Chapter 1

Introduction

1.1. Nanoparticles

The term 'nanoparticle' is used to describe a particle with size in the range of 1 to 100 nm, at least in one of the three dimensions. Because of this very small size scale, they possess an immense surface area per unit volume, a high proportion of atoms in the surface and near surface layers, and the ability to exhibit quantum effects. In this size range, the physical, chemical and biological properties of the nanoparticle change in fundamental ways from the properties of both individual atoms/molecules and of the corresponding bulk material. Nanoparticles exist with great chemical diversity in the form of metals, metal oxides, semiconductors, polymers, carbon materials, organics or biological. They also exhibit great morphological diversity with shapes such as spheres, cylinders, disks, platelets, hollow spheres and tubes, etc. Depending on the material they consist of, nanoparticles can possess a number of different properties such as high electron density and strong optical absorption (e.g. metal particles, in particular Au), photoluminescence (semiconductor quantum dots, e.g. CdSe or CdTe) or phosphorescence (doped oxide materials, e.g. Y$_2$O$_3$), or magnetic moment (e.g. iron or manganese oxide nanoparticles). The unique properties of these various types of nanoparticles give them novel electrical, catalytic, magnetic, mechanical, thermal, or imaging features that are highly desirable for applications in catalysis, biomedicines, and electronics, and environmental sectors.

1.2. Classification of Nanoparticles

Nanoparticles can be classified based upon their sizes, shapes, and materials, and with various chemical and surface properties. There is a constant and rapid growth in this field which adds to the basis of classification. However, the classes of nanoparticles listed below are mainly based upon their constituent materials, and some of their basic properties and current known uses are also described here.

1.2.1. Metal Nanoparticles

Noble metal nanoparticles, such as gold (Au), silver (Ag) and Cu nanoparticles and nanorods, exhibits unique electric, photonic and catalytic properties like local surface
plasmon resonance (LSPR) [1, 2], surface-enhanced Raman scattering (SERS) [3] and surface-enhanced fluorescence (SEF) [4]. The strong plasmon resonance band of the noble metal NPs in the visible region has been used in the development of biosensors for use in colorimetric detection of analytes [5-7]. The light absorption by NPs is related to the incident light interaction with the surface of the nanoparticle. When light of a specific energy interacts with the surface of noble metal NP, an intense localized field is induced. The coupling of the NPs conduction band electrons with the electric field of incident light, at a resonant frequency, generates a localized plasmonic oscillation on the surface of the NPs, designated by surface plasmon resonance (SPR) or localized SPR (LSPR) [8].

1.2.2. Metal Nanoclusters

Similar to metal nanoparticles, study of metal nanoclusters has also received considerable attention in recent years because they bridge the evolution of properties from isolated atoms to nanoparticles and even to the bulk [9, 10]. Providing the “missing link” between atomic and nanoparticles behaviour in noble metals, the fluorescent, water-soluble metal nanoclusters offer complementary transition energy size scalings at smaller dimensions. Their robust, discrete, size-dependent emission makes them ideal fluorophores for single-molecule spectroscopic studies. Their transition energies have been found to scale with the inverse of the cluster radius based on the spherical jellium model [11], valid for metals with free electrons such as gold and silver. Due to the similarity in electronic structure of metal clusters and single atoms, the metal clusters are also called “multi-electron artificial atoms” [12, 13].

According to the spherical jellium model, a metal cluster is represented as uniform, positively charged sphere with electronic shells filled with free electrons. These free electrons are provided by the valence electrons of metal atoms, and they delocalize and form spherical electron shells surrounding the positively charged core. Due to a strong electron screening effect, valence electrons of noble metal atoms are considered free after neglecting electron-electron and electron-ion interactions [14]. Distinct from the electronic structure of single atoms, cluster electron density is independent of the number of free electrons in the metal clusters. However, analogous to single atoms, free electrons in metal clusters are also delocalized for electronic shells surrounding the atoms and subject to the Pauli Exclusion Principle. The jellium model predicts that the emission energy of metallic
nanoclusters follow a power law of the number of atoms in the nanoclusters with no adjustable parameters by the simple scaling relation of $E_{\text{fermi}}/N^{1/3}$ in which $E_{\text{fermi}}$ is the Fermi energy of bulk metal and $N$ is the number of atoms in the nanoclusters. It has been successfully applied to small gold nanoclusters [15], describing accurately the size-dependent electronic structure and relative electronic transitions of the small clusters [11].

1.2.3. Magnetic Nanoparticles

Magnetic nanoparticles are of great interest for researchers from a wide range of disciplines, including magnetic fluids [16], catalysis [17], biotechnology/biomedicine [18], magnetic resonance imaging [19], data storage [20], and environmental remediation [21]. Two key issues dominate the magnetic properties of nanoparticles: finite-size effects and surface effects which give rise to various special features. Finite-size effects result, for example, from the quantum confinement of the electrons, whereas typical surface effects are related to the symmetry breaking of the crystal structure at the boundary of each particle. Magnetic nanoparticles can be utilized in versatile ways, very similar to those of nanoparticles in general. However, the magnetic properties of these particles add a new dimension where they can be manipulated upon application of an external magnetic field. This property opens up new applications where drugs that are attached to a magnetic particle to be targeted in the body using a magnetic field. Here, we briefly introduce different kinds of magnetic nanoparticles.

1. 2. 3. 1. Iron Oxides

Iron oxides have received increasing attention due to their extensive applications, such as magnetic recording media, catalysts, pigments, gas sensors, optical devices, and electromagnetic devices [22]. By definition, superparamagnetic iron oxide particles are generally classified with regard to their size into superparamagnetic iron oxide particles (SPIO), displaying hydrodynamic diameters larger than 30 nm, and ultra small superparamagnetic iron oxide particles (USPIO), with hydrodynamic diameters smaller than 30 nm. Among several crystalline modifications of anhydrous ferric oxides there are two magnetic phases, namely, rhombohedral hematite ($\alpha$-Fe$_2$O$_3$) and cubic maghemite ($\gamma$-Fe$_2$O$_3$). In the $\alpha$-structure, all Fe$^{3+}$ ions have an octahedral coordination, whereas in $\gamma$-Fe$_2$O$_3$ having the structure of a cation-deficient AB$_2$O$_4$ spinel, the metal atoms A and B occur in tetrahedral and octahedral environments, respectively. The oxide $\alpha$-Fe$_2$O$_3$ is
antiferromagnetic at temperatures below 950 K, while above the Morin point (260 K) it exhibits so-called weak ferromagnetism. Among all iron oxides, magnetite Fe₃O₄ possess the most interesting properties because of the presence of iron cations in two valence states, Fe²⁺ and Fe³⁺, in the inverse spinel structure. The cubic spinel Fe₃O₄ is ferrimagnetic at temperatures below 858 K. This inverse spinel structure for magnetite was first suggested to explain the fast electron hopping-continuous exchange of electrons between Fe²⁺ and Fe³⁺ in the octahedral positions at room temperature, rendering magnetite an important class of half metallic material.

1.2.3.2. Manganese Oxides

During the past few decades, manganese oxides have been widely exploited because of their promising applications in many fields, such as catalysis [23], molecular adsorption [24, 25], ion exchange [26], supercapacitors [27], magnetic applications [28], and secondary batteries. Among the manganese oxides, the hausmannite Mn₃O₄ is the most stable oxide at high temperature relative to other manganese oxides, such as MnO₂ and Mn₂O₃. The compound is known to be an active catalyst for the oxidation of methane and carbon monoxide [29], decomposition of waste gases, the selective reduction of nitrobenzene [30], and the combustion of organic compounds at temperatures of the order of 373-773 K. These catalytic applications provide a powerful method of controlling air pollution. Most recently, hollow Mn₃O₄ nanoparticles have been utilized as positive MRI contrast agent (exploiting their room temperature paramagnetism) with enhanced relaxivity attributed to an increased water-accessible surface area and the flexibility of further functional surface modifications [31, 32]. Mn₃O₄ is also a starting material in the preparation of soft magnetic materials, such as manganese ferrite for dioxy-magnetic cores in transformers for power supplies [33], in the lithiation of Li–Mn–O electrode materials for rechargeable lithium batteries [34], and in a corrosion-inhabiting pigment for epoxy-polyamide-based and epoxy-ester-based primers and top coatings.

In recent years, mixed-valent perovskite manganese oxides of general formula Ln₁₋ₓAₓMnO₃ (Ln and A are lanthanide and alkaline-earth cations, respectively) have attracted much attention for their remarkable interrelated structural, magnetic and transport properties induced by the mixed valence (3+ and 4+) of the Mn ions. In particular, they exhibit very large negative magnetoresistance, called colossal magnetoresistance (CMR),
in the vicinity of metal–insulator transition for certain compositions. In the perovskite structure, the MnO$_3$ network of corner-shared MnO$_6$ octahedra is at the origin of an incredible amount of spectacular physical properties which are driven by competition between double-exchange ferromagnetism (DE-F) [35] and a natural tendency towards orbital and charge ordering phenomena [36]. The Jahn–Teller (J-T) Mn$^{3+}$O$_6$ octahedra, with a $t_{2g}^3e_g^1$ electronic configuration for Mn$^{3+}$, can be either flattened or elongated depending on the $e_g$ orbital filling, $d_{x^2-y^2}$ or $d_z^2$, respectively. According to the super exchange rules [37], depending on the orbital configurations, Mn$^{3+}$–O–Mn$^{3+}$ is either antiferromagnetic (AF) or ferromagnetic (F). Starting from LaMnO$_3$, the creation of Mn$^{4+}$ cations ($t_{2g}^3e_g^0$), which lie in much less distorted MnO$_6$ octahedra than Mn$^{3+}$O$_6$, can be induced by Ln$^{3+}$1-xA$_{2+}$x divalent substitution. This is responsible for the ferromagnetic double-exchange, Mn$^{3+}$–O–Mn$^{4+}$. In the La$_{1-x}$Sr$_x$MnO$_3$ series, the ferromagnetism becomes metallic as soon as $x > 0.15$, [38] i.e. as the 3D percolation threshold is reached, and the Curie temperature reaches a maximum $T_C = 371$K value for $x = 0.40$ [38].

### 1.2.4. Quantum Dots

An important field of research, for the past fifteen years, quantum dots are typically composed of combinations of Group II and IV elements or Group III and V elements of the periodic table. They have been developed in the form of semiconductors, insulators, metals, magnetic materials or metallic oxides. Semiconductor quantum dots (QDs) are tiny light-emitting particles on the nanometer scale, and are emerging as a new class of fluorescent labels for biology and medicine. QDs are nearly spherical semiconductor particles with diameters on the order of 2–10 nanometers, containing roughly 200–10,000 atoms. The semiconducting nature and the size-dependent fluorescence of these nanocrystals have made them very attractive for use in optoelectronic devices, biological detection, and also as fundamental prototypes for the study of colloids and the size-dependent properties of nanoparticles [39]. Bulk semiconductors are characterized by a composition-dependent bandgap energy, which is the minimum energy required to excite an electron to an energy level above its ground state, commonly through the absorption of a photon of energy greater than the bandgap energy. Relaxation of the excited electron back to its ground state may be accompanied by the fluorescent emission of a photon. Small nanocrystals of semiconductors are characterized by a bandgap energy that is
dependent on the particle size, allowing the optical characteristics of a QD to be tuned by adjusting its size. In comparison with organic dyes and fluorescent proteins, QDs are about 10–100 times brighter, mainly due to their large absorption cross sections, 100–1000 times more stable against photobleaching, and show narrower and more symmetric emission spectra. In addition, a single light source can be used to excite QDs with different emission wavelengths, which can be tuned from the ultraviolet [40], throughout the visible and near-infrared spectra [41], and even into the mid-infrared [42]. The group II-VI QD nanocrystals such as CdSe, CdTe, CdS [43], ZnS [44], and ZnSe have been studied extensively over the past decade, and QDs with a CdSe core and ZnS shell are currently commercially available.

1.3. Synthesis of Nanoparticles

Nanoparticles can be synthesized by a variety of methods using gas, liquid or solid phase processes. These include gas phase processes of flame pyrolysis, high temperature evaporation, and plasma synthesis; microwave irradiation; physical and chemical vapor deposition synthesis; colloidal or liquid phase methods in which chemical reactions in solvents lead to the formation of colloids, molecular self-assembly, and, mechanical processes of size reduction including grinding, milling and alloying.

Gas phase synthesis approaches are based on homogeneous nucleation of a supersaturated vapour and subsequent particle growth by condensation, coagulation and capture. The supersaturated vapour can be generated in many ways depending on the chemical nature of the material, but typically by heating a solid and evaporating it into a carrier gas phase.

Vapour deposition methods are based on forming a vapour by pyrolysis, followed by reduction, oxidation and allowing the deposition of the vapour on a surface. Starting from initial nuclei existing as islands on a surface, the growth is controlled by various ways to produce nanoparticles. An important example of this approach is the production of carbon nanotubes.

Colloidal methods are based on precipitation processes in solution. For example, solutions of different ions can be mixed under controlled conditions of temperature and pressure to form insoluble precipitates. By controlling the nucleation and growth kinetics, particles of various sizes and morphologies can be produced. The method has been
implemented in bulk solutions and also in confined systems such as reverse micelles. To control the process of nucleation, ultrasonic or sonochemical effects have also been employed. A wide range of metal, metal oxide and organic nanoparticles have been produced by colloidal wet chemical approach.

All of the above synthesis approaches start at the molecular level to build up or create the nanoparticles. In the opposite direction, mechanical size reduction methods such as grinding and milling have also been employed to generate nanoparticles. These methods are the traditional approaches to produce fine particles and they have been able to generate nanoparticles from minerals such as clay, coal and metals. To avoid particle aggregation in the course of the size reduction process, the grinding and milling operations are often carried out with colloidal stabilizers.

1.4. Surface Modification of Nanoparticles

Once the nanoparticles are produced and purified to a satisfactory level it is often necessary to introduce surface modifications. The surface modifications can be for the purposes of (a) passivating a very reactive nanoparticle, (b) stabilizing a very aggregative nanoparticle in a medium (which may be a solvent or a polymer melt) where the nanoparticles are to be dispersed, (c) functionalizing the nanoparticle for applications such as molecular recognition, or (d) promoting the assembly of nanoparticles. Most commonly used surface modification methods include grafting thiolated surfactants or polymers, adsorption of charged surfactants, charged ligands or polymer brushes, attachment of biological molecules such as DNA, peptides, proteins, antigens, streptavidin or coating a continuous polymer film on nanoparticles.

1.5. Multifunctional Nanoparticles

The emerging fields of nanotechnology and nanoengineering provide a path to design and fabricate nanoparticles for their diverse applications. Particularly, nanotechnology offers tremendous potential for future biomedical technology. Due to their unique characteristics including superparamagnetic or fluorescent properties, and small size comparable to biomolecules, nanostructured materials have emerged as novel bio-imaging, diagnostic, and therapeutic agents for the future medical field. The use of combinations of different nanostructured materials will allow the development of novel multifunctional nanomedical
platforms for multimodal imaging, and simultaneous diagnosis and therapy. For example, the combination of magnetic resonance imaging (MRI) contrast agent and fluorescent organic dye can allow the detection of cancer through non-invasive MRI and the optical guide of surgery. The encapsulation of MRI contrast agent and anti-cancer drug in a nanostructured matrix has the potential to allow for simultaneous diagnosis and targeted chemotherapy. There are many possible combinations of the various imaging and therapeutic modalities, which make it possible to accomplish multimodal imaging, and simultaneous diagnosis and therapy. Moreover, the conjugation of targeting moieties on the surface of these multifunctional nanoparticles gives them specific targeted imaging and therapeutic properties.

1.6. Scope and Objective

The interface of biology and inorganic nanoparticles represents one of the fastest growing and most promising areas of nanotechnology. The innovative use of engineered nanoparticles in medicine, be it in therapy or diagnosis, is growing dramatically. This is motivated by the current extraordinary control over the synthesis of complex nanoparticles with a variety of biological functions (e.g. contrast agents, drug-delivery systems, transducers, amplifiers, etc.). Engineered nanoparticles are found in the bio-context with a variety of applications in fields such as sensing, imaging, therapy or diagnosis [45]. As the degree of control to fabricate customized novel nanoparticles evolves, new applications, devices with enhanced performance or unprecedented sensing limits can be achieved. The major applications of nanoparticles in the biomedical field can be mainly divided into imaging and therapy. Most of the clinically used imaging and therapeutic modalities are small molecules, such as the gadolinium complexes used as T1 MRI contrast agents and anticancer chemical drugs. The limitations of these small molecules are their very short blood circulation time and non-specific biodistribution, which causes many unwanted side effects. Nanostructured materials can be employed to overcome these limitations [46]. For example, the blood circulation times can be increased significantly by the size control and surface modification of nanoparticles and by conjugating targeting molecules, such as antibodies and peptides, on their surface. However, several challenging issues still circumvent widespread biomedical uses of advanced nanotechnology. For example, novel multifunctional nanoparticles and improved treatment strategies are required to meet the
needs of real-time, non-invasive imaging in living subjects or humans, and those of satisfactory drug delivery and therapeutic efficiency in vivo. Secondly, standardized nanoplatforms to be applied to diagnostic or therapeutic investigations of various diseases still have to be developed and formulated. The development of multifunctional nanoparticles with precise biological/chemical functions having economic, healthcare and environmental benefits are a key focus in nanobiotechnology and could have profound impact on many research areas, ranging from molecular imaging to medical diagnostics/therapeutics, chemical conversion and energy production. Several novel nanoparticles have recently been described for their unique optical, magnetic, electronic and structural properties. Considerable efforts have also been directed towards rational surface modifications to modulate their complicated surface chemistry, high-specificity and efficient targeting. However, despite recent advancement, much works still need to be done in order to achieve, (i) hydrophilic and biocompatible nanoparticles that are intrinsically luminescent, with surface chemistry adaptable to varied biological/chemical applications, (ii) selective and specific labeling of live cells and biomolecules. Since, nanoparticles can display distinct biological effects compared to bulk materials of the same chemical composition, the physico-chemical characterization of nanoparticles and the understanding of their interaction with biological media are essential for optimizing the properties of nanoparticles. The ‘nano-bio’ interface comprises the dynamic physicochemical interactions, kinetics and thermodynamic exchanges between nanoparticles surfaces and the surfaces of biological components (for example small biomolecule, protein, DNA etc.). Moreover, nanotechnology-based approaches are being explored for a variety of biomedical applications such as for drug delivery, bioimaging, tissue engineering, and biosensors. A substantial number of these approaches employ nanoscale materials or bio-nanoparticles for developing unique functionalities required by the biomedical systems. For this field to evolve, it is necessary to understand the dynamic forces and molecular components that shape these interactions. The key focus of this thesis is (a) to explore how the interactions between nanoparticles and biological systems modify the fundamental forces that govern nanoparticle properties as well as their interactions, (b) development of ligand functionalization approaches to control the surface chemistry of nanoparticles in order to gain a better understanding of the origin of surface-induced
optical, magnetic and catalytic properties, since, subtle differences in ligand functional groups or the structural position of the functional groups can dramatically change the optical, magnetic and catalytic responses of the nanoparticles, (c) development of multifunctional nanoprobes with precise biological functions along with novel reactivity and selectivity towards a desired chemical transformation having direct biological and medical significance.

In this thesis, we will present a molecular functionalization strategy to solubilize one of the promising manganite nanoparticles La$\text{_{67}}$Sr$\text{_{33}}$MnO$_3$ (LSMO) in aqueous environments. The electronic structural modification of the NPs imparted through functionalization and subsequent water solubilization reveals multiple absorption bands in the UV-vis region. Using the absorption band of the functionalized nanoparticles, we have monitored their interaction with other biologically important ligands such as 4-nitrophenylanthranilate (NPA) and a DNA base mimic, 2-aminopurine (2AP). Förster resonance energy transfer (FRET) of the covalently attached probe NPA with the capped NPs confirm their attachment with the surface functional group (–OH) of the citrate ligand, whereas, the FRET of 2AP, with the nanoparticles confirm the surface adsorption of the 2AP molecules. In another work, we have observed that surface treatment of the tartrate/citrate functionalized highly water soluble LSMO nanoparticles, lead to the emergences of multi-color photoluminescence (from blue to red region of the spectrum) when it is addressed with different excitation wavelengths, where the respective excitation wavelengths have a direct correlation with the observed UV-vis absorption bands. Using a multitude of spectroscopic tools we have investigated the mechanistic insight behind the origin of different absorption bands and emergence of multicolor photoluminescence from the functionalized nanoparticles.

In the study on Mn$_3$O$_4$ nanoparticles, we have demonstrated their surface modification induced multiple photoluminescence and room temperature ferromagnetic activation. Moreover, employing a systematic variation of the ligands, their functional groups and the structural position of the functional groups, we have identified the necessary and sufficient structural requirement of the surface co-ordinating ligands, to induce such unprecedented optical/magnetic responses from the nanoparticles.
One of the challenges for using nanoparticles in biological studies is to design nanoparticles which are water-soluble with surface chemistry adaptable to varied biological applications. For this purpose, different ligands have been exploited to impart biocompatibility and bioactive functionalities to nanoparticles through surface modification with biomolecules. In this direction, in one of our studies, we have exchanged TOPO (trioctylphosphine oxide) ligand of CdSe/ZnS core/shell quantum dots (QDs) with an amino acid L-arginine (Arg) at the toluene/water interface and eventually rendered the QDs from toluene to aqueous phase. We have studied the interaction of the water soluble Arg-capped QDs (energy donor) with ethidium bromide (EB) labeled synthetic dodecamer DNA (energy acceptor) using picosecond resolved FRET technique.

With respect to bulk materials, clusters are of fundamental interest due to their own intrinsic properties but also because of their intermediate position between molecular and materials science. Compared with common fluorophores such as organic dyes and semiconductor quantum dots, where practical deployment can be limited by relatively poor photostability (for organic fluorophores) or toxicity concerns (e.g., quantum dots), fluorescent metal clusters are promising alternatives for the design of novel bioimaging probes because of their ultrafine size, excellent photostability, and low toxicity. So, there is a strong interest in the development of synthesis methods for highly fluorescent metal clusters. In this regard, in one of our studies, we have demonstrated the synthesis and characterization of novel super-paramagnetic iron clusters in hemoglobin matrix that are highly luminescent, having quantum yield of ~10% at 565 nm. Using mass spectrometry, we have tentatively assigned that the clusters synthesized in solution consist of 8, 10 and 13 number of Fe atoms. We believe that this new material holds promise for fundamental applications like catalysis, imaging and sensing.

1.7. Summary of the Work Done:

1.7.1. Surface Modification of Nanoparticles for their New Functionality and Better Acceptability in the Biophysical Studies:

1.7.1.1. Emergence of Multicolor Photoluminescence in La_{0.67}Sr_{0.33}MnO_{3} Nanoparticles [47]: In the present study, we report the emergence of multicolor
photoluminescence in a mixed valence manganite nanoparticle La$_{0.67}$Sr$_{0.33}$MnO$_3$ (LSMO NP), achieved through electronic structural modification of the nanoparticles upon functionalization with a biocompatible organic ligand, sodium tartrate. From UV-vis absorption, X-ray photoelectron spectroscopy (XPS), time-resolved photoluminescence study and Raman spectroscopic measurements, it is revealed that ligand-to-metal charge transfer transitions from highest occupied molecular orbital (HOMO, centered in tartrate ligand) to lowest unoccupied molecular orbital (LUMO, centered in Mn$^{3+/4+}$ of the NPs), and d-d transitions involving Jahn-Teller sensitive Mn$^{3+}$ ions in the nanoparticles plays the central role behind the origin of multiple photoluminescence from the ligand functionalized LSMO nanoparticles.

1.7.2. Synthesis of Biocompatible Nanoparticles with Novel Optical & Magnetic Properties and their Characterization:

1.7.2.1. Rational Surface Modification of Mn$_3$O$_4$ Nanoparticles to Induce Multiple Photoluminescence and Room Temperature Ferromagnetism [48]: Surface modification can have a significant influence on the materials behavior at the nanoscale and can lead to nanostructures with novel properties. In the present contribution, we demonstrate surface modification induced multiple photoluminescence and room temperature ferromagnetic activation of Mn$_3$O$_4$ nanoparticles (NPs). Employing a systematic variation of the ligands, their functional groups and the structural position of the functional groups, we have identified the necessary and sufficient structural requirement of the surface co-ordinating ligands, to induce such unprecedented optical/magnetic responses from the NPs. Using a multitude of spectroscopic techniques, we have investigated the mechanistic insight behind this emergence of multiple photoluminescence (PL), and it is revealed that, the presence of a $\alpha$-hydroxy carboxylate moiety in the ligands is necessary to activate the Jahn-Teller (J-T) splitting of Mn$^{3+}$ ions on the NPs surface and the corresponding d-d transitions along with ligand-to-metal charge transfer transitions (LMCT, associated with Mn$^{2+/3+}$-ligand interactions) plays the deciding role. Whereas, the presence of a carboxylate group in the surface coordinating ligands is sufficient to activate the room temperature ferromagnetism of the NPs. Moreover, it has been observed that the ligands induce smallest crystal field splitting energy (CFSE) resulted in the strongest ferromagnetic activation of the NPs. Finally, the functionalized material has been
identified as an efficient catalyst for the photo-degradation of a model cationic organic dye. Apart from the fundamental scientific interest, these results represent a promising route for the rational designing of Mn$_3$O$_4$ NPs adaptable to diverse applications.

1.7.3. Surface Functionalization of Nanoparticles and their Interaction with Small Organic Molecules:

1.7.3.1. Functionalization of Manganite Nanoparticles and their Interaction with Biologically Relevant Small Ligands: Picosecond Time-Resolved FRET Studies [49]:
In this study, we report molecular functionalization of one of the promising manganite nanoparticles La$_{0.67}$Sr$_{0.33}$MnO$_3$ (LSMO) for their solubilization in aqueous environments. The functionalization of individual NPs with biocompatible citrate ligand as confirmed by fourier transform infrared (FTIR) spectroscopy, reveals that citrates are covalently attached to the surface of the NPs. UV-vis spectroscopic studies on the citrate functionalized NPs revealing an optical band in the visible region. Uniform size selectivity (2.6 nm) of the functionalization process is confirmed from high resolution transmission electron microscope (HRTEM). In the present study we have used the optical band of the functionalized NPs to monitor their interaction with other biologically important ligands. Förster resonance energy transfer (FRET) of a covalently attached probe 4-nitrophenyl anthranilate (NPA) with the capped NPs confirm the attachment of the NPA ligands with the surface functional group (-OH) of the citrate ligand. The FRET of a DNA base mimic, 2-aminopurine (2AP), with the NPs confirms the surface adsorption of 2AP. Our study may find its relevance to study interaction of the individual manganite NPs with the drug/ligand molecules.

1.7.4. Synthesis of Amino Acid Modified Fluorescent Quantum Dots in Aqueous Solution and their Interaction with Biological Macromolecules:

1.7.4.1. Preparation of Water Soluble L-Arginine Capped CdSe/Zns QDs and their Interaction with Synthetic DNA: Picosecond-Resolved FRET Study [50]: In the present contribution, we have exchanged TOPO (trioctylphosphine oxide) ligand of CdSe/ZnS core/shell quantum dots (QDs) with an amino acid L-arginine (arg) at the toluene/water interface and eventually rendered the QDs from toluene to aqueous phase. We have studied the interaction of the water soluble arg-capped QDs (energy donor) with ethidium (EB) labeled synthetic dodecamer DNA (energy acceptor) using picoseconds
resolved Förster resonance energy transfer (FRET) technique. Furthermore, we have applied a kinetic model developed by M. Tachiya to understand the kinetics of energy transfer and the distribution of acceptor (EB-DNA) molecules around the donor QDs. Circular dichroism (CD) studies revealed a negligible perturbation in the native B-form structure of the DNA upon interaction with arg-capped QDs. The melting and the rehybridization pathways of the DNA attached to the QDs have been monitored by the CD which reveals hydrogen bonding is the associative mechanism for interaction between arg-capped QDs and DNA.

1.7.5. Novel Synthesis of Biocompatible and Highly Luminescent Metal Cluster and their Characterization:

1.7.5.1. Atomically Precise Luminescent Iron Clusters in Solution [51]: Metal clusters, composed of a few atoms at the core, exhibit unique properties and have potential applications. Although atomically precise clusters of noble metals have been synthesized, analogous systems of reactive metals, such as iron, have not been realized in solution due to high reactivity. Here we report the synthesis and characterization of novel iron clusters in hemoglobin matrix that are highly luminescent (quantum yield 10% at 565 nm). The super-paramagnetic iron clusters, after successful ligand exchange from protein and phase transfer from water to chloroform using tri-octylphosphineoxide (TOPO), were detected as $[\text{Fe}_{10}(\text{TOPO})_2(\text{H}_2\text{O})_3]^+$, $[\text{Fe}_{13}(\text{TOPO})_2(\text{H}_2\text{O})]^+$ and $[\text{Fe}_8(\text{TOPO})(\text{H}_2\text{O})_2]^+$ by mass spectrometry. This study lays the groundwork for exploiting unique properties of soluble iron clusters.

1.8. Plan of Thesis:

The plan of the thesis is as follows:

Chapter 1: This chapter gives a brief introduction to the various kinds of nanoparticles, their synthesis and surface functionalization, as well as the scope and motivation behind the thesis work. A brief summary of the work done is also included in this chapter.

Chapter 2: This chapter provides an overview of the dynamical and steady-state tools, the structural aspects of biologically important systems (proteins, DNAs) and probes used in the research.

Chapter 3: Details of instrumentation, data analysis and experimental procedures have been discussed in this chapter.
Chapter 4: This chapter demonstrate the possibility of electronic structural modifications of manganite nanoparticles (La$_{0.67}$Sr$_{0.33}$MnO$_3$, and thus the resulting novel optical properties) by charge transfer through functionalization with small organic ligands.

Chapter 5: Rational surface modification strategy to induce multiple photoluminescence, room temperature ferromagnetism and novel photocatalytic property to a transition metal oxide nanoparticle has been discussed in this chapter.

Chapter 6: This chapter deals with the molecular functionalization of a promising manganite nanoparticle La$_{0.67}$Sr$_{0.33}$MnO$_3$ (LSMO) and their interaction with biologically relevant small ligands.

Chapter 7: A convenient approach for preparing water-soluble, biocompatible QDs following a liquid-liquid interfacial ligand exchange method has been discussed in this chapter.

Chapter 8: This chapter offers the synthesis of highly luminescent and water-soluble Fe quantum clusters, starting from Hemoglobin (Hb), a Fe-containing metalloprotein which acts as the iron source as well as the protecting agent.
References


