called gold mesoflowers (Fig. 2C–E), with star-shaped appearance and nanostructured stems with pentagonal symmetry was reported by the same authors.³⁴ They demonstrated that NIR-IR absorption exhibited by gold mesoflowers can capture a significant amount of heat, thereby reducing the temperature rise in an enclosure exposed to sunlight. Multiple attributes such as magnetism and Raman enhancement was achieved using bimetallic⁴⁶ and magnetic⁴⁷ mesoflowers. Jena and Raj demonstrated a seedless, surfactantless synthesis route for the synthesis of fluorescent marigold like nanoflowers (Fig. 2B).³³

Polymers have also been used to synthesize metal nanoparticles.⁴⁸ Here the polymer acts as both reducing as well as stabilizing agent and nanoparticles are formed in-situ in the polymer matrix. Recently, stable mercury nanodrops and nanocrystals were synthesized in a poly(vinyl alcohol) thin film using mild thermal annealing.⁴⁹ Various optical and nonlinear properties of such polymer encapsulated nanoparticles in view of their potential applications have been reviewed recently.⁵⁰ A mirror image relation was observed in surface plasmon coupled CD spectra of gold nanoparticles grown on D- and L-diphenylalanine nanotubes. This unique phenomenon was rationalized by Jino George and George Thomas to be a result of orientational asymmetry of GNPs driven by chiral molecules on nanotubes.⁵¹ Sharma *et al.* have extensively investigated the stability, dynamics, dewetting and morphology of ultrathin nano-films and nanoparticles with a combination of theoretical, numerical and experimental techniques.²³ Catalysis using a reusable ‘Dip Catalyst’ employing silver nanoparticles embedded in a polymer thin film was demonstrated by Hariprasad and Radhakrishnan.⁵²

2.1.1.1 Noble metal quantum clusters. Chemistry of gold-sulphur interface on monolayer protected clusters (MPCs) has long attracted research interest. These materials have a nanosized metal core containing hundreds or thousands of atoms with monolayers of surfactants/ligands on its surface. The metal core made of dense packing of metal atoms forming nanocrystals with specific lattice planes on its surface.⁵³

Intensive research on thiolate protected noble metal plasmonic systems have culminated in the discovery of a new type of material, composed of a few atoms, called quantum clusters (QCs) or sub-nanoclusters. They are composed of tens to hundreds of atoms having a core size in the sub-nanometer regime. They possess discrete electronic energy levels and thereby show “molecule-like” optical transitions in absorption and emission

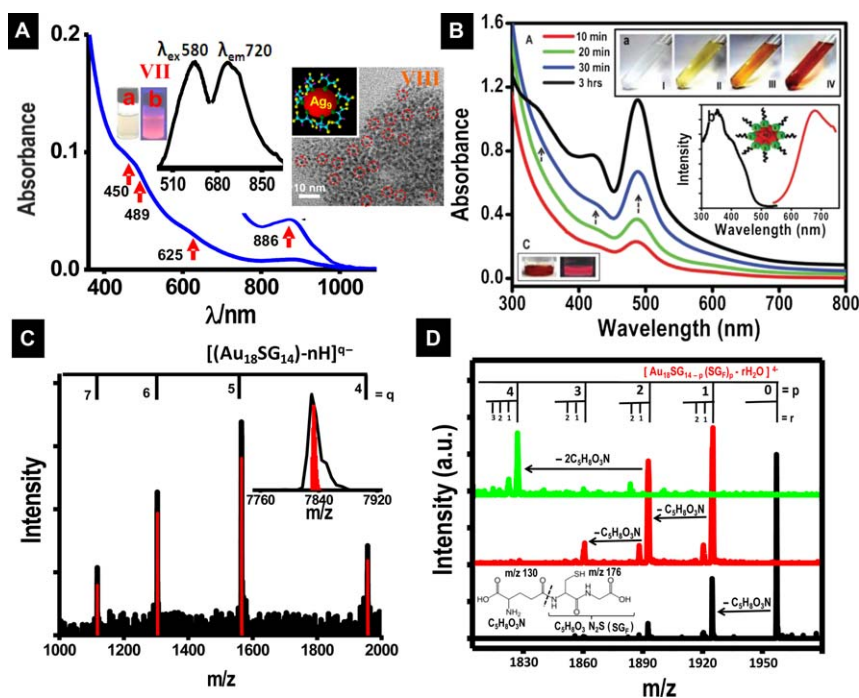


Fig. 3 (A) TEM image, UV-vis absorption spectra and luminescence spectra of $\text{Ag}_9(\text{H}_2\text{MSA})_7$ quantum clusters (adapted from Ref. 65). (B) UV-vis absorption spectra, luminescence profile of the as-synthesized $\text{Ag} \sim 75$ clusters. Photographs of the solution during various stages of reduction and that under UV light and visible light are shown in the inset (adapted from Ref. 67). (C) ESI MS spectrum of $\text{Au}_{18}\text{SG}_{14}$ in the negative mode (adapted from Ref. 62). (D) MS/MS spectra of $[\text{Au}_{18}\text{SG}_{14}]^{4-}$ with increasing collision energy.

behavior (Fig. 3A–B). Due to quantum confinement, they behave totally differently from metallic nanoparticles of the same element and are often considered to bridge the gap between atomic and nanoparticle behaviors. While theories such as Mie theory are used to describe optical properties of plasmonic nanoparticles, jellium model and time dependent density functional theory calculations explain molecule-like cluster dependent systems more precisely. Luminescence and bio-compatibility exhibited by these systems hold great promise in biological studies.⁵⁴ Among the diverse $\text{Au}:\text{SR}$ clusters synthesized, $\text{Au}_{25}(\text{SR})_{18}$ continues to be the most studied cluster due to its extraordinary stability and interesting optical, electronic and geometric properties. Habeeb Muhammed *et al.* observed fluorescence resonance energy transfer (FRET) between the metal core and ligand in dansyl chromophore functionalized $\text{Au}_{25}(\text{SG})_{18}$ cluster.⁵⁵ In another study, reactivity of $\text{Au}_{25}\text{SG}_{18}$ to externally added chloroaurate ions and various metal ions was investigated.⁵⁶ While addition of chloroaurate ions resulted in rapid decomposition of cluster to insoluble gold thiolate polymer, addition of metal ions did not show such an effect. Ligand exchange of $\text{Au}_{25}\text{SG}_{18}$ (SG-glutathione thiolate) was demonstrated by Shibu *et al.* for the first time.⁵⁷ Monodisperse Au_{25} clusters embedded in silica were synthesized from polydisperse glutathione-protected gold clusters (Au_mSG_n) by reaction with (3-mercaptopropyl)trimethoxysilane.⁵⁸ Dipeptide nanotubes have

been uniformly coated with glutathione protected Au₂₅ clusters and effect of electron beam irradiation on the growth of the clusters to form nanoparticles has been studied.⁵⁹ Various other clusters were also synthesized using diverse protocols. An interfacial route was developed for the synthesis of a bright-red-emitting Au₂₃ cluster from Au₂₅(SG)₁₈ via core etching, the resultant fluorescent Au₂₃ clusters were used for bioimaging of human hepatoma cells.⁶⁰ Clusters such as Au₁₅ could also be made in confined spaces such as cyclodextrin cavities (CD),⁶¹ by core etching of larger clusters and simultaneous trapping of the clusters formed inside the CD cavities. Recently a direct one step route based on slow reduction of the metal precursor was demonstrated by Ghosh *et al.* to make red luminescent Au₁₈SG₁₄ (Fig. 3C–D) in hundreds of milligram scale.⁶²

Synthesis of monolayer protected atomically precise clusters of other noble metals, especially silver, is one of the recent interests in this area. Mrudula *et al.* reported the synthesis of luminescent Ag clusters through the interfacial etching of mercaptosuccinic acid (MSA) protected silver nanoparticles, Ag@MSA, with guanine at the water-toluene interface.⁶³ Interfacial etching was also used by Uday and Pradeep to synthesize mercaptosuccinic acid (MSA) protected silver clusters such as Ag₇(MSA)₇ and Ag₈(MSA)₈ from plasmonic Ag@MSA nanoparticles.⁶⁴ A solid state route for the synthesis of Ag₉(H₂MSA)₇⁶⁵ (Fig. 3A) and Ag₃₂(SG)₁₉⁶⁶ in gram quantities has been developed. Here the reagents were mixed in the solid state which negates the effects due to diffusion of reactants in the growth step. Dhanalakshmi *et al.* synthesized a red luminescent silver cluster by the direct core reduction of the most widely studied class of silver nanoparticles, namely silver@citrate. No byproducts such as thiolates were detected during the synthesis resulting in nearly pure clusters. High temperature nucleation and growth of ~Ag₇₅SG₄₀ clusters (Fig. 3B) was reported by Indranath *et al.* recently.⁶⁷ An alloy cluster, Ag₇Au₆(MSA)₁₀ was also synthesized from the precursor, Ag₈MSA₈ using galvanic replacement of Ag atoms by Au(I).⁶⁸ A distorted icosahedral core is predicted for Ag₇Au₆(SCH₃)₁₀ from theoretical calculations.

Protein protected quantum clusters⁶⁹ are yet another category of materials which have wide variety of potential applications in optical and bioimaging areas. Such materials possess immense potential in terms of their utility for biolabelling⁵⁴ due to ease of synthesis and functionalization, biocompatibility, non-photobleaching, long fluorescence lifetimes, low toxicity, *etc.* Various noble metal clusters protected by proteins such as lactotransferrin (Lf)⁷⁰ and bovine serum albumin (BSA)^{71,72} have been reported. Recently, the growth process of these clusters inside the protein templates such as Lf and BSA was investigated using mass spectrometry by Chaudhari *et al.* Yet another ‘green’ approach towards the synthesis of clusters was demonstrated by Adhikari *et al.*⁷³ by reducing silver ion encapsulated peptide hydrogel under sunlight to produce fluorescent silver nanoclusters. Luminescent quantum clusters of copper capped in BSA with Cu₅ and Cu₁₃ cores were reported recently by Goswami *et al.*⁷⁴

2.1.1.2 Nanoparticle assemblies and superlattices. Fabrication of various nanoparticles into one, two, or three dimensional assemblies can lead to

novel properties due to their inter-particle coupling resulting in exotic applications. Such self-assembled superstructures, usually synthesized by lithographic techniques or self assembly protocols, are useful in studying specific properties such as SERS, metal-insulator transition, inter-plasmon coupling, *etc.* A method for the synthesis and assembly of ultrathin nanocrystalline films of metals (gold, silver), metal chalcogenides and oxides at various liquid-liquid interfaces have been developed by Rao *et al.*⁷⁵ The inter-nanoparticle coupling observed in an ordered nanoparticle array can be tuned by the choice of the 'linker' molecule and its properties. Assembly and thermo-mechanical properties of various polymer grafted nanoparticles have been studied by Jaydeep *et al.*^{76,77} Furthermore, choice of the dispersing polymer medium, polymer grafting density, molecular weight, *etc.* determines their utility for realising devices. Chattopadhyay *et al.*

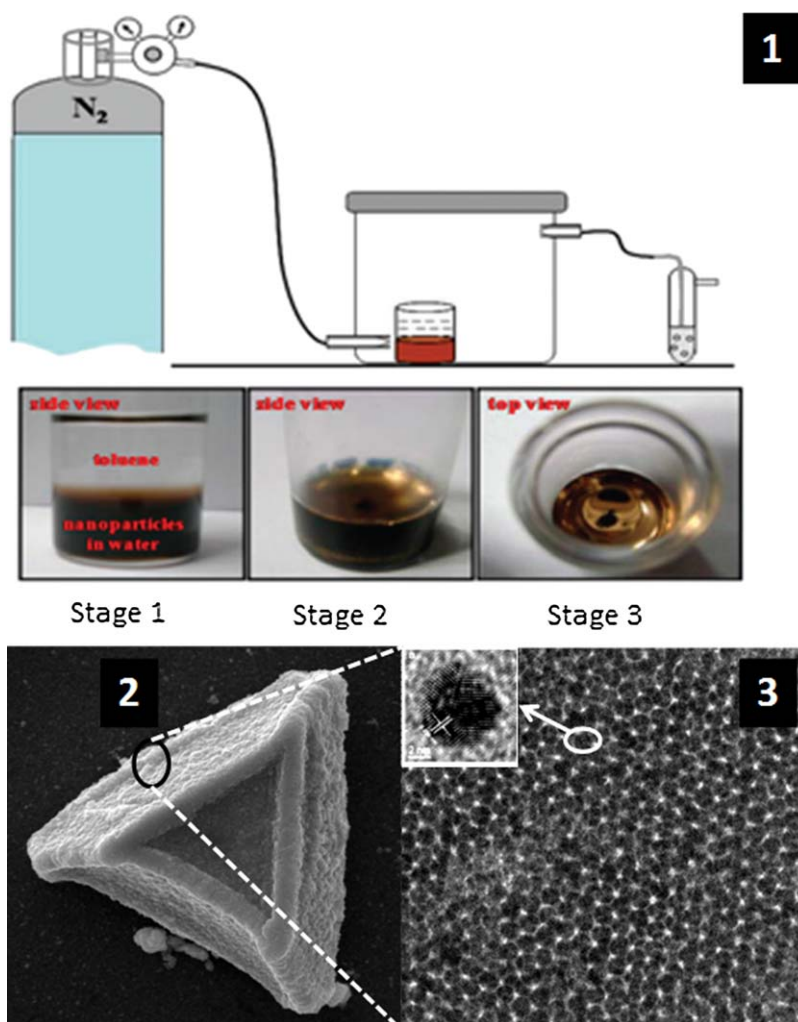


Fig. 4 (1) Cartoon representation of the setup used for the SL formation (adapted from Ref. 86). (2) SEM image of a Au NP superlattice. (3) TEM image of a corner of superlattice. Inset shows TEM image of a single nanoparticle in the superlattice (adapted from Ref. 87).

demonstrated a new form of lithography for imprinting coloured patterns using CdS quantum dots.⁷⁸ Exposure of H₂S gas to a transmission electron microscope grid placed on a poly(vinylpyrrolidone) film leads to a yellow luminescence pattern of CdS nanoparticles on the exposed parts of the film which results in organized arrays of quantum dots in two dimensions. A 2D array of patterned Au-Ag composite nanoparticles was developed using commercially available compact disks (CDs) and digital versatile disks (DVDs) as templates.⁷⁹ Direct write techniques reduce the processing steps involved and provide better control of the properties of nanoparticles. Micro- and nanoscale patterns of various metals anions and their alloys complexed with tetraoctylammonium bromide (TOABr) was realized as direct write precursors in e-beam and soft lithography processes.⁸⁰ Here, the interaction between the anion and TOABr being mainly electrostatic, patterned regions can be easily removed by thermolysis on a hot plate in ambient air. Recently, Radha and Kulkarni developed an electrical rectifier device (diode) using Au nanoparticle array stripes employing the above direct write approach.⁸¹

Well defined arrays of monodisperse nanoparticles having long range order, called superlattices, have been studied.^{82,83} Various synthetic protocols have been reported such as digestive ripening,⁸⁴ self organization at the interface⁸⁵ *etc.* to name a few. Triangular 3D superlattices of gold nanoparticles protected by mercaptosuccinic acid and their fluorescein labeled analogues were reported.^{85,86} Shibu and Pradeep illustrated the applicability of functional gold nanoparticle superlattices⁸⁷ (Fig. 4) as good SERS substrates and these superlattices have been used for gas adsorption.⁸⁶

2.1.2 Inorganic nanostructures. For the past two decade, nanomaterials based technologies have been widely used for the construction of new devices for harvesting light energy. As the particle size decreases below the Bohr radius in a semiconductor material, an increase in the band gap energy is seen due to the confinement of electrons. Hybrid materials made of semiconducting nanomaterials provided innovative strategies for designing light harvesting systems. Various classes of semiconducting nanoparticles such as cadmium chalcogenides (CdS, CdSe, CdSeS), zinc oxides and zinc chalcogenides (ZnS, ZnSe) exhibit amazing properties in the quantum size regime. Kinetics⁸⁸ and mechanism of growth⁸⁹ of ZnO nanocrystals in solution has been studied in detail. Size control of such systems allows tuning of their optical and electronic properties due to variation in their band gap. Doping magnetic impurities like Mn into CdS nanocrystals⁹⁰ and Zn_xCd_{1-x}S alloy nanocrystals⁹¹ allows modification of their inherent properties which can lead to new electronic, optical and magnetic devices. Quantum dot-quantum-well nanostructures having cores/shell ZnS/CdSe/ZnS layers were synthesized (Fig. 5A–B) and their tunable photoluminescence was demonstrated.⁹² Reversible phase transition between wurtzite and zinc blende phases of platelet-shaped ZnS nanostructures by insertion or ejection of dopant Mn(II) ions was reported *via* a thermocyclic process.⁹³ Sarma *et al.* have reported for the first time the generation of white light from a simple Mn²⁺-doped CdS semiconducting nanocrystals (Fig. 5C), by suitably tuning the relative surface-state emissions of the

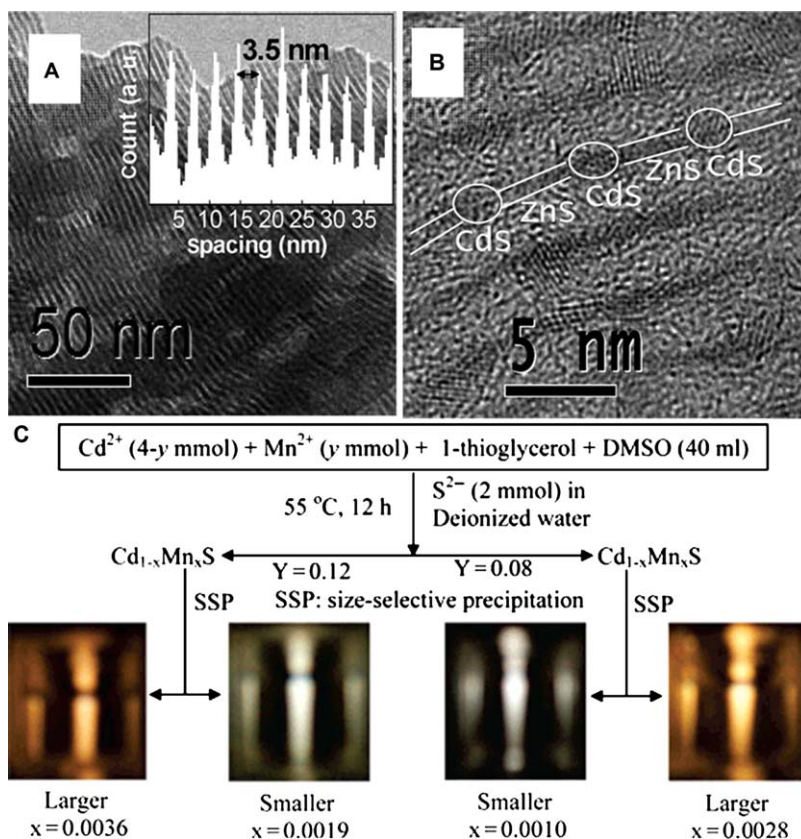


Fig. 5 (A) and (B) are the TEM images of a 2D supercrystalline parallel assembly of $(\text{-ZnS-CdS-ZnS-})_n$ superlattice wires. Inset: statistical distribution of superlattices demonstrating an ultrahigh pitch density of 3.5 nm (adapted from Ref. 95). (C) Schematics of the reaction strategy for making Mn^{2+} doped light emitting CdS nanocrystals (adapted from Ref. 94). Photographs in 'C' showing 0.10 and 0.19% Mn^{2+} -doped CdS NCs producing white light upon excitation at 365 nm, whereas 0.28 and 0.36% doping produces yellow emission upon excitation at 383 nm.

nanocrystal host and the dopant emission.⁹⁴ Zero, one, and two-dimensional shape-dependent confinement in PbS nanostructures resulted in distinguishable far-field optical polarizations due to different geometries.⁹⁵ Shape dependent change in blue-green photoluminescence of ZnO nanostructures was probed by Ghosh *et al.*⁹⁶ An ultrahigh density two dimensional semiconductor superlattice array composed of periodic quantum wells with a barrier width of 5 nm by ZnS and a well width of 1-2 nm by CdS particles was synthesized *via* a general synthesis route.⁹⁷ An electrochemical DNA biosensor for the detection of chronic myelogenous leukemia was achieved using Langmuir-Blodgett monolayers of CdSe quantum dots synthesized on an indium tin oxide (ITO) coated glass substrate.⁹⁸

Intrinsically non-magnetic inorganic materials were found to exhibit room temperature ferromagnetism as their size is brought down to nanoscale. These materials include simple nonmagnetic oxides like CeO_2 , Al_2O_3 , ZnO , In_2O_3 and SnO_2 ⁹⁹ as well as complex superconducting oxides such as $\text{YBa}_2\text{Cu}_3\text{O}_7$.¹⁰⁰ Surface ferromagnetism, which arises from surface defects,

was also observed in NPs of metal nitrides and chalcogenides and is now considered to be a universal phenomenon. A detailed discussion of such systems is available in a review by Sundaresan and C. N. R. Rao.¹⁰¹ Multiferroics, which exhibit ferromagnetism as well as ferroelectricity, are another group of interesting materials. Detailed powder XRD analysis of such a nanocrystalline multiferroic, BiFeO₃, led Vijayanand *et al.* to infer that Fe₃O₄ as the magnetic impurity phase responsible for its high room temperature ferromagnetic moment.¹⁰² Antiferromagnetic coupling along S-Ni-S chain in layered nickel alkanethiolates was probed by John *et al.*¹⁰³

Chemical synthesis of graphene mimics from layered inorganic compounds and their applications is one of the emerging areas of research. Three different chemical routes for the synthesis of graphene analogues of Mo and W disulphide¹⁰⁴ and diselenide¹⁰⁵ was reported by Matte *et al.* Characteristic absence of (002) reflection and shift and broadening of the Raman bands are common feature of these materials. Synthesis of another graphene analogue of BN with control over number of layers along with its property studies was reported by Nag *et al.*¹⁰⁶ All these inorganic graphene analogues exhibit room temperature ferromagnetism. Formation of a new few layer graphene analogue, B_xC_yN_z having a composition between BCN and BC₂N, was achieved by reaction of activated charcoal, boric acid and urea.¹⁰⁷ This material possesses better CO₂ and CH₄ uptake ability than both activated charcoal and graphene. MoS₂ among these materials has been used for application in field effect transistor devices. The reason behind hysteresis observed in these devices was rationalized recently to be a combined effect of absorption of moisture combined with high photosensitivity of MoS₂.¹⁰⁸

2.1.3 Carbon nanomaterials. Carbon nanomaterials with their exciting electronic properties and application possibilities have fascinated scientists over the globe for decades. Graphene, the newest member of the nano-carbon family consisting of a single layer of hexagonally arranged carbon atom array, has caused significant stir in this pool already. Exciting new properties like quantum Hall effect at room temperature, an ambipolar electric field effect along with ballistic conduction of charge carriers, tunable band gap, and high elasticity and associated applications have come about which have turned graphene into a super-material. Indian scientists are not lagging behind to join this excitement and have contributed significantly in developing graphene based new applications.

There have been two main directions of graphene research in the country. Synthesis of graphene and graphene-composites by easy methods and from cheap sources is one of the trends.¹⁶ Other one is concerned with the discovery new properties and novel applications. John *et al.* reported the formation of single and few layer graphene on stainless steel substrates by direct thermal CVD process.¹⁰⁹ Ethanol was used as the source of carbon in this process. Dey *et al.* demonstrated a facile and rapid formation of reduced graphene oxide (RGO) sheets from graphene oxide (GO) using Zn/acid at room temperature,¹¹⁰ whereas a method for the synthesis of water soluble functionalized graphene sheets from GO was reported by Mhamane *et al.* using plant extract.¹¹¹ Production of graphene has also been achieved

by exfoliation using focused solar radiation.¹¹² Microwave irradiation induced co-reduction of graphene oxide and Pt was used to produce graphene supported Pt catalysts. Defect sites on reduced GO are found to serve as anchor points for the heterogeneous nucleation of Pt.¹⁰⁹ Graphene was recently produced from cheap starting materials like sugar¹¹³ and asphalt¹¹⁴ on silica support. This graphene coated sand was found to be very effective in water purification. A review of environmental and biological applications of graphene by Sreeprasad and Pradeep was published recently.¹¹⁵

Multidimensional applications of graphene have been reported from India in the recent years. It has been used in drug delivery as an effective nanocarrier for tamoxifen citrate (TrC), a breast cancer drug.¹¹⁶ It has also been used in catalysis, for the oxidation of alcohols, by linking them with an oxo-vanadium Schiff base.¹¹⁷ Carboxyl and hydroxyl functionalized multilayered graphene, produced from multiwalled CNT has shown unique urea sensing ability.¹¹⁸ Both RGO and graphene nanoribbons (GNRs) are demonstrated to be potent infrared photodetectors.¹¹⁹ Graphene, known to be a quencher was molded into an optical bifunctional material by Gupta *et al.* by linking Eu(III) cations. Electron microscopic characterization of the material is shown in Fig. 6A–D. This material was shown to quench the luminescence of Rhodamine-B while it retained its own red emitting property. This dual nature of the material can be very useful for biosensing and optoelectronic applications.¹²⁰ Graphene has also been used for the fabrication of inexpensive and efficient solar cells. Significant improvement in organic photovoltaic (OPV) characteristics was reported in a blend of graphene quantum dots and a regioregular polymer.¹²¹ Graphene-polyvinyl fluoride polymer composite films were shown to exhibit real time strain response. Nanoscale mechanical deformation in this composite films result in change in the electrical properties of the films and enables it to act as strain sensor.¹²² Saha *et al.* synthesized graphene quantum sheet with dimensions ranging from 2–5 nm. These quantum sheets exhibited

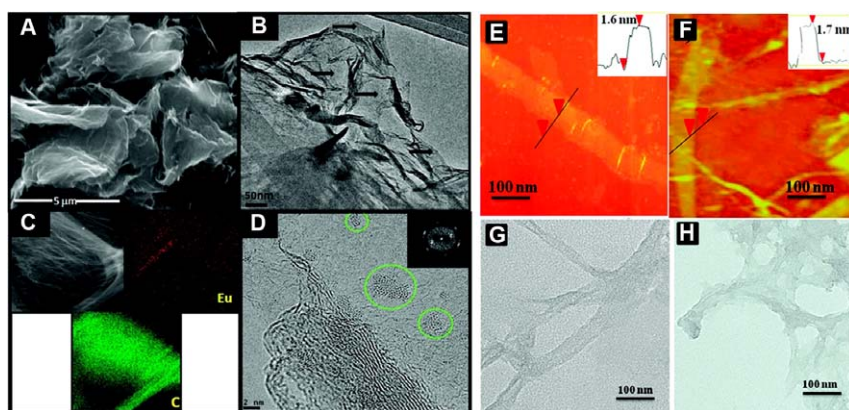


Fig. 6 (A) SEM and (B) TEM images of europium complexed graphene. (C) Eu and C EDS mapping from a selected area. (D) HRTEM image of showing hexagonal graphene lattice. FFT pattern is shown in the inset. (adapted from Ref. 120). AFM image of graphene nanoribbons synthesized by the electrochemical unzipping of MWCNT at (E) 0.7 and (F) 0.5 V. TEM images of (G) partially and (H) completely transformed MWCNT (adapted from Ref. 129).

exceptional magnetoresistance which can be used in spintronic devices.¹²³ Use of graphene for hydrogen storage was demonstrated where hydrogen was found to be chemically linked with sp^3 -carbon.¹²⁴ A new type of gas sensor was fabricated by Pd-Pt nanoparticle-graphene composite by monitoring the change in conduction of graphene layers upon gas adsorption.¹²⁵ Graphene oxide has even been used as a carbocatalyst for Michel addition reaction.¹²⁶ Covalently linking graphene with emerging materials with functions such as quantum clusters will generate new possibilities.¹²⁷ Use of graphene for water purification and in devices are covered under sections 3.1 and 3.4, respectively.

Carbon nanotubes (CNTs), much like graphene, have been shown to exhibit novel phenomena and been used for a diverse array of applications. Voggu *et al.* reported a simple, yet effective method for the separation of metallic and semiconducting single walled CNT (SWCNT) from a solution containing potassium salt of coronene tetracarboxylic acid. Metallic tubes precipitate while semiconducting ones remain in solution, which can be used for the separation of these two varieties even without centrifugation.¹²⁸ Electrochemical unzipping of multi-walled CNT (MWCNT) to produce high quality graphene nanoribbons (GNRs) was reported by Shinde *et al.*¹²⁹ AFM and TEM images of unzipped GNRs are presented in Fig. 6G–H. Similar unzipping of MWCNT was observed upon shining an excimer laser also.¹³⁰ Decoration of GNRs with very small CdSe QDs was attained recently by *in-situ* electrochemical unzipping of MWCNTs.¹³¹ Viscosity of a flocculated suspension containing of MWCNT at very low weight fractions (approximately 0.5%) was found to jump sharply by four to six orders of magnitude upon varying shear stress. Manipulation of mechanical strength and transport properties of nanostructured composites can be achieved by understanding this phenomenon.¹³² CNTs have been used for molecular detection and removal of toxic chemicals. Electrochemical sensing of ascorbic acid was achieved using a modified gold electrode. The electrode was coated with polyaniline and carboxylated MWCNT was covalently attached to ascorbate oxidase and easy detection of ascorbic acid was possible.¹³³ Femtomolar detection of a herbicide, 2,4-dichlorophenoxy acetic acid (2,4-D) was obtained by conductance modulation in a liquid-gated field effect transistor with SWCNT as an active element.¹³⁴ Mishra and Ramaprabhu fabricated a magnetite-MWCNT (Fe_3O_4 -MWCNTs) nanocomposite and used the supercapacitor nanocomposite for the removal of high concentration of arsenic (both arsenate and arsenite). The composite was also effective for desalination of seawater.¹³⁵ Phosphonated MWCNT has been used in polymer electrolyte fuel cells with polybenzimidazole with enhanced efficiency.¹³⁶ Single-walled carbon nanotubes (SWCNTs) covalently functionalized with uracil were observed to self-assemble into regular nanorings with a diameter of 50–70 nm. These nanorings were formed by two bundles of CNTs interacting with each other *via* uracil-uracil base-pair which is most likely to find application in advanced electronic circuits.¹³⁷ Acid functionalized carbon nanotubes decorated with Rh nanospheres was demonstrated to have superior field emission characteristics in terms of high current density at an ultra-low threshold which is better than both the component structures.¹³⁸ Small interfering RNA was found to strongly bind

to SWCNT surface *via* unzipping its base-pairs which can be used for the delivery of these SiRNAs.¹³⁹

2.1.4 Organic nanostructures. Nanomaterials research in India mostly used to deal with manipulation of inorganic materials until recently. Organic materials, with their tunable photophysical properties are gaining much more attention lately and research on soft nanomaterials like assembled organic frameworks and hydro/organo-gels is growing rapidly in India. Ayyappanpillai Ajayaghosh has used supramolecular chemistry of functional dyes and π -conjugated systems to create nanostructured self-assemblies, organogels, light-harvesting assemblies and chemosensors. Formation of well defined ring and fiber shaped nanostructures through self assembly approach was reported by his group.¹⁴⁰ Folding of chiral π -conjugated oligomer having alternate bipyridine and carbazole moieties connected through acetylenic bonds into helical form was reported by the same group. Defolding of helical conformation was observed in presence of transition metal ions, while addition of EDTA helps in regaining the helical conformation.¹⁴¹ Formation of self-assembled aligned fibers using supramolecular gels based on trithienylenevinyls was demonstrated by Prasanthkumar *et al.* which highlighted the role of self assembly and gelation on the electronic property of semiconducting molecular gelators.¹⁴² AFM images and I-V characteristics of such gelators are shown in Fig. 7A–D. They also reported high metallic conductivity in oligo(thienylenevinylene) (OTV) based gelators, which are expected to be good candidates for bulk heterojunction devices.¹⁴³ Rao *et al.* reported the formation of cylindrical micelle in water. These long nanofibers formed by assembly of noncovalent donor-acceptor (D-A) pair forms hydrogel at higher concentration of D-A pair.¹⁴⁴ Concentration dependent spontaneous self-assembly formation in octupolar oxadiazole derivatives to produce spheres to fibrous gels was reported by Varghese *et al.*¹⁴⁵ They also studied the photophysical and liquid crystalline behaviour of these self organized structures.

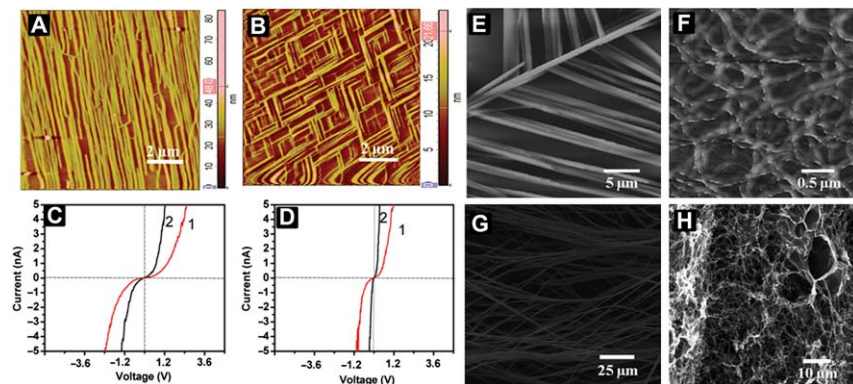


Fig. 7 AFM images of (A) TTV4 and (B) TTV5 from decane drop casted on freshly cleaved mica surface (adapted from Ref. 142). *I-V* curves of undoped (C) and doped (D) xerogels of OTV1 (1) and OTV2 (2) (adapted from Ref. 143). AFM (E and F) and SEM (G and H) of organogels formed in different organic solvents (adapted from Ref. 150).

Differences in gelation habits of organogels from derivatives of oligo(p-phenylene vinylene) (OPV) was linked to the fact that whether they can establish hydrogen bonds with adjacent OPV molecules or with the solvent.¹⁴⁶ Tunable excited-state properties of a π -acceptor- π -donor-type fluorophore with a bipyridyl moiety was exploited by Sreejith *et al.*¹⁴⁷ to respond to different analytes. Ultratrace level detection of TNT was attained very recently by a similar method which uses organogel paper strips.¹⁴⁸ Naked eye detection of fluoride ions using a fluorescent organogel was reported by Rajamalli and Prasad.¹⁴⁹ The detection process includes a reversible gel-sol transition associated with change in color in presence of fluoride ions. Vidyasagar *et al.* found that two sugar-based supergelators can congeal oils to produce highly transparent gels having low UV transmittance and high visible transmittance which make them suitable for soft optical devices.¹⁵⁰ AFM and SEM characterization of these gels is presented in Fig. 7G–H. A method for reversible shape transformation of organic waveguides to form 2D nanosheets, 1D nanotubes, and 0D nanorings was reported recently by Chandrasekhar *et al.*¹⁵¹ Both nanotubes and nanosheets act as waveguides and changes direction of incident laser light in a shape-dependent manner. The nanosheets were turned into nanotubes and subsequently into nanorings with the addition of water to the solvent, whereas nanotubes were converted back to nanosheets through ultrasonication. CD studies revealed the induction of chirality into π -stacked dialkoxynaphthalene (DAN)-fiber made up of achiral building blocks through supramolecular co-assembly with helical naphthalenediimide (NDI)-fiber.¹⁵² Organogel-hydrogel transformation by a simple method was achieved by Kar *et al.*¹⁵³

Integration of graphene^{154,155} and other carbon nanostructures¹⁵⁵ with these organogels has been achieved. The composites formed through supramolecular interaction exhibit higher rigidity than the parent gel systems. Synergistic effects in these composites enable them to exhibit interesting optical, mechanical, thermal and electrical properties and opens up a new door of possibilities.

2.2 Theoretical and computational inputs

Computational materials science provides valuable insights into the structure and bonding in a material which in turn dictate its spectroscopic property and reactivity. In nanomaterials, where quantum confinement results in the emergence of new phenomena, theoretical and computational inputs are of larger significance for a better understanding of the systems. Computational material scientists in India have provided immense support towards understanding of experimental results which has helped in the growth of nanoscience and nanotechnology in the country.

Possibility of using few layer graphene for chemical storage of hydrogen was probed through first-principles calculations.¹²⁴ This study offers insight into the mechanism of dehydrogenation of hydrogenated graphene produced by Birch reduction. The dehydrogenation was proposed to occur through a possible reconstruction and relaxation of the hydrogenated graphene lattice, which showed the presence of sp^3 C–H bonds. First-principles simulations have also been used to determine structure, phonon dispersion,

and elastic properties of graphene analogues of BN.¹⁰⁶ Metal oxide and magnetic NPs were found effective in tailoring electronic structure of graphene. First principles calculations linked charge transfer between the NPs and graphene with the change in electronic and magnetic properties.¹⁵⁶ Calculations have shown that the unusual pesticide uptake capacity of graphene is due to the interaction between the two mediated by water.¹⁵⁷

Interaction between single walled carbon nanotube (SWCNT) and α -helix was probed using classical molecular dynamics (MD) simulation by V. Subramanian *et al.*¹⁵⁸ Breakage of hydrogen bonds in the α -helix was observed, which leads to conformational transitions ($\alpha \rightarrow$ turns). His group also tried to relate the curvature of carbon nanomaterials (NMs) with their α -helix breaking tendency.¹⁵⁹ Their results show that the extent of helix breakage induced by carbon nanomaterials is inversely proportional to their curvature; *i.e.*, the tendency for helix breaking is minimum for the CNT and maximum for the graphene sheet. Srinivasu and Ghosh used *ab-initio* first-principles calculations to investigate lithium-dispersed two-dimensional carbon allotropes, *viz.* graphyne and graphdiyne, for lithium and hydrogen storage applications.¹⁶⁰ They have also shown that these planar carbon allotropes can be used in nanoelectronics as tuning their band gap is possible by varying the number of acetylenic bridging units.

Significant effort has also been directed towards understanding the structure, bonding and reactivity of metal clusters through computational methods and tools. Most of these studies have been directed towards the study of gold clusters. Pundlik *et al.* investigated the electronic structure and magnetic moment of gold quantum clusters (Au_n ; $n = 12, 13, 24, 25$) using first-principles plane-wave density functional theory.¹⁶¹ Stability and magnetic moment in these clusters were explained in terms of degeneracies of the HOMO and LUMO levels and Jahn-Teller activity. Probing of reactivity¹⁶² and finite temperature behaviour¹⁶³ of Au_n clusters were demonstrated by Sourav Pal. Mammen *et al.* demonstrated that the morphology of gold clusters can be tuned through doping of the substrate taking Au_{20} as a model cluster.¹⁶⁴ DFT calculations showed that catalytically active planar geometry of Au_{20} is favored over its tetrahedral geometry if the MgO substrate is doped with Al. Reactivity enhancement of a closed-shell Au_8 cluster was observed by Jena *et al.* when an Au atom was replaced by a H atom.¹⁶⁵ H-doping enhances the binding efficiency of O_2 with the cluster and reduces the barrier for CO oxidation. Computational study of other metal clusters has also been reported. Size dependent reactivity of aluminium clusters with N_2 was reported by Kulkarni *et al.*¹⁶⁶ Structural stabilities of small 3d late transition metal clusters was probed by first principles DFT calculations by Datta *et al.* While Co was found to show unusual stability in hexagonal closed pack stacking, other metals prefer icosahedral structures. This structural preference was reported to be a combined effect of magnetic energy gain and s-d hybridization.¹⁶⁷ Molecular dynamics simulation has been used in understanding the clustering of ionic liquids at room temperature by Sarangi *et al.*¹⁶⁸

Among other computational studies related to nanoscience, it is notable to mention the work of distance dependence of FRET by Swathi and

Sebastian where they have shown non- R^{-6} type behavior in the case of graphene.¹⁶⁹

3 Applications of nanomaterials

3.1 Environmental applications and sensing

Inherent properties of nanostructured materials such as large surface area and surface energy, presence of catalytic/reactive sites and modified electronic structures are used for several environmental applications. It is either enhancement of the bulk properties to increase the overall efficiency or enhancing the kinetics of a given event to make it happen at acceptable temperature or completely new phenomena at the nanoscale which can lead to applications. In the case of nanoscale matter, the quantity of material required for a given application is much smaller. Because of this, noble metal NPs, once considered impossible to be used for mundane applications such as water purification, are increasingly recognized as useful and affordable solutions. This is also due to the realization that noble metals in the bulk have been used for millennia for applications such as water disinfection and risks of toxicity are relatively less with them in comparison to artificial nanomaterials. This can be illustrated with the example of silver which has been a potent antibacterial material in the ionic form. Nanoparticles of silver under favourable conditions can release silver ion (Ag^+) at a steady concentration of around 40 ppb at around 300 K.¹⁷⁰ This concentration of Ag^+ is antibacterial for a wide spectrum of bacteria, if incubated for a few hours. A practical Ag^+ releasing composition requires only 40 $\mu\text{g/L}$ or 40 mg/kL of microbially safe water. This amounts to a composition of nearly 432 mg for 3600 L of water, approximately the yearly drinking water consumption for a small family (10 L/day). Considering an effective release of 10% of silver, the consumable cost required for such a device is within the affordable limit of everyone. Combining the chemistry of diverse nanomaterials for capturing heavy metal contaminants, pesticides, organics and anions, a nanomaterials based drinking water solution is indeed possible. The advantage of such a solution is also from the point-of-use application in countries where reliable piped-water supply is not available. These solutions work in the absence of electricity, another added advantage. Although materials involved are complex in their structure and function, they can be made with simple approaches and therefore production can be decentralized. Due to all these advantages, a few such solutions have already been implemented in India with home-grown technologies.

The use of noble metal NPs in water purification for applications other than microbial disinfection was first reported in 2003.¹⁷¹ The chemistry reported can be summarized as reductive de-halogenation of chlorocarbons (halocarbons in general) in water solutions occurring at room temperature over silver nanoparticles wherein the C–Cl bond is cleaved with the formation of AgCl . UV-visible spectroscopic analysis of this reactivity is shown in Fig. 8A. A series of chemical events occur on the nanoparticle and amorphous carbon is observed as a product. This chemistry was soon extended to halogenated pesticides at high efficiency.^{172,173} A concentration of 50 ppb chlorpyrifos was reduced to less than 0.5 ppb upon passing over a

filter made of supported noble metal particles which can be observed from the gas chromatogram presented in Fig. 8B. On stable supports, no NP release was observed in water. In commercial implementation of the technology, NPs are used along with activated carbon so that reaction byproducts, desorbed species, *etc.* can be removed from drinking water. A photograph of such a filter is shown in Fig. 8C. The interaction of pesticides on NPs is being explored even today from which new insights on molecular steps are available.¹⁷⁴ There are several related technologies in the market place. One involves the anchoring of NPs on cheaper substrates such as rice husk silica and to make ceramic candles. It is also worthwhile to mention the use of porous structures such as clay bricks (terracotta) for antimicrobial applications. Several filtration technologies have also come about such as polysulfone based domestic nanofilters for removing microbial contamination and ceramic filters for the removal of particulate matters

The most recent developments in this area tend to use graphene for such applications. Most of these efforts have been concentrated on using the exceptional surface area of 2D graphene (RGO/GO) to use it as an adsorbent. An *in situ* strategy to synthesize and immobilize graphenic adsorbent materials onto sand particles was recently reported by Sreepasad *et al.* starting from asphalt. The synthesized adsorbent was reusable for several cycles and it was found to be highly effective for the adsorption of dyes and pesticides from water.¹¹⁴ Sen Gupta *et al.* obtained similar graphene-sand composites using sugar as the source of graphene.¹⁷⁵ Raman spectroscopic evolution, SEM images and EDS analysis of pesticide

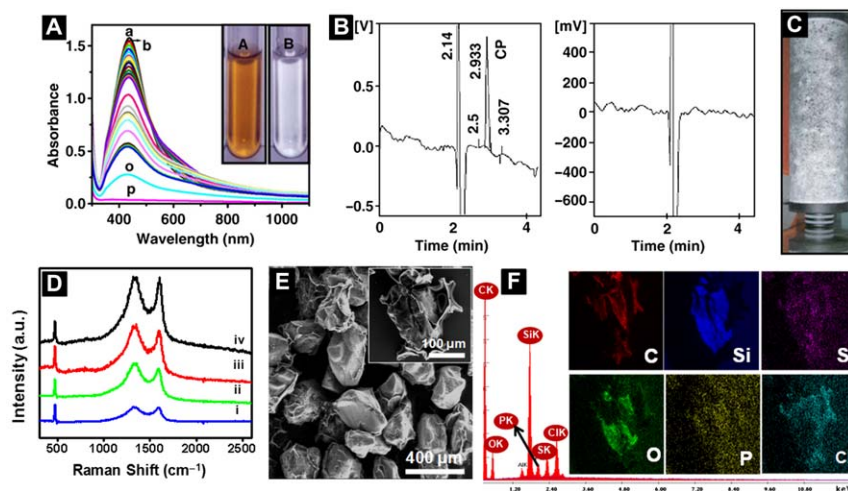


Fig. 8 (A) Variation of UV-visible absorption spectrum of Ag NP with the addition of carbon tetrachloride (adapted from Ref. 171). (B) Gas chromatogram of 50 ppb chlorpyrifos extracted in hexane before after passing through silver NPs supported on alumina. Disappearance of CP peak indicates the complete degradation of CP by Silver NPs (adapted from Ref. 173). (C) Photograph of a pesticide filter device made by using supported NPs. (D) Raman spectra of graphene-sand composite made from sugar under different heating conditions. (E) SEM image of graphene-sand composite made from sugar. Inset shows one graphene coated sand particle after absorption of chlorpyrifos. (F) EDS analysis showing adsorption of pesticide chlorpyrifos on the graphene-sand composite (adapted from Ref. 113).

adsorption by the composite are shown in Fig. 8D–F. Ramesha *et al.* demonstrated the use of GO and RGO for the removal of different anionic and cationic dyes from aqueous solutions.¹⁷⁶ Maliyekkal *et al.* found that RGO and GO can function as efficient adsorbent for pesticides and thereby can be used for the removal of pesticides from water.¹⁵⁷ The adsorption capacities reported for different groups of pesticides like chlorpyrifos (CP), endosulfan (ES) and malathion (ML) were as high as ~1200, 1100 and 800 mg/g, respectively. RGO showed 10–20% higher affinity compared to GO, indicating that increased surface oxygen functionality reduces the affinity of graphenic surface to pesticides. Theoretical calculations indicated the dependence of adsorption on the presence of water molecules. A versatile strategy for the synthesis of various metal/metal oxide graphene composite at room temperature and the utility of these composites for the removal of heavy metals were demonstrated by Sreepasad *et al.*¹⁷⁷ A green strategy was also devised to immobilize these composites onto cheap substrate like sand for easy post treatment handling. An abundant and environmental friendly biopolymer, chitosan was used for immobilization, thus avoiding harsh reactants and reaction conditions. Practical utility of these composites was showed in the form of enhanced removal efficiency over some common adsorbents. A graphene based composite consisting of antibacterial bio-polymer chitosan and a bactericidal protein was fabricated recently utilizing the rich abundance of functional groups.¹⁷⁸ The composite showed a tendency to form self-standing films which can aid in coating this composite onto suitable substrates for its practical applications in water treatment.

Water purification also requires ultrasensitive detection of ultratrace contaminants. Plasmonic noble metal nanoparticles are already known to be promising sensors for organic impurities^{172,179} and toxic metal ions.¹⁸⁰ Quantum clusters of noble metals have recently been used as nanosensors for toxic ions like Cu(II),¹⁸¹ Hg(II)¹⁸² and As(III)¹⁸³ with very high sensitivity.

Sensor research in India has extended to areas of security and safety as well. The national program on explosives utilizes nanomaterials and Microelectromechanical Systems (MEMS) based detection strategies. Ramgopal Rao has used various nanomaterials based sensors for low level detection of vapors of nitro compounds and explosives.^{184–186} Venkatramaiah *et al.* recently developed a fluoranthene based fluorescent chemosensor for ppb level detection of picric acid.¹⁸⁷ In this context, spectroscopy based sensors using self assembled nanostructures⁸⁶ and anisotropic nanomaterials^{46,188} have shown potential applications. Ajayaghosh *et al.* developed an attogram sensor for TNT using fluorescent organogelator.¹⁴⁸ Several orders of magnitude improved visual sensing of TNT was demonstrated recently using mesoflowers.¹⁸⁹

3.2 Nano and energy

Increasing demand for energy remains one of the major problems of humankind. With the limited and decreasing reserve of fossil fuels, research on clean alternate energy sources is increasing globally. A significant part of research activities have gone into exploring new ways of energy production. In a developing country like India with its huge population, demand for

energy is huge. Yet, India lags far behind in alternate and renewable energy production in comparison to developed countries and its developing neighbors. There has been some activity in the last few years in India to use nanomaterials for energy production, storage and waste energy harvesting; most of which started with the initiatives of Nano Mission of the Department of Science and Technology.

Various nanomaterials have been used in solar cells to increase their conversion efficiency. Kaniyoor *et al.* used a polyelectrolyte based soft functionalization technique to produce functionalized graphene and used it for efficient tri-iodide reduction.¹⁹⁰ Sudhagar *et al.* reported 145% increase in the performance of hierarchical nanostructured TiO₂ photoanode through N-ion implantation in a CdSe QD sensitized solar cell.¹⁹¹ Possibility of replacing Pt with cheap alternatives like graphene supported Ni NPs was reported by Bajpai *et al.*¹⁹² Guchhait *et al.* were able to increase the conversion efficiency of PbS based solar cells by several folds by the introduction of TiO₂ nanostructures.¹⁹³ Resonance energy transfer in ZnO NP-based in dye sensitized solar cell and the effect of high energy photons in solar radiation on such a cell was probed by Makhal *et al.*¹⁹⁴ Nanomaterials have also found their way into fuel cell research. Iron nitride-doped carbon nanofiber was produced by Palaniselvam *et al.* to use as cathode electrocatalyst for proton exchange membrane fuel cells. Unique cup-stake structure of this material had resulted in more number of active sites which in turn increased the oxygen reduction efficiency.¹⁹⁵ They also produced an artificially designed membrane incorporating phosphonated MWCNTs and were able to obtain 50% improved proton conductivity for polymer electrolyte fuel cell.¹⁹⁶ Ghosh and Raj produced flower-like Pt NPs supported on MWCNTs by an *in-situ* wet chemical route. The material was demonstrated to be catalytically active for both oxygen reduction and methanol oxidation.¹⁹⁷ Rao and Viswanathan observed high power density as they fabricated a membrane electrode assembly incorporating ultrasmall Pt NPs into carbon electrodes.¹⁹⁸

Nanoscale thermoelectric materials have attracted attention due to their increased conversion efficiency than the bulk counterparts. Silver chalcogenides are an interesting class of narrow band gap semiconductor for thermoelectric applications. Samal *et al.* demonstrated a room temperature solution phase method for the synthesis of Ag₂Te NWs by the direct reaction of Te NWs with AgNO₃ and examined their thermoelectric performance.¹⁹⁹ Formation of heterostructured dumb-bell shaped NWs in this system by simple post-synthetic annealing was reported by Som and Pradeep.²⁰⁰ Datta *et al.* reported the synthesis of nanocrystalline Bi₂Te₃ and Sb₂Te₃ and their alloys with spherical and flake-like morphology and examined their thermoelectric performances.²⁰¹ Paul *et al.* examined the enhancement of thermoelectric properties of PbTe through energy filtering with embedded Ag nanodots. Their study revealed that energy filtering of the carriers was facilitated by embedded Ag nanodots.²⁰²

Prakash *et al.* develop a new route to synthesize nanodimensional Li₄Ti₅O₁₂ by solution combustion method, in a single step within a minute. The Li₄Ti₅O₁₂ produced by this method were used in the lithium ion batteries with high capacity.²⁰³

Materials for the storage of hydrogen are one of the hot areas of research as hydrogen is considered as the fuel for future. The Hydrogen Energy Centre, Banaras Hindu University has been one of the pioneering centres for hydrogen storage research in the country. Their achievements in this regard can be found in a review by O. N. Srivastava and colleagues.²⁰⁴ His group showed that CNT-Mg₂Ni composite possesses higher hydrogen storage capacity as well as faster desorption kinetics than Mg₂Ni alone.²⁰⁵ CNTs²⁰⁶ and graphene nanoribbons (GNRs)²⁰⁷ were shown to be excellent catalysts for the release of hydrogen from sodium alanate. Recently few layer graphene was demonstrated to be capable of storing hydrogen by Subrahmanyam *et al.* About 5 wt% of hydrogen can be stored in the few layer graphene which is released upon UV or excimer laser irradiation.¹²⁴

3.3 Catalysis

Nanostructures possess high surface energy due to their high surface to volume ratio and presence of these high energy surfaces makes them interesting candidates for several catalytic reactions which are not observed in their bulk counterparts. Catalysis in nanoscale happens on the active sites present on the nanoparticle surfaces and their activity is governed by nanoparticle size, shape, crystal structure and support used. Metal, semiconductor and hybrid nanomaterials have been used in the recent years for catalysing various chemical reactions in India. Metal nanoparticles on oxide support are well known catalysts for various chemical reactions and microwave assisted synthesis are widely used for these catalysts. Anumol *et al.* recently shed light on the mechanism of formation of these metal NPs on oxide support considering both thermodynamic and kinetic aspects of metal ion reduction.²⁰⁸ Microwave assisted co-reduction synthesis of graphene-Pt NP was reported from the same group. This material was shown to be catalytically active for methanol oxidation and hydrogen conversion reactions.²⁰⁹ Nanoparticles have been used for the catalytic reduction and coupling of organic molecules. Tarasankar Pal successfully used Ag/Au core shell NPs for the reduction of nitroaromatics.²¹⁰ Use of monoclinic CuO nanoflowers for oxidative phenol coupling reactions was reported by the same group.²¹¹ Use of anisotropic Au NPs entrapped in mesoporous boehmite films as reusable catalysts for both inorganic and organic redox reactions was demonstrated by Jana *et al.*²¹² Magnetically recoverable copper ferrite NPs were used as catalysts for reduction of ketones into corresponding secondary alcohols with up to 99% enantiomeric excess by Lakshmikantam *et al.* These NPs were also quite effective for the asymmetric reduction of alpha and beta keto esters.²¹³ Chakravarti *et al.* demonstrated the use of highly basic MgO NPs immobilized over mesoporous carbon for the selective synthesis of sulfinamides.²¹⁴ Venkatesan and Santhanalakshmi used Au/Ag/Pd trimetallic NPs for the Sonogashira C–C coupling reaction.²¹⁵ Datta *et al.* Synthesized small (less than 7 nm) Au NPs in the channels of mesoporous carbon nitride support. These supported NPs were reported to be selective catalysts for the three-component coupling reaction of benzaldehyde, piperidine, and phenylacetylene for the synthesis of propargylamine.²¹⁶ Bej *et al.*

demonstrated the use of Pd NPs for borylation of aryl and benzyl halides which was further used for Suzuki–Miyaura coupling reaction to produce unsymmetrical biaryls and diarylmethanes in solvent free environment.²¹⁷

3.4 Device structure

India, though has become one of the leaders in nanomaterials synthesis and characterization over the span of a decade, there have been very few efforts in molding these materials in the form of devices to take advantage of their unique, yet intriguing optical and electronic properties. In the following, we point to a few recent efforts.

Top gated graphene transistor was fabricated for the first time by A. K. Sood and colleagues. A very high doping level was attained which was monitored using Raman spectroscopy.²¹⁸ Simultaneous injection of p- and n-type carriers in a bilayer graphene channel was demonstrated by Chakraborty *et al.*²¹⁹ Fabrication of ultralow noise field-effect transistor using multilayer graphene was demonstrated by Pal and Ghosh.²²⁰ Low temperature electrical transport phenomena in MoS₂ field-effect transistor devices was examined by Ghatak *et al.* with varying MoS₂ layer thickness. While 2D variable range hopping was observed at higher temperature, resonant tunneling at localized sites results in oscillatory conductivity at low temperature.²²¹ Magnetic anisotropy studies on Fe films grown on cubic GaAs and GaAs/MgO was reported by Sakshath *et al.* Pronounced uniaxial magnetic anisotropy rather than fourfold symmetry dictated by cubic crystalline symmetry of Fe was observed for a layer Fe thicknesses less than 20 monolayer.²²² An optical waveguide based sensor capable of detecting minor variations of refractive index was designed by coating Au NPs on a C-shaped polymer waveguide. This chip fabricated by Prabhakar and Mukherji utilizes localized SPR of Au NPs for detection of even minor variation in refractive index and is suitable as an affinity biosensor.²²³ A microfluidic immunosensor chip capable of visual detection and quantification of waterborne pathogens like *E. coli* and *S. typhimurium* at low concentrations was fabricated by Agrawal *et al.*²²⁴ A single polymer layer based device capable of multicolor sensing was fabricated by Gautam *et al.*²²⁵

3.5 Soft lithography

Creation of nanostructures in an organized fashion can be achieved in several ways. The traditional approach of lithography has been the dominant way but new approaches have come in the recent years. Among them the instability patterns produced by diverse physical phenomena have been extensively used by Ashutosh Sharma to create sub-micrometer structures. Using a topographically patterned stamp, Mukherjee and Sharma created instability patterns which are ordered.²²⁶ Phenomena such as dewetting have also been used to create such structures. Self-organized dewetting of ultrathin polymer film in presence of a mixture of solvents can create sub 40 nm ordered nano-droplet patterns.²²⁷ Such structures could lead to patterned organic structures as demonstrated in an earlier paper.²²⁸ Understanding such instabilities have implication to several branches of soft materials science. Therefore, it is being intensely pursued in the recent years.

Soft lithographic patterns using nanomaterials can create ultra-small structures. These structures can be of metal, alloy, oxides and nitrides using inorganic precursors as demonstrated by a recent report Kulkarni *et al.*²²⁹ Utilizing the sharp thermal decomposition of Pd-thiolates, patterned Pd₄S structures have been generated by the same group.²³⁰ Extending the very same method, it is possible to create InAs nanostructures.²³¹ Patterning can also generate femtoliter cups.²³² Electrocondensation of attoliter water droplets in such cups can be visualized by atomic force microscopy.²³³ Specific phases can be grown by methods even without the use of lithography. Kinetic control can be used in this context. A GaN NW network has been generated by this approach.²³⁴ Reduced adatom diffusion leading to supersaturation and associated dislocation have been shown to create such structures.

4 Nano-bio interface, nanomedicine and nanotoxicity

Biological organisms have adapted their best forms to survive in the conditions they live in. Cell, the best working self-replicating micro-compartment ever known, with millions of soft nanomachines dispersed in it, wandering due to Brownian motion and yet functioning precisely due to molecular recognition, sets the hardest target ever to be understood by human endeavors. As we discussed above, 'size' is the key factor which relates nanotechnology to biology and it sets biology to be an inspiration and an example for functional nanotechnology. On the other side, novel properties of nanomaterials help solve many biological/medical problems. Scientists all over the world work in both the directions at the nano-bio interface where in one direction, they try to understand, exploit or mimic, the biological molecules/structures for the development of nanoscience and technology and in the another, they try to understand the interaction of nanomaterials with biological systems and apply nanomaterials for solving biological problems. In the sub-continent too, research at the nano-bio interface has been active in both the directions mentioned above.

In the peninsula which is the second most populous in the world, nano-biology or nanobiotechnology have been of crucial importance due to, 1. rapidly growing population in need of healthcare provisions (*e.g.* according to a recent published report in *The Lancet*, around 55,000 people died in 2010 due to cancer²³⁵), 2. Multitude of issues of agriculture such as drought and floods, lands lost in vigour due to intensive use of chemical fertilizers or pesticides, increasing farmer suicides, desire to increase the quantity food produced and 3. Need to have affordable storage and transport solutions for agricultural products. The above mentioned problems as a whole or in part are a reflection of the global scenario for which nanotechnology could provide solutions. The contemporary nano-bio research areas range from investigations on 1. understanding the interaction of nanomaterials with prokaryotes, eukaryotes and biological macromolecules and their concomitant effects and 2. exploitation of nanomaterials in understanding or solving problems of biology and medicine (translational research). Below we present a brief collection of representative literature which are categorized into the themes (i) understanding the nano-biointerface, (ii) DNA nanotechnology, (iii) targeted drug and gene delivery and regenerative medicine, (iv) nano in agriculture and (v) nanotoxicity.

4.1 Understanding the nano-bio interface

Several groups in the country try to understand the nano-bio interface (especially interaction of nanomaterials with biomolecules and the mechanism of biomolecules mediated synthesis of nanomaterials) by various spectroscopic techniques such as electronic, vibrational and time resolved analysis of the macromolecule-nanoparticle interface. Pal and colleagues have worked on probing the nano-bio interactions using time resolved spectroscopic techniques²³⁶ such as quantum dot-DNA interaction, metal cluster-protein and V_2O_5 molecular magnet-protein interaction. Recently Pal and Pradeep have reported the formation HgO intermediate which is reported to be necessary during the formation of HgS quantum dots in the protein, bovine serum albumin (BSA).²³⁷ Interaction of gold nanoparticle with heme protein and the concomitant conformational changes have been studied by Pradeep's group.²³⁸ They have attempted to understand the mechanism of formation of noble metal clusters in functional proteins using MALDI MS which revealed that clusters grow *via* the initial uptake of Au^{3+} ions, which get reduced to Au^{1+} and subsequent incubation leads its reduction to Au(0) (Fig. 9). During this process, inter-protein metal ion transfer occurs with time dependent conformational changes of the protein. At the nano-bio interface, how the formation of metal nanostructures inside a protein affects the secondary structure of the

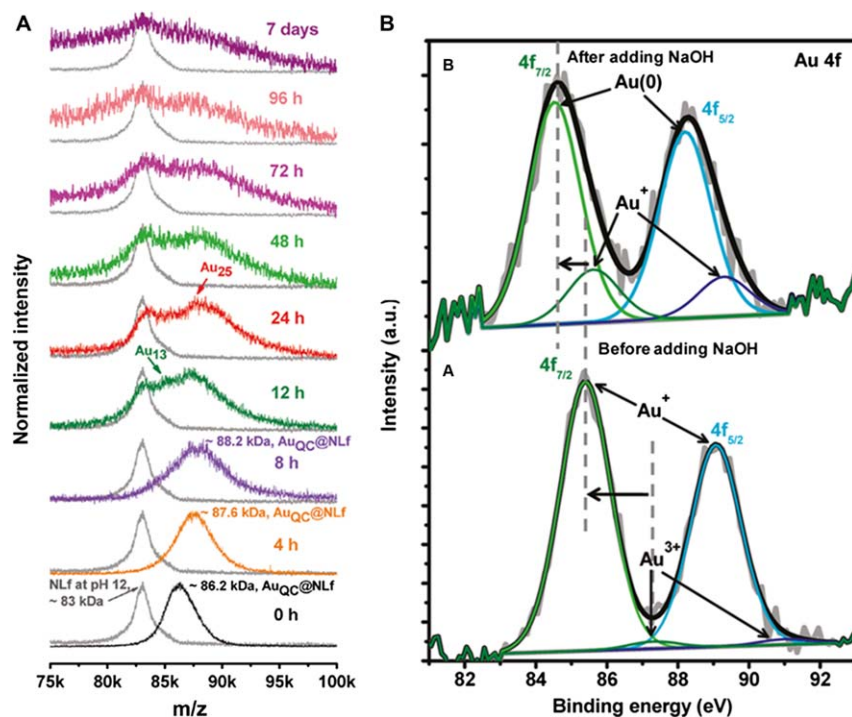


Fig. 9 A) Time dependent MALDI MS data of growth of luminescent gold quantum clusters Au_{25} in the protein lactotransferrin indicating the emergence of free protein and interprotein metal ion transfer. B) XPS spectra showing the presence of Au^{1+} state before the addition of NaOH and Au(0) after the addition of NaOH (adapted from Ref. 239).

macromolecule also has also been studied.^{70,74,239} Previously, Sastry and colleagues studied the thermodynamics of interaction of DNA and PNA bases with gold nanoparticles using isothermal titration calorimetry.²⁴⁰ Gupta *et al.* studied the mechanism of amyloid fibril disruption using biphenyl ether-conjugated CdSe/ZnS core/shell quantum dots.²⁴¹ Kundu *et al.* studied the change in bacterial size and magnetosome features for *M. magnetotacticum* (MS-1) under high concentrations of zinc and nickel.²⁴² Dasgupta and co-workers designed a colorimetric experiment based on the conformational changes induced by gold nanoparticles in a protein, and used it as a tool to sense protein conformational changes by colorimetry.²⁴³

4.2 DNA nanotechnology

Though started in 1980s in the world arena, DNA nanotechnology has been practiced only by a few people in India in recent times. Krishnan and colleagues are active in this area where they use genetic blue print material as bricks to create novel structures. One of the widely appreciated works of Krishnan is to probe the intracellular pH of cells using DNA actuators.^{244–246} Krishnan *et al.* encapsulated a fluorescent biopolymer that functions as a pH reporter within the synthetic, DNA-based icosahedral host and showed that the encapsulated cargo (FITC conjugated dextran–FD10) is up-taken by specific cells in *Caenorhabditis elegans*, a multi cellular living organism widely used in translational medicine research. Recently, together with Koushika, she was able to probe the intracellular pH of *C. elegans*.²⁴⁷ Krishnan also has worked on creating pH-toggled DNA architectures through reversible assembly of three-way junctions.²⁴⁸

4.3 Nanomedicine: targeted delivery and imaging

An Indian traditional medicine, *Jasada Bhasma* was found to contain non-stoichiometric zinc oxide nanoparticles by Bellare and co-workers thus providing the link between the ancient medicinal practices of India and nanotechnology.¹ Today we can see the influence of nanomaterials in various areas of medicine such as targeted drug/gene delivery, imaging, wound dressing and tissue engineering.²⁴⁹ Receptor mediated delivery has become another active research area.²⁵⁰ Sahoo and co-workers have extensively worked on targeted therapy, they have conjugated EGF (epidermal growth factor) antibodies to rapamycin loaded PLGA NP and used for targeted therapy of breast cancer and in another study they have treated Bcr-Abl+ leukemia cells by targeting.^{251,252} Sahoo and co-workers treated pancreatic cancer cells with herceptin (HER2)-conjugated gemcitabine-loaded chitosan NP.²⁵³ Gupta and co-workers used polyethylemine conjugated with chondritin sulfate NP for gene delivery.²⁵⁴ Chennazhi and colleagues made fibrin nano constructs and used them as a controlled and effective gene delivery agent.²⁵⁵ Sahoo *et al.* demonstrated that the paracetamol-Ag nanoparticle conjugate mediated internalization of plasmid DNA in bacteria.²⁵⁶ Dash and colleagues characterized the antiplatelet properties of silver nanoparticles and proposed it to be a potential antithrombotic agent.²⁵⁷ Sahoo *et al.* has made dual drug loaded super paramagnetic iron oxide nanoparticles for targeting human breast carcinoma cell line (MCF-7).²⁵⁸ Pramanik and co-workers made nanoconjugated vancomycin which showed

efficacy against vancomycin resistant *S. aureus*, where folic acid conjugated nanopolymer acted as effective delivery agents inside the bacterial cell.²⁵⁹ Ali *et al.* developed a dry nanopowder inhaler made of atropine sulphate and used it as antidote for organophosphorous poisoning.²⁶⁰ Maitra and colleagues made multifunctional gadolinium oxide doped silica nanoparticles for gene delivery.²⁶¹ Desmukh and colleagues made highly stable Eudragit R 100 cationic nanoparticles containing amphotericin B for ophthalmic antifungal drug delivery.^{262,263} Previously, Mittal *et al.* used PLGA nanoparticles loaded with sparfloxacin for sustained ocular drug delivery.²⁶⁴ Gupta and co-workers synthesized linear polyethylenimine (PEI) and used as efficient carrier of pDNA and siRNA both *in vitro* and *in vivo*.²⁶⁵ Pathak *et al.* used the nano sized PEI-chondritin sulphate for tumor gene therapy and evaluated their bio-distribution and resultant transfection efficiency.²⁵⁴ Jain *et al.* used mannosylated gelatin nanoparticles loaded with anti-HIV drug didanosine for organ specific delivery.²⁶⁶ Dasgupta and co-workers conjugated AuNPs to α -crystallin protein and reported that the conjugate could prevent glycation even in the presence of strong glycating agents.²⁶⁷ Wilson and co-workers used chitosan nanoparticles as a new delivery system for the anti-Alzheimer drug tacrine.²⁶⁸ Recently nanomaterials based imaging and imaging-guided therapy have become active. Surolia and co-workers probed the mechanism of biphenyl ether mediated amyloid fibril disruption by BPE-QD conjugates and also traced senile plaque in the brain of transgenic mice.²⁴¹ Sarkar and co-workers used carbon nano onions as a tool to study the life cycle of the common fruit fly, *Drosophila melanaogaster*.²⁶⁹ Pramanik and co-workers made magneto-fluorescent nanoparticles conjugated with folic acid and targeted folate receptor over expressing cancer cells and isolated them using magnetically activated cell sorting (MACS).²⁷⁰ Highly fluorescent noble metal quantum clusters have become potential imaging tools of late.^{54,271} Pradeep and co-workers conjugated streptavidin to the QC, Au₂₃ and imaged HeLa cells and in another study they have conjugated folic acid to BSA protected Au₃₈ and imaged folic acid receptor positive cancer cells.^{272,273} Manzoor and colleagues have demonstrated folate receptor specific targeted delivery and flow cytometric detection of acute myeloid leukaemia by protein protected fluorescent gold quantum clusters.^{274,275} Manzoor and co-workers have conjugated folic acid with various nanomaterials and used for targeted imaging namely with multimodal hydroxyapatite, Y₂O₃ nanocrystals based contrast agents doped with Eu³⁺ and Gd³⁺, ZnS QD and BSA protected AuQCs.²⁷⁵⁻²⁷⁹ Pramanik and co-workers combined multimodal imaging, targeting and pH dependent drug delivery in a single nanosystem by conjugating folic acid methotrexate to ultra small iron oxide nanoparticles coated with N-phosphonomethyl iminodiacetic acid (PMIDA).²⁸⁰

4.4 Regenerative medicine

Very few groups in India have been doing research on this vital and lucrative topic. Mandal and co-workers has grown hydroxyapatites on physiologically clotted fibrin on gold nanoparticles.²⁸¹ Jayakumar and colleagues have made sodium alginate/ZnO/polyvinyl alcohol composite nanofibers for wound dressing.²⁸² Selvamurugan and co-workers made bio-composite scaffolds

containing chitosan/nano-hydroxyapatite/nano-copper-zinc for bone tissue engineering.²⁸³ Kalkura and co-workers synthesized hydroxyapatite nanorods by a microwave irradiation method for the treatment of bone infection.²⁸⁴ Recently Singh *et al.* used nano-biphasic calcium phosphate ceramics for bone tissue engineering and evaluated the osteogenic differentiation of mesenchymal stem cells on the substrate.²⁸⁵ Ghosh and colleagues made silk fibroin scaffolds combined with chondroitin sulfate developed with precise fiber orientation in lamellar form for tissue engineering of the annulus fibrosus part of the intervertebral disc.²⁸⁶ Sethuraman and colleagues demonstrated that aligned nanofibers of PLGA-PHT (poly (lactide-co-glycolide)-poly (3-hexylthiophene)) can be used for neural regeneration by *in vitro* cell studies.²⁸⁷ Potential applications of fibrous scaffolds containing micro and nanoscale fibers in regenerative medicine have been discussed in detail by S.V. Nair and colleagues.²⁸⁸

4.5 Agriculture

Novel strategies for plant transformation to resist flood, salinity and drought, disease and pest control, minimal and efficient use of fertilizers are few crucial needs for increased productivity for Indian agriculture, not leaving the efficient storage of agricultural products. Scientists have been promoting the use of nanotechnology in agriculture for these objectives and these are evident from various reviews and recent research.^{289–291} Samim and co-workers prepared ultra-small sized (20–50 nm diameter) calcium phosphate (CaP) nanoparticles encapsulated with a reporter gene, pCambia 1301, and transfected *Brassica juncea* L. This CaP NP method was shown to be much efficient than *Agrobacterium tumefaciens* mediated genetic transformation.²⁹² Prasad and co-workers used carbon supported gold nanoparticles as gene carrying bullets in ballistic gene transformation method. They have tested the nano bullets on *Nicotinia tabaccum*, *Oriza sativa* and *Leucaena leucocephala* and have shown that it has better gene delivery efficiency and less damage than conventional micrometer sized gold particles.²⁹³ Prasad and co-workers have shown that ZnO nanoparticles could enhance the growth and yield of ground nut (*Arachis hypogaea*) compared to the bulk ZnO counterparts.²⁹⁴ Nandy and colleagues have shown that CNTs could have beneficial role on mustard plant (*Brassica juncea*) growth.²⁹⁵ Sarkar *et al.* have shown that water soluble carbon nanotubes stimulate the growth of *Cicer arietinum*.²⁹⁶

4.6 Nanotoxicity

Nanotoxicology has become one of the active areas of research in the country in the past decade and is well promoted among biologists and toxicologists.^{297–299} Comet assay, which a simple yet sensitive visual technique for the assessment of DNA damage in cells, and an important tool in toxicity evaluation, is discussed in a recent book.³⁰⁰ Since there is a thin line between chemical toxicity and nano toxicity where the former is due to the intrinsic chemical nature of the matter and the latter is purely based on size and associated emergent properties (the size limitation for the term nano is continuously changing, at present a NM is that having size between 1 and 100 nm in its characteristic dimension), a beginner

may miss to distinguish between them. Here, we give importance to the size dependent toxicity behavior (*e.g.* carbon is non toxic while CNTs are^{301,302}) and not to chemical moiety based toxicity where chemical nature is predominant than the size, but it is also known that the stabilizing ligands also influence the toxicity of a given nanoparticle. Size does matter in the case of soft organic nanomaterials also, such as dendrimers and polymer NM for enhanced intracellular uptake which is due to the large surface area created at the nanoscale, such enhanced uptake would influence the toxicity, here the toxicity is not only due to the chemical nature of the polymer or dendrimer but size also plays a role indirectly by means of facilitating enhanced uptake. In India toxicity of nanomaterials on both prokaryotic and eukaryotic organisms has been investigated. Some of the tested nanomaterials are carbon nanostructures, metal NPs, metal oxides NPs, semiconductor QDs and polymeric particles.

4.6.1 Studies on prokaryotic and plant systems. Mukerjee and co-workers tested titanium dioxide (TiO₂) nanoparticles on two trophic levels plants *Allium cepa* and *Nicotiana tabacum*, Comet assay and DNA laddering experiments showed TiO₂ NP to be geno toxic and it was further confirmed by the presence of micronuclei and chromosomal aberrations.³⁰³ In another study, the same group showed that MWCNT are genotoxic to *Allium cepa*.³⁰⁴ Mukerjee and co-workers studied the toxicity of Al₂O₃ nanoparticles on microalgae *Scenedesmus* sp. and *Chlorella* sp and concluded that inhibition of growth and decrease in chlorophyll content occurred in NP treated algae and showed enhanced toxicity for alumina.^{305,306} Manivannan and co-workers have reported that of ZnO NPs are selectively toxic towards Gram positive bacteria.³⁰⁷ Dash *et al.* investigated the toxicity of silver nanoparticles to bacteria in detail and found that bacterial death is due to cell lysis. They observed many changes in phosphotyrosine profile of putative bacterial peptide and proposed that it could have inhibited bacterial signaling and growth.³⁰⁸ While several NM are shown to be toxic to bacteria, it has a gainful side that it can be used as antimicrobial materials.³⁰⁹

4.6.2 Studies on animal systems. Testing the toxicity of NM on animal and humans are of paramount importance. Several toxicological studies dealing with *in vitro* cellular systems and *in vivo* animal studies have been performed.

4.6.2.1 In vitro cell systems. Chaudhuri and colleagues showed that Au NPs can induce platelet aggregation and platelet response increases monotonically with NP size.³¹⁰ This could provide a measure of thrombotic risk associated with nanoparticles. Dasgupta and co-workers studied the role of purinergic receptors in platelet-nanoparticle interactions and reported that pro-aggregatory effect of NPs are ADP dependent and purinergic receptors also have role to play in the observed effect. They also showed that the usage of clopidogrel can prevent NP induced thrombotic responses.³¹¹ Reddanna and co-workers studied the molecular mechanism of inflammatory responses of RAW 264.7 macrophages upon exposure to Ag, Au, Al NP and carbon black. They have observed the maximum inflammatory responses such as increased IL-6, reactive oxygen species (ROS) generation,

nuclear translocation of NF- κ B, induction of cyclooxygenase-2 (COX-2) and TNF- α for Ag NP followed by Al NP while no such inflammatory response was seen for Au NP indicating the bio compatibility of Au NP.³¹² Ahmad and co-workers compared the autophagy and cytotoxicity of iron oxide NP in normal human lung fibroblast cell (IMR-90) and lung cancer cell (A549) and found that ROS generation, mitochondrial damage and increased autophagy in lung epithelial cancer cells and not in normal cells.³¹³ Dasgupta and co-workers demonstrated that Au NP can be selectively toxic to different cell lines. They reported that Au NP were toxic to A549 cells while being non toxic to BHK21 (baby hamster kidney) and HepG2 (human hepatocellular liver carcinoma) cells.³¹⁴ Rahman and co-workers reported the oxidative damage induced by MWCNT in A549 cells.³¹⁵ Manzoor and co-workers reported that carboxyl functionalization could mitigate the toxicity of pristine graphene.³¹⁶

4.6.2.2 In vivo studies. Palaniappan *et al.* used Raman spectroscopy as a tool to investigate the bio molecular changes occurring in TiO₂ NPs exposed zebrafish (*Danio rerio*) liver tissues.³¹⁷ Murthy and co-workers reported that repeated administration of ZnO nanoparticles on the skin of Sprague-Dawley rats lead to loss of collagen when compared to the untreated site of the skin.³¹⁸ Patravale and co-workers studied the toxicity of curcumin loaded polymeric nanoparticles of Eudragit S100 and found it to be non toxic.³¹⁹ Jain and co-workers studied the toxicity of functionalized and non functionalized fifth generation polypropylenimine (PPI) dendrimers and reported that former were non toxic and latter were severely toxic.³²⁰ Sil and co-workers recently studied the molecular mechanism of oxidative stress responsive cell signaling in Cu NP induced liver dysfunction and cell death *in vivo*. They have found that Cu NP led to increased transcriptional activity of NF- κ B, upregulation of expression of phosphorylated p38, ERK1/2 and reciprocal regulation of Bcl-2 family proteins. Disruption of mitochondrial membrane potential, release of cytochrome C, formation of apoptosome and activation of caspase 3 was also seen, conforming the role of mitochondrial signaling.³²¹

Critically looking at the present scenario, based on the published work and from the discussion above, a bright future for nano-bio in India is predictable. There are certain areas in the field of nanobio, well represented from the Gandhian land compared to certain vital areas which are less represented viz nano in medicine, artificial biomimetic structures (artificial retina for example), molecular biology of nanotoxicity, protein corona on nanoparticle surface, *in situ* real time investigation of NP-cell interaction, *etc.* Certain areas like nano based functional man-made cellular systems are yet to start, while it has already started in western countries. Nanomedicine is only at the bench level and it is yet to reach the beds, and this is expected for a new technology at its foetal stage.

5 Nano and industry

India in principle has a lot to offer towards the large and growing market of nanotechnology. Till date most of the investments to the R&D programme

on nanotechnology in India have been through governmental agencies. Availability of young professionals at cheaper price is attracting attention and investments from industries in the recent years. Whereas R&D activities in nanoscience and nanotechnology have grown larger and larger over the years, India needs more number of people with techno-managerial skills to bridge between industry and educational institutes for successful transfer of technology.

The advantages of R&D in India have already attracted giant multinational companies like GE, GM and IBM who have already set up R&D centres in India.³²² Nano-tex has set a tie-up with Madura Garments, an Indian textile major recently and has plans to set up R&D to carry out research on NPs and textiles.³²² There are several other companies in India working on the synthesis of nanomaterials like nanosilver powders for making conductive paste (Auto Fibre Craft), nano silica products (Bee Chems), CNTs and graphene (Quantum Corporation and Nanoshel), protective nano-coatings for various surfaces (Nilima Nanotechnologies), *etc.*³²³ Bilcare has developed nonClonable, a security system which uses optical and magnetic properties of NPs.³²³ Dabur Pharma is working on drug delivery using polymeric NPs which is in the advanced stages of clinical trials.³²³ Saint-Gobain Glass manufactures SGG NANO, a glass coated with multiple layers of nanoscale metallic oxides/nitrides which possesses advanced energy efficient solar control and thermal insulation properties.³²³ We have already outlined the nanotechnology efforts related to water purification earlier (section 3.1).

Lack of competent product marketing, sales and distribution skills are the major drawbacks in the Indian nano industries. Hilaal Alam, CEO of Qtech Nanosystem commented on this issue: "India has got (the) potential to become a service provider for (global) nanotechnology industry; but not a pipeline for new products. Majority of investment in India up till now has gone in services sector and into building a testing and characterization infrastructure."³²²

6 Nano and education

Almost every institutes/universities in India has a nanotechnology programme. In most cases nanotechnology education is imparted at senior undergraduate level in the form of a completely new course or part of an existing course. At the masters level, specific nanoscience and nanotechnology programmes offering M. S. and M. Tech degrees are also available. A rather different course entitled M. Sc. Tech. is also offered by some institutions. Besides these, integrated B. Tech.-M. Tech. programmes are also initiated. A detailed discussion on the status of nanotechnology education at IITs (Indian Institute of Technologies) can be found elsewhere.³²⁴ While the first few batches from such nanotech programmes have already come out, in most of the institutions they are at advanced level of completion. As nanotechnology is diverse, most institutions have tried to specialize their degrees based on the expertise available. Nanomaterials, bionanotechnology and nanomedicine are the common specializations being offered. As industrial opportunities are limited, most of the graduates

have opted to stay with research as their career option. The steady output of PhDs in the area was commented upon earlier.

7 Future of nano-research in India

Science at the nanoscale is making numerous surprises and it is impossible to predict the future. This is true in the Indian context too. However, from the current trends, nature of investments made and the human resource available, it is expected that new materials and their modifications will continue to be the major focus in the immediate future. Applications in areas of societal relevance is getting momentum not only due to the implications but also because of the fact that it is practiceable in almost every institution as several experiments are possible with minimum infrastructure. Exciting new materials – graphene, soft materials, clusters, gels, porous materials, anisotropic nanostructures, functionally graded nanostructures, *etc.* – will continue to be active. An aspect that is apparent in current science is the greater involvement of synthetic organic chemists in nanoscience. These efforts are directed towards self organization, patterning, composites, luminescence, biology and the like.

Indian research at the nanoscale will generate new excitements if there is a greater possibility for device fabrication. These developments need not necessarily be using nanoscale patterning. In areas of sensors the range of activities in the country in national security, disease identification, environmental monitoring, water purification, *etc.* the need for demonstrable devices is large. Applications of traditional knowledge using nanomaterials will be significantly advantageous wherein new formulations are likely.

All the developments will have their ultimate impact only if materials are made and tested in quantities. There is a need to make nanomaterials of relevance to applications available to people. For this piloting facilities have to come up. Field applications and data from such studies will be possible only this way.

Society is keenly observing new breakthroughs. The nation is sensitized on this area through various media, new programmes and also due to the largely younger population. There is a realisation that a vast majority of Indians will live in the Nanotechnology-enabled society as the average age of India by 2020 is expected to be 29. The new society has to understand the benefits and risks and therefore societal relevance of nanoscience and its implications will be discussed more and more. With the availability of instrumental resources across the country, nanoscience will not only capture the imagination of people but also enable them to do something relevant. However, for this to happen sustained funding and longer term commitment is essential. Industry has to be ready to absorb the developments happening in the soil.

8 Conclusions

Nanoscience presents an explosive, diverse and highly promising science in India, just as in any part of the world. The most active area is related to the developments in materials. There is a strong overlap of computational

materials science with the nanoscience activity. Although nanoscience has not yet resulted in industrial products in several nations, early signs of applications are available in India. Surprisingly this turns out to be on one of the most pressing needs of the nation, namely water purification. The applications of nanomaterials on several of the national needs such as security, environment, health, *etc.* are visible. However, intense efforts in areas such as energy have not happened, although no area is not unrepresented. Nanoscience has got into pedagogy in several universities and the first few batches with NS&NT specialization have already come out. Nano has got into the regional language literature and the nation is pregnant with hope from this new branch of science.

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