Chapter 1

General Introduction

Introduction

1.1 Nanoparticles

Nanoscience and nanotechnology are recent, revolutionary development in science and engineering that are evolving at a very fast pace. It is driven by the desire to fabricate materials with novel and improved properties that is likely to impact virtually all the areas of the physical and chemical sciences, materials sciences, biological sciences and health sciences. Particles with sizes in the range of 1-100 nm, at least in one dimension, are called nanoparticles. The word "nano", generally, means a billionth (10^9) part of one meter. It is derived from a Greek word "nanos" meaning dwarf (extremely small). Nanoparticles are a number of atoms or molecules bonded together (these particles usually contain 10^6 atoms or less) and intermediate in size between individual atoms and aggregates large enough to be called bulk material. As the nanoparticles are larger than individual atoms and molecules but are smaller than bulk solid, those obey neither absolute quantum chemistry nor the laws of classical physics and therefore, materials in the nanometer size regime show the behavior which is intermediate between that of a macroscopic solid and that of an atomic or molecular system. There are two major phenomena those are responsible for these differences. First, as the size of a particle is reduced, the number of atoms at the surface of the particle increases compared to their bulk i. e., surface-to-volume ratio increases. Second, as the size of the material becomes equal to or falls below the nanometer length scale that characterizes the motion of its electrons and thus its properties, become sensitive to the size of the particles. The effect specific to the small size of nanoparticles is called the quantum size effect that opens up the opportunity to create materials and devices with entirely new properties. Due to these factors, materials in the nanometer size regime exhibit novel optical, electronic, catalytic, magnetic properties.[1, 2] Nanoparticles get adsorbed and self-assembled on to the liequid/liquid interfaces due to unbalanced or residual forces on the particle surface (also known as surface energy). Self-organization of nanoparticles generates a variety of structures, including chains, sheets, vesicles, three-dimensional (3D) crystals or more complex 3D architectures.[3]

1.2 Self-Assembly of Nanoparticles at the Liquid/Liquid Interface

Liquid-liquid interface is the junction of two immiscible liquids, it is a heterogeneous system involving two solvents of different solvation characteristics. The interface between two immiscible liquids is a unique environment, where, the structural, dielectric, dynamic, thermodynamic, adsorption-desorption and other surface properties and even chemical environments are also different from those of the bulk liquids. Processes occurring at this interface underlie many important phenomena in chemistry and biology. For example, the transport and exchange of mass across the liquid interface between lipid bilayer membranes and aqueous body fluids play key roles in life activity. All energy conversion processes in living organisms occur by nature at liquid interfaces. These interfaces are also fundamental to a variety of industrial applications, including, separation and extraction processes, phase transfer catalysis, electrochemical processes, and drug delivery in pharmacology.[4, 5] The study of the liquid/liquid interface dates back to, at least, the beginning of the last century. In the past 100 years, the experimental and theoretical developments have significantly enriched our knowledge and understanding of the properties of the interface between two immiscible liquids, mainly in two aspects: (i) the structure of the interface, including, the electrical double layers and potential distribution across the interface between two immiscible electrolyte solutions and the microscopic structure of the interface; (ii) the electrochemical reactions at the interface, including, adsorption at the interface and charge transfer across the interface. The structure of the interface remains a rather controversial and interesting topic. Knowledge of the interfacial structure is a prerequisite for understanding the chemical reactivity at the interface. Verwey and Niessen[6] proposed the first model describing liquid/liquid interface as two back-to-back diffuse layers, in between which an inner layer of solvent molecules was later considered to exist. The resulting model, which is called modified Verwey-Niessen model, has been extensively used. Nowadays, microscopic information about the interface is mainly obtained from computer simulations together with up-to-date experimental techniques, such as, nonlinear optics, neutron and x-ray scattering and infrared spectroscopy. Electrochemical reactions at the interface include molecular adsorption at the interface and charge transfer across the interface. The first study of a charge transfer process can be traced back to 1902 when Nernst and Riesenfeld observed the transfer of ions across the water/phenol interface using electrochemical methods.[7] However, progress of research on fluid interface has ever been very slow due to the unknown interfacial structure and potential distribution across the interface and, experimentally, to the large ohmic potential drop in the organic phase. The chemical control of the polarizability of liquid/liquid interface by Gavach *et al.*[8] and the invention of the 4-electrode potentiostat with ohmic drop compensation by Samec *et al.* [9] have motivated a new round of research interest. In the past three decades, there has been a tremendous increase in research in the field of liquid/liquid interface with the emergence of various new techniques, such as, scanning electrochemical microscopy (SECM), microelectrode, and the combination of electrochemical and surface specific spectroscopic techniques. Various reviews and books have been published, concerning the advances in this field.[10]

Interfaces between two immiscible liquids are frequently encountered in natural as well as artificial processes. It is well established in literature that colloidal particles get adsorbed on to liquid-liquid interfaces driven by reduction in interfacial energy. One example is emulsion in which very small droplet (in colloidal range) of one fluid dispersed in the other continuous liquid. Emulsions have important practical interest because of their applications in food, cosmetics and pharmaceutical industries. The most well known examples of emulsions, includes, milk, mayonnaise and lotion etc. In 1907, Pickering first discovered that colloidal solid particles could stabilize an emulsion droplet by getting adsorbed at the interfaces between two immiscible liquids.[11] This type of emulsion was named as 'Pickering' emulsion. 'Pickering' emulsions have extensive applications in many industrial processes. For instance, food, emulsions are commonly stabilized by proteins or other large biological macromolecules. In crude oil refining industries, the oil-brine emulsions are stabilized by clays, asphaltenes and other dispersed particles. Secondly, a simple model of adsorption energy, ΔE, of a single particle at the interface was introduced by Pieranski and Koretskii *et al.*[12, 13] In this model, adsorption energy is obtained by calculating the change in total interfacial energy when a particle moves from one fluid to the lowest-energy position at the interface. Figure 1.1 is a schematic representation showing a spherical particle at an oil-water interface. Here, R is the particle radius, Z the vertical distance from the center of the particle to the interface, γ_0 the interfacial tension of the oil-water interface, and γ_1 and γ_2 are the interfacial tensions of the particle-water and particle-oil interfaces, respectively. There are three contributions to the interfacial energy of the particles: (1) energy of the particle-water interface: $E_1 = \gamma_1 . 2\pi R^2(1 + Z/R)$, (2) energy of the particle-oil interface: $E_2 = \gamma_2 . 2\pi R^2(1 + Z/R)$, (3) negative energy of missing oil- water interface: $E_2 = \gamma_2 . 2\pi R^2(1 + Z/R)$, (3) negative energy of missing oil-water interface: $E_0 = -\gamma_0 . \pi R^2(1 - (Z/R)^2)$. The total interfacial energy, $E = \pi R^2 \gamma_0 [(Z/R)^2 + 2(a-b)(Z/R) + 2(a+b) - 1]$ where, $a = \gamma 1/\gamma 0$, $b = \gamma 2/\gamma 0$. When, $Z/R =$

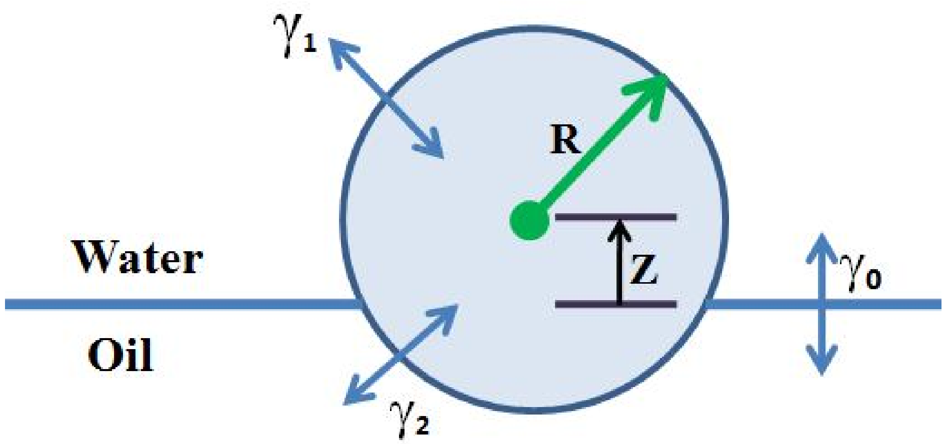

Figure 1.1. Schematic representation showing a spherical particle with radius R get adsorbed at oil/water interface.

$b–a = (\gamma_2 - \gamma_1)/\gamma_0$, the total interfacial energy has a minimum $E_{\min} = \pi R^2\gamma_0[2(a+b) - 1 - (a–b)^2]$. For a particle not adsorbed at the interface (in water, $Z/R>1$; in oil, $Z/R < -1$), total interfacial energy $E' = \pi R^2\gamma_0 \cdot 4b$ or $\pi R^2\gamma_0 \cdot 4a$, respectively. When a particle binds to the interface from water, the binding energy, $\Delta E = E' - E_{\min} = -\pi R^2\gamma_0 [1 - (\gamma_2 - \gamma_1)/\gamma_0]^2$. For plausible choices of γ_1 and γ_2, the model predicts $\Delta E \approx -10^6\ k_BT$ for R = 1 µm, where, k_BT is the product of Boltzmann's constant and the absolute temperature, T = 298 K.[13] The values of γ_1 and γ_2 can be, experimentally, measured at a flat surface with same chemical properties as the particles.[14]

Recently, emphasis has been given to exploit the nanoparticle assemblies in different field of applications, including, devices designed from nanoparticle assemblies. For example, emulsion-based method was applied to assemble colloidal particles into microstructures or multi-component clusters ('supraparticles').[15, 16] In this method, particles were gathered, assembled and fixed together in the restricted, colloidal size in 3D space provided by emulsion droplets. Similarly, by fusing latex particles at the interfaces of emulsion droplets, a new form of particle called 'colloidosomes' was developed for encapsulation.[17] The 'colloidosomes' are hollow, elastic shells whose permeability and elasticity could be precisely controlled. The generality and robustness of these structures and the potential for cellular immunoisolation were demonstrated by the use of a variety of solvents, particles and effectors. To endow the capsules with special properties, temperature-sensitive microgel particles was use to fabricate 'colloidosomes' which expanded and contracted upon heating and cooling. These ‘colloidosomes’ might be useful for controlled release or as microscopic actuators. Self-assembly of nanoparticles has attracted much attentions because of its applications in fabricating nanoscopic materials with unique electronic, optical and magnetic properties.[18-22] Fluid interfaces are ideal templates for assembling nanoparticles into two dimensional structures by exploiting the nature of the liquid-liquid interfaces. At the interfaces, nanoparticles are mobile and defects free (i. e., defects of the

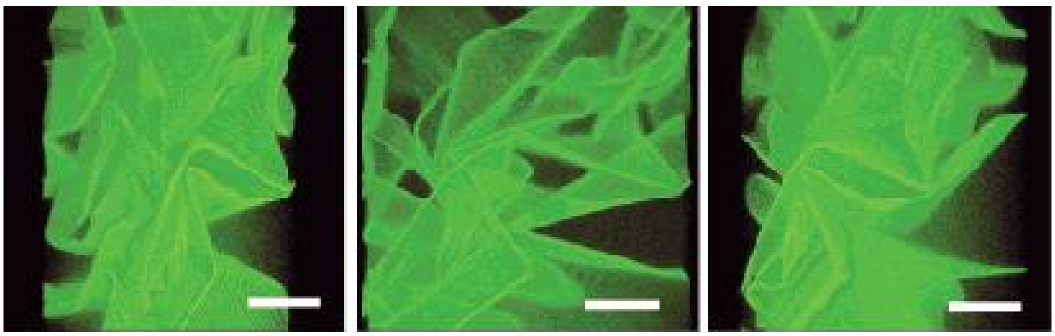

Figure 2. Confocal microscope image of a nanoparticle sheet prepared by cross-linking the associated organic ligands. The scale bar is 50 μm. (Reproduced from Lin *et al.*[25])

structures could be automatically rectified). The liquid interfaces also offer a potential for chemical manipulation of adsorbed nanoparticles. Nanoparticle assemblies at liquid-liquid interfaces offer novel and inexpensive routes to superstructures with novel and improved properties. There have been many studies showering light on this topic over last the few decades. The first study investigated the assembly of cadmium selenide nanoparticles at oil-water interfaces.[23] Lin and coworkers achieved size-dependent interfacial encapsulation of CdSe nanoparticles and provided an easy access to chemical modification of nanoparticles by reaction of attached ligands with reagents in both liquids. The structure of adsorbed nanoparticles at the interfaces was studied in-situ by grazing-incident small angle x-ray scattering and ex-situ by scanning force microscopy and transmission electron microscopy. The results showed that nanoparticles formed a densely packed monolayer with liquid-like ordering at the interfaces. The adsorbed nanoparticles were crosslinked to generate mechanically stable capsules and membranes, which remained the integrity even when removed from the interfaces (Figure 1.2).[24] This work offered a simple and facile route for the fabrication of ultrathin, composite organic-inorganic membranes. Duan and coworkers“ study on Au, Ag and Fe_2O_3 nanoparticles showed that the attached ligands played a crucial role in self-assembly process and demonstrated the possibility to form nano-alloy films at the liquid interfaces.[25] In another study, Duan and coworkers fabricated magnetic nanoparticle colloidosomes with nanoscale selective permeability based on interfacial assembly of Fe_3O_4 nanoparticles.[26, 27] These robust and water-dispersible colloidosome allowed encapsulation of various water soluble materials. Bigioni and coworkers achievied highly ordered gold nanoparticle monolayer at water-air interfaces by controlling the evaporation of water.[28]

The liquid/liquid interfaces also acts as a viable platform for nanoparticle self-assembly. Recently, Reincke and co-workers reported that, the introduction of ethanol can pull hydrophilic citrate-stabilized Au-nanoparticles into the water/heptane interface, leading to a closely packed monolayer.[29] Most recently, Kumar *et al.* observed that aromatic molecules, such as, benzene and anthracene present in the organic phase strongly bind to aqueous gold nanoparticles.[30] This process leads to the immobilization of the gold nanoparticles in the form of a highly localized film at the interface. Meanwhile, Duan *et al.* reported the assembly of hydrophobic and hydrophilic nanoparticles at water/oil interfaces by capping the nanoparticles with organic ligands.[31] These reports demonstrate a promising way to create a 2D arrangement of hydrophobic or hydrophilic nanoparticles at water/oil interfaces.

During last few years, special attention has been given in the investigation of colloidal nanoparticles adsorbed at fluid interfaces. The main driving force behind this interest is the wide range of applications of such assemblies. Owing to their small dimensions their properties are significantly different from the properties of macroscopic materials. Hence, metallic and semiconductor nanoparticles have been chosen as building blocks for materials with novel mechanical, optical, electronic and magnetic properties.[32] The self-assembly of nanoparticles at the liquid–liquid interfaces has enabled the preparation of high quality two-dimensional crystals.[33] Particles adsorbed at interfaces also play a vital role in several industrial applications [34, 35]. It has been known for many years that, the large stability of particles at interfaces can be exploited to tune the stability of emulsions. At the same time it is now well established that particles at interfaces can be used to study also some basic problems in condensed matter physics, such as the physical behavior of two-dimensional crystals.[36–38] Considering the surface energies of the particle–air, particle–water and air–water interfaces Pieranski noted that the activation energy for particle detachment scales quadratically with the colloid radius, being of the order of 107 times the thermal energy for polystyrene microparticles adsorbed at the water–

air interface. This high stability enables the formation of two-dimensional,[36, 39] and pseudo-two-dimensional structures.[40] The strong repulsions between the colloids, necessary to prevent coagulation in the colloidal solutions, can be introduced through steric interactions or surface charges.

1.4 Self-Assembly of Nanoparticles at the Liquid-Liquid Interface in 2D

In recent years, nanoparticle self-assembly processes at fluid interfaces have received considerable attention because of their importance encountered in separation and cleaning of oil, cosmetic preparation, waste water treatment and for storage and controlled release of various ingredients in the fields of medicine, pharmaceutics and agriculture.[41] When nanoparticles get self-assembled onto two dimensional interfaces (i.e, flat surface) a membrane like structures could be obtained which founds lots of important applications in natural biological systems as well as in artificial systems like, ultra-filtration, sensor, separation and controlled release etc. The fabrication of membranes via self-assembly of nanoscale materials is also a topic of interest for their application in delivery vessels, size-selective separation and purification, sensors and catalysts, scaffolds for tissue engineering, low dielectric constant materials for microelectronic devices, antireflective coatings and proton exchange membranes for polymer electrolyte membrane fuel cells etc.[42--46] It is well-established in the literature that nanoparticles strongly segregate to the interface of immiscible fluids, driven by a reduction in interfacial energy.[47] Localisation of nanoparticles at liquid-liquid interfaces by manipulating the particle surface energy offers tailor-made assemblies which have opened a new window to fabricate interfacially structured hybrid materials with unique properties.[48] However, while the nanoparticles are decorated with functional ligands for designing the hierarchical self-assembly, the assemblies can be stabilised and transformed into robust materials as the nanoparticles possess a range of surface-binding properties while the attached ligands can be tuned to tailor interaction with the surroundings and by performing suitable chemistry to the functional groups present in the attached ligands. Based on this conceptive, nanoparticle-decorated membranes with sizes ranging from micrometers to millimetres have been designed with highly controllable permeability due to the presence of a close-packed layer of colloidal particles linked together to form a solid shell at fluid interfaces under benign reaction conditions. A variety of cross-linking strategies have been pursued for designing two-dimensional arrangement of both hydrophilic and hydrophobic nanoparticles at oil-water interfaces for example interdigitation of ligands, vanderwaal's force, ionic interactions etc.[42-44] We have exploited the formation of covalent bond between the attached ligands to stabilise and to impert machanical strength and robustness to the membranes in oeder to expands their effectiveness and field of applications. We have used different types of surface functionalized metal and metal oxide nanoparticls to synthesize the membranes. These systems feature useful attributes including enhanced mechanical stability and controlled pore size distribution as well as the optical, fluorescent and magnetic properties depending on their precursor particles.[49-51] As a result, the application of this compatible chemistry is of great interest at the interface of materials science, chemistry and biology.[52 - 54]

1.5 Self-Assembly of Nanoparticles at the Liquid-Liquid Interface in 3D

In recent years, self-assembly processes based on selective control of non-covalent and covalent interactions[55] for synthesizing nanoparticle-decorated membranes and capsules at fluid interfaces has attracted researchers due to their potential applications in controlled encapsulation and release.[42-43,56-57] The self-assembly of colloidal particles at fluid interfaces offers a straightforward pathway for fabricating novel materials that have attracted immense interest in academic, scientific, and industrial fields due to their advanced technological applications, e. g., targeted delivery vehicles, tracking, diagnostics, microreactors, filters, biomedical engineering, catalysis, and so forth.[41,56,57] About a century ago, Pickering discovered that colloidal solid particles could be adsorbed onto the liquid−liquid interface to stabilize emulsion droplets to minimize the Helmholtz free energy.[46,47] As a result, colloidal particles localize at the interface, forming a shell made up of colloidal building blocks (both organic and inorganic) leading to the fabrication of microcapsules which makes it possible to achieve significant control over the physical properties of nanodimensional shells.[42−44] The effectiveness in stabilizing the droplets depends on parameters such as the particle size, interparticle interactions, and particle wettability by both the aqueous and oil phases.[58] Due to the advancement of nanoscale synthesis strategies,[59] nanoparticles with diverse morphologies and chemical composition could be exploited for the fabrication of microcapsules with distinct functionalities. These hollow microcapsules provide a means of encapsulation and open up the possibility of harnessing controlled nanoparticle release in a range of novel applications.[60]

Several approaches have been found in the literature to fabricate stable capsules using nanoparticles based on the interfacial assembly of nanometer-sized objects in three dimensions. Duan and coworkers[27] fabricated magnetic-nanoparticle-decorated capsules at the interfaces of water-in-toluene droplets by gelating the water phase with agarose, and the permeability of the capsules can be tailored through the variation of the dimension of the colloidal particles. Koo and colleagues[61] reported the preparation of magnetic microcapsules, based on double emulsions comprising a chloroform core and an iron oxide (γ-Fe_2O_3) nanoparticle-embedded polymer shell, which are reversibly swellable upon repetitive drying and hydration. Samanta and colleagues[62] reported the fabrication of magnetic colloidosomes by cross-linking alkyneand azide-functionalized Fe_3O_4 nanoparticles at a water–oil interface using click chemistry under ambient conditions. Shi *et al.*[63] have reported the combination of a layer-by-layer selfassembly method utilizing dendrimer chemistry to fabricate targeted shell-cross-linked iron oxide NPs for in vivo magnetic resonance imaging of tumors. Zhou *et al.*[64] have synthesized superparamagnetic Fe_3O_4 nanoparticles prepared by a classical coprecipitation method to prepare magnetic Pickering emulsions and investigated the effects of the particle concentration, oil/water volume ratio, and oil polarity on the type, stability, composition, and morphology of these functional emulsions. Hu *et al.*[65] synthesized iron oxide-containing double-emulsion capsules that can release hydrophilic doxorubicin and hydrophobic paclitaxel remotely triggered by a highfrequency magnetic field and energy via internalized iron oxide nanoparticles for magneto-chemotherapy/hyperthermia with multiple drugs. Kong and colleagues[66] have described hollow capsules containing the desired anticancer drugs together with magnetic nanoparticles, which can provide a powerful magnetic vector for penetration into a tumor and on-demand drug release upon external radio frequency stimulus. Gorin and colleagues[67] have reported nanocomposite microcapsule shells composed of iron oxide together with gold nanoparticles and established the effect of a magnetic field on the microcapsule concentration along with the sensitivity of the capsules to laser irradiation. On the basis of these perspectives, we have employ gold and iron oxide nanoparticles as the constituent particles for the preparation of microcapsules because the interfacial communication between the nanoscale Au and Fe_3O_4 results in a multimodal platform with magnetic − plasmonic bifunctionality.[68,69] Moreover, the magnetism of Fe_3O_4 NPs is enhanced via interfacial interaction with Au NPs, making the capsules more magnetic in nature.[70] The unique properties of both the iron oxide and gold result in a versatile platform for use as MRI contrast agents and a nanoheater.[71] Therefore, the capsule wall consisting of both Au and Fe_3O_4 contains both magnetically and optically active NPs, which show high potential applications to drug delivery and biomedical imaging.[72-74] In this work, we have reported the fabrication of composite microcapsules consisting of plasmonic gold and magnetic iron oxide nanoparticles at a water−toluene interface by ligand polymerization. The formation of the capsules has been characterized by UV − vis spectroscopy, Fourier transform infrared spectroscopy, optical microscopy, transmission electron microscopy, and scanning electron microscopy images. The response of the MCs in the presence of a bar magnet indicates that the capsules can be manipulated using an external magnetic field. To study the efficacy of these assemblies, the permeability of the capsule wall has been unraveled using dye molecules of three different sizes, and the size-selective permeability of the capsule wall has been demonstrated.

1.6 Self-assembly of Nanoparticles Leading to Different Morphologies

In recent years, the self-assembly of nanoscale objects has paved the way towards a simple and general strategy to organise nanoparticles into higher order architectures.[75] Such processes require adequate stabilization of the nanoparticles at interfaces with a high degree of organizational selectivity.[75,76] Amongst the three different approaches that are currently exploited to effect ordering of nanoparticles by the self-assembly processes, liquid–liquid interfaces offer an important alternative scaffold for colloidal crystallization into higher ordered nanostructures.[76] A number of innovative approaches have been explored to engender interfacial ordering effects for the organization of nanometer-size objects into both two and three dimensions, including membranes,[77] capsules,[78] core–shell structures,[79] heterodimeric alloyed nanostructures,[80] Janus particles,[81] and giant supramolecular assemblies[82] with distinct functionalities. Nanoobjects made with the semiconductor zinc oxide (ZnO) have attracted immense interest due to its direct wide band gap (3.37 eV), high exciton binding energy (60 meV) and the opportunity to vary its properties by morphological tuning.[83] One-dimensional semiconductor nanostructures (nanowires and nanorods) have attracted special interest due to their fascinating physical properties and potential applications in electronic and photonic devices,[84] room temperature UV laser, dye sensitized solar cell, light emitting diode, varistor, sensor, laser, field emission displays, as high efficient green phosphor, as an UV photodetector materials etc. Due to its present importance and upcoming applications, it is obvious that, tremendous interest has been given to explore various synthetic methods for different particle size, shape and hierarchical assemblies.

In conclusion, the self-assembly of nanoparticles can give rise to varieties of hierarchical architectures depending on the synthetic condition. For liquid–liquid interfaces, reduction in the interfacial energy is the dominated driving force, which is essentially enthalpically driven. Given the wide range of synthetic methods for well-defined nanoparticles of many types, the selfassembly of nanoparticles into hierarchically ordered structures, using interfacial interactions to advantage, represents a rich new area for fabricating optical, acoustic, electronic, and magnetic materials.

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