INTRODUCTION

1.1 Nanotechnology

Nanotechnology is the study, investigation, and creation process of functional and useful materials, devices, and systems through control of matter at the nanometer (nm) scale, generally between 1 to 100 nm in at least one dimension. The study of physical properties of nanoscale materials has led to numerous new applications. The word “Nanotechnology” was originated from a Greek word which means "dwarf" i.e. one billionth of a meter (1nm = 10^{-9} m). The nanoscale is unique because nothing solid can be made any smaller. It is also unique because many of the mechanisms of the biological and physical world operate on length scales from 1 to 100 nm. At these dimensions materials exhibit different physical properties, thus scientists expect that many novel effects at the nanoscale will be discovered and used for breakthrough technologies.

A number of important breakthroughs have already occurred in nanotechnology. These developments are discovered in materials and products used throughout the world. Some examples are devices in computers that read from and write to the hard disk, catalytic converters in automobiles that help to remove air pollutants, certain sunscreens, and cosmetics that transparently block harmful radiation from the sun. Still, many scientists believe that they have only scratched the surface of nanotechnology’s potential and it will have a major impact on medicine and health care; energy production and conservation; environmental cleanup and protection; electronics, computers, and sensors; and world security and defense.

To grasp the size of the nanoscale, consider the diameter of an atom, the basic building block of the matter. The hydrogen atom, one of the smallest naturally occurring atoms, is only 0.1 nm in diameter. In fact, nearly all atoms are roughly 0.1 nm in size, too small to be seen by human eyes. We know that atoms bond together to form molecules, the smallest part of a chemical compound. Molecules that consist of about 30 atoms are only about 1 nm in diameter. Molecules, in turn, compose cells, the basic units of life. Human cells range from 5,000 to 200,000 nm in size, which means that they are larger than the nanoscale. However, the proteins that carry out the internal operations of the cell are just 3 to 20 nm in size and so have nanoscale dimensions. Viruses that attack human cells are about 10 to 200 nm, and the molecules in drugs used to fight viruses are less than 5 nm in size.
1.2 Synthetic Strategies

There are two different approaches to synthesize nanocrystals (NCs): the top-down physical processes and the bottom-up chemical methods (Figure 1.1). In the "bottom-up" approach, materials and devices are built from molecular components which assemble themselves chemically by principles of molecular recognition. The term molecular recognition refers to the specific interactions between two or more molecules through noncovalent bonding such as hydrogen bonding, metal coordination, hydrophobic forces, van der Waals forces, pi-pi interactions, electrostatic and electromagnetic effects. The host and guest involved in molecular recognition exhibit molecular complementary. In the "top-down" approach, the nanoobjects are constructed from larger entities without atomic-level control.
The size or shape control of semiconductor NCs can be accomplished by adjusting the space in which the NCs grow (e.g., in templates).

Creating nanostructured materials based on bottom-up method is a fast-growing field of research. Of particular interest are two-dimensional arrays of NCs, which have been shown to display unique optoelectronic, magnetic, or catalytic properties that can be tuned by varying their size and/or interparticle separation distance. Advanced functional materials incorporating well-defined NCs architectures have potential for practical applications in many areas, including miniaturized nanoelectronics, ultrafast quantum computing, high-density memory/data storage media, ultrasensitive chemical sensing/biosensing, generation of high-efficiency catalytic substrates, and high-throughput templating for the growth/attachment of other types of bio- or inorganic nanomaterials.

Synthesis of protein protected NCs are of particular interest to understand the protein’s specificity and binding capabilities. One of the most widely used proteins is Bovine Serum Albumin (BSA) (Figure 1.2). Serum albumin is the most abundant protein in blood plasma and it serves as a vehicle for intracellular transportation. Serum albumin is of great importance in pharmacology as the conjugation of drugs to albumin decreases their toxicity.

**Figure 1.2. Structure of BSA showing its three homologous domains.**
It has also been reported that BSA conjugated NCs show improved stability against flocculation, increased quantum yield, and low toxicity. BSA can then be conjugated for the targeting purpose. Typically, bioconjugation of NC is a multistep process. This requires the modification of NC surface with a linker that can recognize the biomolecule and can also protect the NC from uncontrolled growth and aggregation.

The synthesis of NCs of metals and metal alloys by biological molecules is known as biomineralization. Over millions of years of evolution, nature has evolved mechanisms to produce such NCs for a wide variety of purposes. Diatoms produce exquisitely intricate porous silica shells with nanoscaled spikes (Figure 1.3, left panel), pores and valleys, and sponges produce spicules that are utilized for structure and protection. Bacteria synthesize crystalline magnetic NCs for navigation and orientation. Algae, plants and bacteria produce metal NCs (Figure 1.3, right panel) as a consequence of detoxification pathways. In many cases, the NCs are produced under genetic control, resulting in specific morphologies, sizes, and crystallinities of the structures and particles.

For appropriate biocompatible applications of bioconjugated chalcogenides, carefully designed synthetic routes involving biological molecules such as amino acids, proteins, and biopolymers are required. Colloidal synthesis of nanochalcogenides is an exciting branch of synthetic inorganic chemistry in which surface active compounds provide charge and steric stabilizations for the growing nucleating centers in order to attain desired morphologies. Many groups have followed this route to obtain fine morphologies at
relatively much elevated temperatures. However, in order to synthesize biomaterials involving biomolecules, it is desirable to have relatively low temperature (<100 °C) synthesis where biofunctionalities could be retained.

Bioconjugated NCs\textsuperscript{35-38} have become the focus of intensive research due to their applications in drug delivery, biological labeling, luminescence tagging, etc. Semiconductor chalcogenides have been widely used as optical filters, optical recording materials, thermoelectric cooling materials, sensors, solar cells, superionic materials, and laser materials\textsuperscript{39-42}. Lead selenide (PbSe) is an attractive semiconducting material that has been employed to produce photoresistors, photodetectors, photovoltaic absorbers, photographic plates, and so forth. PbSe has been the subject of particular attention because of its narrow band gap (in bulk) of 0.28 eV (at room temperature) and strong quantum confinement effects due to its large Bohr radius ($r_B \approx$ 46 nm)\textsuperscript{43-54}. Many recent reports\textsuperscript{55-62} have focused on the synthesis of various shapes, and physics of PbSe NCs. Cadmium selenide (CdSe), another calcogenide, has a much lower $r_B$ in comparison to PbSe. It is equally important material to use in opto-electronic devices, laser diodes, nanosensing, biomedical imaging and high-efficiency solar cells\textsuperscript{63-65}. Considering the rapid miniaturization of technology in all fields, we have synthesized important chalcogen-based materials, i.e. PbSe and CdSe at the nanoscale using aqueous solution phase synthesis at relatively mild temperature of 85 °C with particular emphasis on their biocompatible applications.

Bovine Serum Albumin (BSA) has been chosen due to its important characteristic features. It is an important blood protein with molecular weight of 66500 Da and is composed of 580 amino acid residues\textsuperscript{66,67} (Figure 1.2). BSA contains one single cysteine and eight disulfide bonds. The overall shape of BSA is oblate ellipsoid which contains three structurally homologous domains I, II, and III. It is a water soluble and weak reducing agent and has already been used as a capping/stabilizing agent for the synthesis of semiconductor nanomaterials and various noble metals\textsuperscript{68-70}. BSA binds endogenous as well as exogenous substrates in its hydrophobic pockets\textsuperscript{71}. It is well-known that protein denaturation is often followed by a massive "unfolding" of the protein. Native BSA is a globular protein which undergoes structural changes and transforms into its unfolded or tertiary configuration. This secondary structure consists of hydrogen bonded $\alpha$-helices and $\beta$-sheets, and is called the large-scale structure. The latter structure even proved to be a better capping/stabilizing agent.
We have recently observed\(^7\) that (Figure 1.4), there is a significant capping/stabilizing difference between the native and denatured states of BSA. The unfolded or denatured BSA is much efficient in controlling the crystal growth.

1.3 The Importance and Use of Biomolecules in the Synthesis of Nanomaterials

Now-a-days, people are becoming more and more interested in materials with recognition properties toward biological macromolecules, such as protein and nucleic acids. Biomolecules are the subject of particular attention due to their nanoscale dimensions, their various and distinctive molecular structures and functionalities, and their specificities and versatility in recognition and assembly. The conjugation of nanoparticles (NPs) with biomolecules could provide electronic or optical transduction of biological phenomena in the development of novel biosensors\(^{73,74}\). A nanometer scale has significant relevance to the biological systems, where many proteins are in the nm size similar to those of NPs, thus the two classes of materials are structurally compatible. Enzymes, antigens and antibodies, and biomolecular receptors have dimensions in the range of 3-20 nm. Because of several fundamental features, biomaterials are the important future building blocks for NP architectures. For example, biomaterials display specific and strong complementary
recognition interactions and thus to self-assembly. Various biomolecules contain several binding sites and this allows the multidirectional growth of NP structures. Proteins may be genetically engineered and modified with specific anchoring groups. This facilitates their aligned binding to NPs or the site-specific linkage of the biomaterial to surfaces. Consequently, the directional growth of NP structures may be dictated. Deoxyribonucleic acid (DNA) may be synthetically prepared in complex rigidified structures that act as templates for the assembly of NPs by electrostatic binding to phosphate groups. Enzymes are catalytic tools for the manipulation of biomaterials. For example, the ligation process of nucleic acids provides effective tools for controlling the shape and structure of biomolecule-NP hybrid systems. In this context, it has been found that Mother Nature has developed unique biocatalytic replication processes and the use of these biomolecule-NP conjugates may provide an effective system for the formation of nanostructures of specific shapes and compositions.

The importance of functionalized NPs for biomedical applications cannot be overestimated. For example, targeted entry into cells is an increasingly important area of research\textsuperscript{75}. The nucleus is a desirable target because the genetic information of the cell and transcription machinery resides there. Gold (Au) NPs\textsuperscript{76} (20 nm) were modified with shells of BSA which were conjugated to various cellular targeting peptides to provide functional NPs that penetrate the biological membrane and target the nuclei. Various NPs are applied as drug-delivery agents to tumors in the analysis and medical treatment of cancers\textsuperscript{77}. The functionalization of NPs with biomolecules effects the change in the shape and hence the properties of the NPs. Upon adsorption of vitamin C on TiO\textsubscript{2} NPs, the optical properties of the particles were red-shifted by 1.6 eV as a result of charge transfer that originates from the specific binding of the electron-donating modifier to corner defects on the surface of the NPs\textsuperscript{78}. The solubility of NPs in water can be greatly improved by the functionalization of their surfaces with highly hydrophilic biomolecules\textsuperscript{79}. A biomolecule can speed up or slow the rate at which a monomer is generated, changing its concentration and, in turn, its solubility equilibria or crystal nucleation and growth rates. Au NPs modified with long chain alkanethiols are only soluble in low-polarity organic solvents. Furthermore, Au NPs that are modified with biomolecules such as tiopronin or coenzyme A give excellent solubility in water\textsuperscript{79}.
Biomolecule-directed mineralization can lead to the formation of biomineralized hybrid structures with improved performance in nature. The presence of a biomolecule can also change the course of crystal nucleation or growth. A biomolecule that coordinates strongly to a metal center could, of course, prevent crystallization altogether. Alternatively, a biomolecule can bind selectively to certain facets, speeding or slowing monomer addition to that facet relative to others, which results in non-thermodynamic and often highly anisotropic crystal shapes. Biomacromolecule surface recognition by NPs as artificial receptors provides a potential tool for controlling cellular and extracellular processes for numerous biological applications such as transcription regulation, enzymatic inhibition, delivery and sensing. The size of NP cores can be tuned from 1.5 nm to more than 10 nm depending on the core material, providing a suitable platform for the interaction of NPs with proteins and other biomolecules. The conjugation of NPs with biomolecules such as proteins and DNA can be done by using two different approaches, direct covalent linkage and non-covalent interactions between the particle and biomolecules. The most direct approach to the creation of integrated biomolecule-NP conjugates is through covalent attachment. Direct covalent linkage can be achieved either through chemisorptions of the biomolecule to the particle surface or through the use of heterobifunctional linkers. Chemisorption of proteins onto the surface of NPs can be done through cysteine residues that are present in the protein surface. The combination of one-dimentional (1D) NCs with biomolecules paves the way to novel nanobioelectronic elements that could, for instance, transport bioelectronic signals along that 1D nanowires. The combination of nanoobjects, nanotools, and nanotemplates with biomolecules gives new ideas of bioelectronics to open new doors of nanobioelectronics. This is the reason to synthesize and to see the properties of biomolecule–nanoparticle/nanorod hybrid systems as well as the organization of these systems as functional devices.

1.4 Review of Literature

Gao et al. used a simple biomolecule-mediated process to the direct growth and assembly of CdS nanorods. Many kinds of biomolecules such as amino acids (glycine, serine), peptides (glycyl-glycine, glutathione), protein (gelatin, lysozyme), protein metabolism product (guanidine), RNA base (uracil), and pyrimidine (uridine) have been utilized. A series of complex CdS nanorod-based structures have been synthesized in high
yields, including three-dimensional (3D) and two-dimensional (2D) leaflike structures and flower-like structures by assembly of CdS nanorods. The product’s morphology and structure have been confirmed to correspond to the used biomolecule’s type and structure. By controlling biomolecule’s structure and type, reactant’s concentration, ratio of inorganic compound to biomolecule, heating method, and reaction temperature, CdS nanorod-based 3D leaves, 2D leaves, or flowers could be obtained with predominantly single morphology. This study shows that the structures of biomolecules appear to direct the morphology of complex nanostructures of inorganic materials such as CdS and could theoretically lead to more complex and useful nanostructures of many other materials. Yang et al.96 described the small-biomolecule (glycyl glycine)-directed synthesis of single-crystalline Ag nanoplates. It was found that the ratio of glycyl glycine to AgNO₃ was the key to forming Ag nanoplates. The
nanoplates were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscopy (TEM). Zhou et al.\textsuperscript{97} reported the preparation of a compact, functional quantum dot (QD)-DNA conjugate, where the capturing target DNA is directly and covalently coupled to the QD surface.

Bakshi et al.\textsuperscript{72} first reported the PbS NCs synthesized in aqueous phase within a temperature range of 40-80 °C in the presence of native and denatured states of BSA as the capping/stabilizing agent. The purpose of this study was to design bio-nanomaterials whose shape and structure depend on the nature of protein biomacromolecules. Due to the water soluble nature of BSA, it acts as a capping as well as stabilizing agent for colloidal PbS NCs, while thermal denaturation of BSA effectively alters this property. An important dependence of NC morphology on the native to denatured states of BSA has been observed where latter state proves to be quite effective in controlling the NC shape and size. At 40 °C, large spherical PbS NCs are obtained and their size decrease as temperature is increased to 80 °C. Tong et al.\textsuperscript{98} reported a simple biomolecule-assisted synthesis of ZnS nanostructured spheres assembled from ZnS NCs with the controllable crystal phase and morphology. L-Cysteine, a biomolecule, was used as the sulfur source and played a key role in the formation of ZnS nanostructured spheres. Wu et al.\textsuperscript{99} studied a biomolecule-assisted hydrothermal route for generating SnO\textsubscript{2} with diameters <10 nm. SnO\textsubscript{2} is an n-type semiconductor with the free exciton Bohr radius of 2.7 nm. The degradation of rhodamine B (RhB), an organic dye in aqueous suspension is selected as a probe reaction to evaluate the catalytic activity of semiconductor photocatalytic performance. Zheng et al.\textsuperscript{100} reported the nanocrystalline ZrO\textsubscript{2} with narrow size distribution and mean size of about 8 nm by the L-lysine assisted hydrothermal method. The structural and morphological characterizations were studied by XRD and TEM, and physicochemical characterizations were carried out by using infrared spectra (IR), UV-visible spectra, and photoluminescence (PL) spectra.

Sarkar et al.\textsuperscript{101} studied the development of semiconductor CdS NCs (QDs of average diameter less than 2 nm) directly conjugated to a transporter protein human serum albumin (HSA) as fluorescent biological labels. This study is likely to attract widespread attention as a powerful tool for the study of protein folding. Liu et al.\textsuperscript{102} prepared PbS fishbone-like architectures by using a biomolecule (L methionine)-assisted approach in a mixture solvent made of ethanolamine (EA) and distilled water. The as-prepared PbS products were
examined by using XRD, field emission scanning electron microscope (FESEM), TEM, high resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED) and PL. *Chen et al.*\(^{103}\) reported well-defined hexangularly faced CdS nanorod arrays which were fabricated via a facile one-step and non template hydrothermal approach in large scale by using biomolecules of glutathione as capping agents. Structural and morphological evolutions of CdS nanorod arrays were studied by SEM, TEM, and XRD. A formation mechanism of CdS nanorod arrays via this one-step synthesis was tentatively studied by investigating the effects of synthesis parameters on the nanorod arrays. The growth process of CdS nanorod arrays was discussed further from the absorption spectra of CdS nanorod arrays obtained at different reaction times.

*Zuo et al.*\(^{104}\) prepared nanocube-based pagoda-like PbS hierarchical architectures which were fabricated by hydrothermal treatment of Pb(Ac)\(_2\) and L-cysteine solution. It was suggested that a biomimetic mineralization process happened during the growth of the hierarchical architectures. The biomolecule, L-cysteine, exerts coordination, oriented nucleation of crystals, and the morphology modulating effect. By studying the intermediates of the reaction, they observed that 4-fold symmetric star-shaped microcrystals were formed at first, and a second nucleation process resulted in the generation of nanocube-based pagoda-like hierarchical architectures. *Xiang et al.*\(^{105}\) reported Ag\(_2\)S nanospheres which were synthesized by a hydrothermal reaction using L-cysteine as the sulfur source and chelating reagent. The XRD and X-ray photoelectron spectroscopy (XPS) confirmed that the products were monoclinic α-Ag\(_2\)S. The optical absorption spectra of the Ag\(_2\)S nanospheres showed very broad absorption peaks centred at about 515 nm in wavelength. PL spectra exhibited emission peaks centered at about 637 nm in wavelength accompanied by weaker shoulder peaks at nearly 590 nm in wavelength when the sample was excited with a wavelength of 490 nm. *Mi et al.*\(^{106}\) designed a novel “green” chemical route to prepare nanostructured Bi\(_2\)Te\(_3\) in near-critical water using the biomolecule alginic acid as reductant.

*Zhao and Qi*\(^{107}\) have also carried out synthesis of star-shaped PbS NCs by the thermal decomposition of thioacetamide (TAA) in aqueous solutions of lead acetate in the presence of the cationic surfactant (CTAB) and the anionic surfactant sodium dodecyl sulfate (SDS). A low-magnification SEM image of the PbS product obtained after a reaction time of 5h, indicates the exclusive formation of uniform star-like NCs. The related XRD pattern
shows sharp peaks corresponding to cubic PbS with a rock salt structure, confirms the formation of pure PbS NCs. Reaction temperatures of 190-250 °C and multicomponent surfactant mixtures result in a nearly defect-free crystal lattice and high uniformity of nanowire diameter along the entire length. In addition to straight nanowires, zigzag, helical, branched, and tapered nanowires as well as single-crystal nanorings can be prepared in one-pot reactions by careful adjustment of the reaction conditions. Wang et al.\textsuperscript{108} gave a novel and simple one-step solid-state reaction in the presence of a suitable surfactant. They have synthesized PbS NPs with the diameters of 10-15 nm by using the above method. The PbS NPs were characterized by XRD, TEM, HRTEM, UV-visible absorption, and XPS. The role of surfactant C\textsubscript{18}H\textsubscript{37}O(CH\textsubscript{2}CH\textsubscript{2}O)\textsubscript{10}H (abbreviated as C\textsubscript{18}EO\textsubscript{10}) in the formation of PbS NPs was discussed, and the results indicated that C\textsubscript{18}EO\textsubscript{10} played an important role in the preparation of PbS NPs. Gautam and Seshadri\textsuperscript{109} employed a new solvothermal route for the preparation of NCs of PbS and PbSe, involving a reaction of lead stearate with sulfur or selenium and tetralin (tetrahydronaphthalene) in toluene solvent. The NCs were characterized by powder XRD and electron microscopy. The use of surfactant Triton X-100 resulted in both nanorods and nanoparticles of PbSe. Wang et al.\textsuperscript{110} prepared cross-shaped PbS crystals composed of six pods by refluxing. Parameters affecting the morphology of PbS have been investigated systematically. Results reveal that various PbS structures including cubic, truncated octahedral, flower-shaped and dendritic crystals were obtained by changing the sulfur and lead source, the solvent or the surfactant.

Zhu et al.\textsuperscript{111} reported the PbSe NPs of about 12 nm in size. They have prepared them by a pulse sonoelectrochemical technique from an aqueous solution of sodium selenosulfate and lead acetate. The PbSe NPs were characterized by TEM, XRD, absorption spectroscopy, diffuse reflection spectrum, and energy-dispersive X-ray (EDX). Bierman et al.\textsuperscript{112} studied a chemical vapor deposition (CVD) synthesis of hyperbranched single-crystal nanowires of both PbSe and PbS using PbCl\textsubscript{2} and S/Se as precursors under hydrogen flow. Multiple generations of nanowires grow perpendicularly from the previous generation of nanowires in an epitaxial fashion to produce dense clusters of a complex nanowire network structure. The flow rate and duration of the hydrogen co-flow in the argon carrier gas during the CVD reactions are found to have a significant effect on the morphology of the PbSe/PbS grown, from hyperbranched nanowires to micrometer-sized cubes. Pietryga et al.\textsuperscript{113} reported the
synthesis of PbSe colloidal QDs with efficient, particle-size-tunable, narrow band width mid-IR photoluminescence at energies as low as 0.30 eV. Bulk PbSe has a band gap of 0.26 eV at room temperature, so PbSe QDs have the potential to provide PL in the mid-IR energy range. All QDs were characterized by PL and absorption spectroscopy, as well as by TEM. Pietryga et al. had synthesized and further used PbSe QDs to produce heterostructured NCs (PbSe/CdSe/ZnS core/shell) with bright, stable infrared emission. PbSe QDs, provide efficient emission over a large spectral range in the infrared, but their application has been limited by instability in emission quantum yield and peak position on exposure to ambient conditions and hence this is overcome by making these core shell structures.

Ren et al. synthesized the hexagonal selenium (Se) nanowires by using a simple vapor-phase growth with the assistance of the silicon powder as a source material, which turned out to be very important in the growth of the Se nanowires. The morphology, microstructure, and chemical compositions of the nanowires were characterized using various means such as XRD, SEM, TEM, XPS, and Raman spectroscopy. XRD patterns of the samples demonstrate that the nanowires have a pure hexagonal Se phase. EDS and XPS results confirmed that the nanowires consist of Se, while a small amount of Se is in the state of Se-O bonds sheathing the nanowires. TEM and SEM revealed that the length of nanowires is up to several micrometers and the diameter of nanowires can be as thin as 20 nm. HRTEM analysis depicted the detailed crystalline structures of the Se nanowires. Raman spectra of Se nanowires were compared with that of the bulk Se powder. High-yield synthesis of bamboo-raft-like single-crystalline Se superstructures had been realized for the first time by Song et al. via a facile solvothermal approach by reducing SeO₂ with ethylene alcohol in the presence of cellulose acetate. The formation of a raftlike superstructure with various forms is strongly dependent on the temperature, amount of cellulose acetate, reaction time, and even preheating treatment. The suitable amount of cellulose acetate is essential for the formation of elegant and uniform raft Se. The morphology, microstructure, optical properties, and chemical compositions of bamboo-raft-like Se were characterized using the following techniques as XRD, FESEM, TEM, HRTEM, XPS, UV-visible spectroscopy, Fourier Transform Infrared spectroscopy (FTIR) and Raman spectroscopy. Single-crystalline nanobelts and nanowires of trigonal selenium (t-Se) have been selectively synthesized by Ma et al. in micellar solutions of nonionic surfactants. In particular, t-Se nanobelts about 30
In thickness were obtained in micellar solutions of poly(oxyethylene(20)) octadecyl ether (C\textsubscript{18}EO\textsubscript{20}), whereas t-Se nanowires were obtained in micellar solutions of poly(oxyethylene(10)) dodecyl ether (C\textsubscript{12}EO\textsubscript{10}). Elemental t-Se microrods have been synthesized by Mondal et al.\textsuperscript{118} using a facile solution-phase biomolecule approach in the presence of L-cysteine being used as both the ligand for the formation of the complex and a capping agent under hydrothermal conditions. The phase analysis, purity, and morphology of the product have been studied by XRD, SEM and Raman spectroscopy. Xiong et al.\textsuperscript{119} have carried out synthesis of Se nanoneedles with the stem diameter ranging from 100-500 nm and lengths up to tens of micrometers, gradually becoming thinner to form a sharp tip, which were fabricated by reduction of sodium selenite (Na\textsubscript{2}SeO\textsubscript{3}) with poly(vinyl alcohol) (PVA). An interesting feature of the nanoneedles is their tendency to form branches and junctions. The morphology of Se nanoneedles were characterized by using various methods such as XRD, FESEM, TEM, and HRTEM, indicating that the nanoneedles were single crystalline with high purity, structurally uniform, and dislocation-free. Nath et al.\textsuperscript{120} have described the synthesis of Se NPs through the reduction of aqueous selenious acid solution by sodium borohydride. To prevent aggregation of the particles and to offer stability, a non-ionic micelle, Triton X-100, has been introduced into the reaction medium. The NPs were characterized by UV-visible spectroscopy, atomic force microscopy (AFM), and XPS studies. The characteristic catalytic behavior of the Se particles is established by studying the decolorization of methylene blue in the presence of UV light. It has been authenticated from the study that the NPs afforded a complete mineralization process and the rate of dye decolorization varies linearly with the NP concentration. Song et al.\textsuperscript{121} have reported Se/C nanocables through the reduction of Na\textsubscript{2}SeO\textsubscript{3} with glucose in the presence of CTAB under hydrothermal conditions. In the process, glucose acts as a reducing agent and carbon source, and the final morphology of the product was determined by the CTAB concentration. The products are characterized in detail by XRD, EDX, SEM, and TEM. The results show that the obtained products are coaxial nanocables with lengths of 2-6 \( \mu \text{m} \), about 300-500 nm in diameter, and a surrounding sheath about 20-30 nm in thickness. It is of great importance and wide application that the obtained Se/C coaxial nanocables could be tailored freely by an electron beam of TEM. Zhang et al.\textsuperscript{122} have reported solution-phase approach to the large-scale synthesis of faceted single-crystalline Se nanotubes, in the presence of CTAB. Shah et
al.\textsuperscript{123} gave a new simple wet chemical method to synthesize Se NPs (50-100 nm), by reaction of sodium selenosulphate precursor with acrylonitrile monomer, under ambient conditions. PVA has been used to stabilize the Se NPs.

\textit{Bakshi et al.}\textsuperscript{124} reported Au nanoribbons in aqueous phase under ambient conditions by using dimethylene bis(tetradecyldimethyl-ammonium bromide) (abbreviated as 14-2-14) as a capping agent as well as a soft template. A two steps seed-growth (S-G) method was used. The first step of S-G method mainly gave nanorods of high aspect ratio along with NPs of other shapes, but the next step produced mainly fine Au nanoribbons of several micrometers long, 50-150 nm wide, and \( \approx 5 \) nm thick. They were characterized by TEM, XPS, EDX, and XRD. \textit{Sau et al.}\textsuperscript{125} reported the short Au nanorods of average lengths ranging between 20 and 100 nm (with corresponding aspect ratios of 2 and 4). These nanorods were characterized by dark-field microscopy, UV-visible spectroscopy, and TEM. \textit{Jana et al.}\textsuperscript{126} followed S-G method to produce Au NPs of diameters 5-40 nm. The particle size can be controlled by varying the ratio of seed to metal salt, and thus any size in the range 5-40 nm can be prepared. \textit{Shi et al.}\textsuperscript{127} gave a method to produce core-shell structures consisting of monodisperse polystyrene latex nanospheres as cores and Au NPs as shells. Use of polystyrene spheres as the core in these structures is advantageous because they are readily available commercially in a wide range of sizes, and with dyes or other molecules doped into them. Au NPs, ranging in size from 1-20 nm, are prepared by reduction of a Au precursor with sodium citrate or tetrakis(hydroxymethyl)phosphonium chloride (THPC). \textit{Wei and Qian}\textsuperscript{128} also reported the fabrication of Au NPs by UV photoactivation in the presence of biopolymeric chitosan and the tracing of the Au salt solution aging. Detailed UV-visible spectroscopy study witnessed the evolution of the surface plasma resonance (SPR) absorption during the Au NPs growth. The effect of chitosan in aqueous solution for the Au NPs preparation was investigated in detail. The results indicated the size and distribution of Au NPs could be controlled over by altering the concentration of chitosan, and the Au NPs growth during aging was a chitosan-mediated autocatalytic process. FTIR showed that the hydroxyl in molecular chitosan was oxidized to carbonyl groups in the fabrication of Au NPs after aging and nitrogen atoms are the main sites for the complexation of chitosan with Au atoms. \textit{Huang and Yang}\textsuperscript{129} studied that the Au NPs were prepared by reducing Au salt with chitosan, in the absence/presence of tripolyphosphate (TPP). Here, chitosan acted as a
reducing/stabilizing agent. Sarma and Chattopadhyay\textsuperscript{130} reported the synthesis of Au NPs with tunable longitudinal plasmon band and shape selectivity, mediated by starch in the presence of ultrasonic waves. The synthesis was carried out by reduction of HAuCl$_4$, at various concentrations, using H$_2$O$_2$ as the reducing agent. The conformational changes of BSA in the albumin : Au NP bioconjugates were investigated in detail by Shang \textit{et al.}\textsuperscript{131} by using various spectroscopic techniques including UV-visible absorption, fluorescence, circular dichroism, and FTIR spectroscopies.

Nanocrystalline CdS particles directly conjugated BSA protein were prepared by Meziani \textit{et al.}\textsuperscript{132} by applying the supercritical fluid processing technique, rapid expansion of a supercritical solution into a liquid solvent. The direct conjugation takes advantage of the unique features of the process for NPs formation. The BSA-conjugated CdS NPs in stable aqueous suspension or in the solid state were characterized by using microscopy, XRD, and optical spectroscopy methods. The results show that well-dispersed CdS NPs are coated with BSA in a core-shell-like arrangement and that the protein species associated with the NPs remain functional according to the modified Lowry assay. Highly water soluble and biocompatible L-cysteine-capped CdS NPs having narrow size distribution were synthesized by Chatterjee \textit{et al.}\textsuperscript{133} for the first time by $\gamma$ -irradiation technique without using any additional stabilizer. FTIR study shows that CdS NPs are capped through mercapto-group of cysteine amino acid while its free amino and carboxylate groups make it amenable to bioconjugation. Size and luminescence of the NPs can be well controlled by varying the parameters like radiation dose, pH and concentration of cysteine. He and Urban\textsuperscript{134} gave a communication which outlines a simple two-step approach of modification of 1 nm diameter Au NPs using an aqueous solution of (1,2-dipalmitoyl-$sn$-glycero-3-phosphothio-ethanol) phospholipid. TEM as well as particle size analysis show that, as a result of phospholipid reactions with Au particles, the initial Au NP size increases to 5 nm. Considering the size of the phospholipid and their ability to form liposomes, 5 nm diameter spheres indicate that the phospholipid bilayer was attached to the surface of Au particles and the phospholipid-Au interactions are facilitated by the presence of thiol functionality.

1.5 Research Plan

In view of all these studies, a systematic and comprehensive work to synthesize and characterize metal and semiconductor NPs by using a series of biomolecules such as BSA,
zein protein, phospholipids, DNA, and chitosan has been carried out. The main goal of this study was to achieve the shape controlled synthesis by utilizing the stabilizing as well as surface active properties of these complex molecules which range from high molecular weight proteins to small phospholipids. Various factors such as folding/unfolding of proteins, hydrophilic/hydrophobic properties, and their interfacial adsorption have been compared and discussed to achieve the shape controlled morphologies at nanoscale. Likewise, the material’s properties related to the nucleation and subsequent growth of NPs under the capping and stabilizing effects of these biomolecules have been explored and discussed on the basis of crystal structures of various semiconducting and noble metal NPs. Keeping in view of the film making properties of zein protein, zein conjugated Au NPs have further been used in the environmental friendly biodegradable protein film formation for their industrial applications especially in the food and pharmaceutical industries. It has been shown that Au NPs incorporated zein films have much stronger tensile strength and flexibility than pure zein protein films normally used for such applications. Finally, all reactions have been carried out and standardized in aqueous phase so as to preserve the biofunctionalities of biomaterials in view of environmental concerns and green chemistry. We have carried out the above work to achieve the following objectives:

1. *Synthesis and characterization of metal chalcogenides and noble metal nanocrystals by using various biomolecules as capping or stabilizing agents.*
2. *Evaluation and influence of molecular and structural factors of different kinds of biomolecules on the shape directed synthesis of biomaterials at nanoscale.*
3. *Use of bioconjugated nanomaterials for the synthesis of biodegradable protein films for their industrial applications.*
References

47. Talapin, D. V.; Murray, C. B. Science 2005, 310, 86.
73. Faraday, M. Philos. Trans. 1857, 147, 145.


