CHAPTER 1

Introduction

1.1. Nanomaterials

Nanoscience and Nanotechnology is an umbrella term encompassing a range of varied research area used to indicate the study of novel properties of 1-100 nm size and their wide range of applications. Nanoscience is the investigation of properties of materials with structural features in the nanometer range. The underlying theme of nanotechnology is miniaturization and wide range of properties of nanomaterials. The development of advanced tools for characterizing these nanomaterials has provided scientists with new insights for understanding and developing new devices and clues to design new nanostructured materials for a sustainable usage of raw materials and energy.

Nanomaterials exhibit a number of special properties relative to bulk counterpart. Size affects constitute a fascinating aspect of nanomaterials. Due to small size and a large surface to volume ratio nanoparticles exhibit interesting novel properties. Their fine grain dimensions, significant volume fractions of atoms located at the grain boundaries confer them special attributes [1]. Classical laws of physics fails to explain the origin of these novel properties in this nanoregime [2]. From the elementary quantum mechanics it is known that when the electronic particles or charge carriers are confined in a volume limited by potential barriers that are comparable or smaller than the de Broglie wavelength of the particle, the allowed energy becomes discrete rather than continuous as in bulk materials. This effect of size or spatial confinement is termed as size quantization or quantum confinement. Electrons in the nanoregime experience a confinement in space. Dimensional confinement of electrons in materials leads to the modification of the density of states (DOS) giving rise to shape dependent properties. Based on the dimensional confinement of electrons nanomaterials are generally classified as 2D, 1D, 3D [3]. In 1D the confinement of electrons is imposed only along one axis (e.g., quantum well). In case of 2D electrons are confined only in two directions but are free to move only in one directions (e.g., nanowires, nanotubes). However, in
3D electron experiences confinement in all the three dimensions (e.g., nanoparticles) [3]. Due to the quantum confinement effect, the structural, optical, electrical, and magnetic behavior of the nanoparticles are found to be totally different from their bulk counterparts.

The properties of bulk semiconductors are dependent on the energy gap between its valence band and conduction band. Transition from bulk to nanoregime results in discreteness and the density of states ceases to be continuous. As a result, electrons occupy specific numbers of well-separated states at a given energy [4]. The absorption of energy excites electrons from the valence band to the conduction band, leaving behind holes in the valence band. At low temperatures, these two charge carriers form a weak coupled pair called exciton [5]. The excitons correspond to a hydrogen-like bound state of an electron-hole pair and characterized by exciton Bohr radius defined by [6].

\[
\alpha_B = \frac{4\pi\epsilon_0\epsilon_r\hbar^2}{m^*_e}\left(\frac{1}{m^*_e} - \frac{1}{m^*_h}\right) \tag{1.1}
\]

where, \(\epsilon_r = \) relative dielectric constant
\(m^*_e = \) effective mass of electron
\(m^*_h = \) effective mass of hole
\(m_0 = \) rest mass of electron.

For most of the semiconductors, the exciton Bohr radius is within the range of 1-10 nm. The exciton radius is an important parameter to explain the quantum confinement effect. The effect of quantum confinement on the electronic states was theoretically investigated by Efros and Efros. According to Schmitt-Rink et al. [7], the optical properties show dramatic enhancement when the size is smaller than the excitonic Bohr radius. This is based on the observation that as the dimensionality of the bulk semiconductor is reduced, the density of states becomes intense in narrowing energy bands and ultimately results in discrete energy states [7]. The energy separation between the discrete levels in the semiconductor nanostructures varies inversely to the size of the material [8]. The blue shift in the optical absorption spectra is noticed due to an increase in the band gap of the semiconductor nanostructures.

Semiconductors nanostructured materials have been studied intensely in the
last several years using various physical and chemical methods. Nanosized semiconductors exhibit special thermodynamic, magnetic, photochemical, photo-physical, and electro-physical properties. When semiconductors are in the nanoscale regime, their size has significant effects on their properties. Tuning the size of such semiconductor nanoparticles opens up the prospect to control their characteristics [9]. The size of the nanoparticle strongly affects the semiconductor light wave communication and the resulting processes. These processes depend on the optical absorption of light, dynamics of photogenerated exciton, the consequences of electron-hole recombination, and the photo-chemical reactions in the presence of reagents adsorbed on the semiconductor surface [10]. The size effects in the nanoparticles are classified into two types. The first one is the increased surface to volume ratio and the other is the alteration in the electronic state of the semiconductor due to quantum size effects dominating below a critical size of ~10 nm at room temperature. The critical size which is the threshold for the quantum size effects varies for different semiconductors depending on the chemical structure of the nanoparticle. It is similar to de-Broglie wavelength of free electron [11]. Among the various semiconductor nanocrystalline TiO$_2$ is one of the most widely studied oxide semiconductor. This chapter is focused on the fundamental properties of TiO$_2$. Generally pure TiO$_2$ suffers from problems of large band gap. This drawback limits its application as an efficient photocatalyst under visible light. The fundamental processes involved in photocatalysis as well as the state of the art for pristine and doped TiO$_2$ is also highlighted in this chapter. The dopant induced changes on the optical and magnetic property has also been focused. Because of the lack of detailed information about the effects of metal doping on crystal structures and electronic structures, there is still much dispute. Theoretical analysis by using Density Functional Theory (DFT) has been discussed to clarify the effects of doping in detail.

1.2. Crystal Structure of TiO$_2$

TiO$_2$ belongs to the family of transition metal oxides. There are three commonly known polymorphs of TiO$_2$ found in nature: anatase (tetragonal), brookite (orthorhombic), rutile (tetragonal) [12]. The three different crystal structure can be described in terms of the chains of octahedra. Each Ti$^{4+}$ ion is surrounded by an octahedron of six O$^{2-}$ ions. Anatase is built up from octahedrals that are interconnected by their vertices whereas in
rutile the edges are connected [13]. Anatase TiO\(_2\) consists of arrangement of parallel octahedron, while in the rutile phase some octahedron are distorted by 90\(^o\). The brookite phase of TiO\(_2\) is a bit complicated and is not often used for experimental investigation [14]. In this phase both edges and vertices are connected [12]. Fig.1.1 shows the crystal structure of the different forms of TiO\(_2\).

![Fig.1.1. Crystal structure of (a) anatase (b) rutile (c) brookite](image)

The valence band of TiO\(_2\) is composed of the 2\(p\) orbitals of oxygen hybridized with the 3\(d\) orbitals of titanium while the conduction band is composed of only 3\(d\) orbitals of titanium [15]. In comparison to rutile phase, anatase form of TiO\(_2\) has inherent surface band bending that forms spontaneously in a deeper region with a steeper potential [12]. Surface hole trapping dominates and spatial charge separation is obtained by the transfer of photogenerated holes towards the surface of particle via the strong upward band bending [12]. In the rutile phase the bulk recombination of electron and hole takes place due to which holes very close to the surface are trapped and transferred to the surface [15]. The difference in the bonding arrangement and structure leads to difference in their practical applications, eg anatase is used as good photocatalytic candidate whereas rutile is used as pigments due to effective light scattering [12].

**1.3. Process of Phase transformation**

Temperature has a profound effect on the anatase to rutile phase transformation. There
occurs both phase conversion as well as microstructural modification on annealing at high temperature. A noteworthy feature is that in bulk TiO$_2$ rutile is stable while anatase is metastable [16,17]. The brookite phase of TiO$_2$ transforms into rutile phase with anatase as an intermediate [18,19]. The polymorphic transformation is however quite complex. In nanocrystalline TiO$_2$ the competition between surface energy and the energetic of the polymorphs stabilizes the anatase at smaller particle size and thereby results in a crossover in thermodynamic stability between anatase and rutile phases [18, 20]. Upon heating nanocrystalline TiO$_2$ dehydrate and coarsen as they change from anatase to rutile phase. The transformation from anatase to rutile phase is often followed by contemporaneous presence of a mixed phase that is coexistence of both pure anatase and pure rutile phase. Studies have shown that mixture of both these phases can contribute to enhanced photocatalytic activity [19].

1.4. TiO$_2$ as a photocatalyst.

Photocatalytic mechanisms usually involves light and a catalytically active species [21]. A substance can be taken as a catalyst if it accelerates a chemical reaction without itself undergoing any changes. When light of sufficient energy illuminates the photocatalyst an electron from the valence band is promoted to the conduction band, leaving an electron deficiency or hole (h$^+$) in the valence band and an excess of negative charge in the conduction band (e$^-$). These conduction band electrons and valence band holes undergo redox reactions known as interfacial charge transfer. Overall a photocatalytic reactions may be summarized as follows [22]:

$$(\text{Ox}_1)_{ads} + (\text{Red}_1)_{ads} \xrightarrow{\text{photocatalyst} + \text{hv}} (\text{Ox}_2)_{ads} + (\text{Red}_2)_{ads}$$

In practice the photocatalytic process progress through the presence of aqueous environment. In case of TiO$_2$ the photocatalytic reactions are composed of the following steps [22]:

a). Activation of the photon energy greater than its band gap (3.2 eV) that generates electron-hole pair:

$$\text{TiO}_2 \xrightarrow{\text{hv} \geq 3.2 \text{eV}} e^- + h^+$$
This is a very important step. The efficiency of the photocatalyst is dependent on the wavelength and intensity of illumination source.

b). Adsorption of the compound to be oxidized on the catalyst surface and the lattice oxygen ($O_{L}^{2-}$).

c). Recombination of the photogenerated charge carriers to produce heat.

\[ e^- + h^+ \rightarrow \text{heat} \]

This is the most dominant step. More than 95% of the charge carriers recombine before taking part in a chemical reaction. The recombination takes place either on the bulk or on the surface and the kinetics of the processes determine the efficiency of a photocatalyst.

d). Trapping of the charge carriers on the photocatalyst surface. The charge carrier recombination and trapping determine the overall quantum efficiency of a photocatalyst.

e). Oxidation of the adsorbed compounds. This step is assisted by holes on the surface or by the attack of the hydroxyl radicals generated by photocatalysis.

But being a wide band gap semiconductor TiO$_2$ can utilize only a limited portion of the solar spectrum. This lowers the utilization of the material for practical applications. Extending the absorption of the material to the visible region requires changes in the underlying electronic structure that is closely interrelated to the chemical composition and related atomic arrangements. Doping is an indispensable way to produce favorable changes in the electronic structure while keeping the integrity of the original crystal structure. Reducing the size of the band gap through introduction of energy levels between the valence band and conduction band makes TiO$_2$ to be active under visible light [21].

1.5. Tuning of optical properties of TiO$_2$ by doping.

Investigation of the optical property of the nanomaterial is a very powerful tool to understand the electronic properties of the materials as the energy dependence of the optical properties is related to the band structure. When light of sufficient energy falls on a material, it induces electronic transition from occupied states below Fermi level to
the unoccupied state above Fermi level. The quantitative study of these transitions provides some understanding of the initial and final energy bands and symmetry of the associated wave functions. There are two main types of band gap transition in semiconductors [23]. For direct band gap semiconductors, electronic transition from the valence band to the conduction band is electrically dipole allowed [23] and the electronic absorption as well as emission is usually strong. For indirect band gap semiconductors the electronic transition from the valence band to the conduction band is electrical dipole forbidden and the transition is phonon assisted implying that the energy and momentum of the electron-hole pair are changed in the transition [23]. Anatase and rutile TiO$_2$ is reported to exhibit both direct and indirect band gap, but the indirect band gap transition is preferred over the direct one owing to the fact that the low strength direct transition is forbidden [24,25]. In anatase and rutile TiO$_2$ the indirect allowed transition occurs due to $\Gamma$-$M$ transition from O 2$p$ to Ti 3$d$ level in the Brillouin zone [25,26].

Doping of TiO$_2$ is an important approach in the band gap engineering to change the optical response of the material [12]. Doping involves incorporation of foreign atom into the catalyst matrix of the parent metal oxide. From chemical point of view doping is equivalent to the introduction of defect like Ti$^{3+}$ into the semiconductor lattice. In a bulk crystalline material translational symmetry leads to the formation of electronic energy bands. Introduction of the dopant ions breaks the periodicity of the lattice and perturbs the band structure. The perturbation is actually categorized by the presence of discrete energy levels within the band gap. The introduction of such energy levels in the band gap introduce a red shift in the band gap transition and visible light absorption through a charge transfer between the dopant ion and conduction band or valence band in the crystal field, in turn satisfying the criteria for enhanced photocatalytic activity.

Das.et.al [27] reported band gap reduction in Co doped TiO$_2$ nanoparticles to the exchange interaction between dopant $d$ electron and host $sp$ electrons. Li.et.al [28] in their work on Nd$^{3+}$ doped TiO$_2$ nanoparticles attributed band gap reduction to the formation of electronic states of the Nd$^{3+}$ dopant ion in the host matrix. For efficient photocatalytic process it is worth mentioning that the dopant ion must act as both electron and hole traps. Trapping of either electron or hole is however ineffective as the immobilized charge species rapidly recombines with the movable counterparts. The
recombination process competes with the charge transfer process to absorb species in the volume of the semiconductor particle or on its surface followed by the release of heat. The process in turn adversely effect the photocatalytic mechanism and decrease the overall photocatalytic efficiency.

Another very interesting optical property is the band gap widening due to doping the semiconductor to a high free carrier concentration [29]. Mei.et.al [30] in their work reported that the band gap of TiO$_2$ is increased after Nd doping. They attributed this behavior to Burstein Moss effect [31]. According to this effect when the electron concentration is high enough, the Fermi level of the system passes through the conduction band and there are considerable conduction carriers at the bottom of the conduction band. The electrons in the valence band are excited to above the Fermi level instead of to the bottom of the conduction band that are occupied by the conduction electrons. This results in widening of the band gap of the doped degenerate semiconductors compared to the undoped one. The dopant localized states spread out the band edges producing absorption tail deep in the forbidden gap. The strength of the band tail is characterized by Urbach energy which is an important tool to investigate the perfection of the lattice [32,33]. A schematic of the formation of Urbach energy is shown below, Fig.1.2. The dopant atoms substitute the atomic sites and therefore Urbach tail consists of a mixed signal from lattice distortion and impurity band. The equation for Urbach energy is given by:

$$\alpha = \alpha_0 \exp\frac{E}{E_u}$$

(1.2).

Where $\alpha$ is the absorption coefficient, $E$ is the photon energy and $E_u$ is the Urbach energy [34]. The reciprocal of the slopes of the linear portion below the band gap gives the Urbach energy. The Urbach energy is therefore very important to understand the disorder in a material. The higher the Urbach energy the greater is the disorder in the material [35].

Although the effects of metal ion doped TiO$_2$ is investigated frequently, but it remains difficult to make undeviating assessment and portray a clear conclusions due to diverse experimental environment and different methods for sample preparation and photoreactivity testing. Doping of TiO$_2$ is an essential way to produce constructive changes in the electronic structure while keeping the veracity of the original crystal
structure. Often in nanotechnology the motivation is on providing solutions to real world technological problems. The construction and characterization of the systems that demonstrate the potential for use is often an end goal. Nanotechnology greatly benefits from theoretical inputs. Firstly it is quite impractical to perform experiments quite a large number of times. Secondly experimental results cannot always be straightforwardly interpreted and therefore theoretical analysis is significant to elucidate the vital physics behind the situation and resolve many ambiguities. The behavior of the nanoscale systems is governed according to the Schrodinger equation. With the help of this equation small systems like hydrogen atom can be computed. Approximate methods are therefore needed to acquire information about many atom systems such as molecules or surfaces. With the development in the computational techniques, theoretical investigations of quantum mechanical system has highly risen. Many algorithms have been developed that allow the complicated equations governing quantum mechanical behavior to be answered approximately. Computational physics is a very important tool to provide elucidation and way for continuing and impending future experiment. Density functional theory (DFT) is an exceptionally valuable method to analyze and throw light on doping process and its effect on the electronic structure. Thanks to the spectacularly increased processing powers and more efficient software codes that implements comparable computational techniques performing such calculation very
smoothly compared to the scenario just a decade ago. Yu.et.al [36] with the help of DFT calculation confirmed the red shift of absorption edges and the narrowing of the band gap of Fe doped TiO$_2$ nanorods. Guo and Du [37] reported that addition of copper atom can lead to the enhancement of $d$ states near the upper most part of the valence band of TiO$_2$ and the Ag or Au doping creates some new energy states in the band gap.

1.6. Density Functional Theory (DFT).

Density functional theory (DFT) is an *ab-initio* method used to know the ground state of the atoms, molecules and solids. Solution of many electron Schrodinger equation by traditional wave function presents a difficult task as the wave function is a function of $3N$ spatial coordinates and $N$ spin coordinates, $N$ being the number of electrons in the system. Once the electron density is known the external potential and consequently the Hamiltonian of the system can in principle be uniquely determined.

Density functional theory (DFT) states that all ground state properties are functionals of charge density $\rho$ in which the total energy is given by:

$$ E[\rho] = T[\rho] + U[\rho] + E_{XC}[\rho] \tag{1.3} $$

Where $T[\rho]$ - kinetic energy, $U[\rho]$ - classical electrostatic energy and $E_{XC}[\rho]$-energy due to many body contributions.

The first term represents electron-nucleus attraction. The second term represent the electron-electron repulsion where as the third term corresponds to the nucleus-nucleus interaction. Optimisation of the total energy with respect to variation in $\rho$ leads to set of coupled equations known as Kohn-Sham equations. Density functional theory reduces quantum mechanical ground state many electrons to self consistent one electron form through the Kohn-Sham equation \[38-39\]. This is a very useful approach for the elaboration of the ground state properties of metals, semiconductors and insulators. Kohn and Sham \[39\] formulated mapping of the interacting many body electron system onto a system of non interacting electrons moving in an effective potential due to all other electrons and ions. Basically in density functional theory we have to find a self-consistent solution of Kohn-Sham equation that leads to the ground state density. In practice in order to calculate the band structure of a solid, the Kohn-Sham orbital $\psi_i(r)$ are usually expanded in terms of some chosen basis functions with some
co-efficients that are to be determined variationally. The choice of the basis set leads to the nearly correct solution of the one electron band structure problem.

The one electron energy Kohn Sham equation is given by:

\[
\left[-\nabla^2 + V_{\text{eff}}(r)\right] \Psi_i = \epsilon_i \Psi_i(r) \quad \text{----------------------------------------} \quad (1.4)
\]

The accurate form of exchange correlation is unfortunately not known. So it is very necessary to introduce some approximation and the most successful and well tested is so called the local density approximation (LDA) [38] and Generalized Gradient Approximation (GGA). In constructing LDA functionals it is assumed that the density is homogeneous and the total exchange-correlation energy is found by integrating the corresponding exchange correlation energies.

The Generalized Gradient Approximation (GGA) is used widely to provide the accuracy required for density functional theory to be used in various types of analysis. In GGA the exchange correlation energy depends not only on the electron density \( \rho(r) \) at a particular point but also on the gradient of the charge density \( \nabla \rho(r) \). The GGA tends to improve the accuracy of DFT calculations somewhat.

1.6.1. Pseudopotentials.

It is a very well known fact that the physical properties of solids are dependent on the valence electrons to a much greater than core electrons. The pseudopotential exploits this by removing the core electrons that are highly localized and by replacing the strong ionic potential by a weaker pseudo potential that acts as a set of pseudo function rather than true valence wave functions. The physical reason behind the pseudo potential is very simple , the core electrons wave functions of an atom remains unchanged inspite of placing into different chemical environment, the true atomic potential can be replaced by pseudo potentials that effectively reproduces the effect of core electrons. The combination of pseudo potential and plane wave is very important for the electronic structure calculations.

1.6.2. Projected Augmented Wave.

The projected augmented wave is computationally very efficient technique used in \textit{ab-initio} electronic structure calculations. In this method an augmentation sphere is
included surrounding each nucleus in the lattice and outside this augmentation sphere
the wave functions are represented with smooth normal plane waves. Within the
augmentation sphere the wave functions are presented with projectors and auxiliary
localize wave functions just in case of ultrasoft pseudopotentials. In PAW all electron
wave function can be preserved. The full wave functions oscillates heavily around the
nucleus, hence all integrals in the PAW method are evaluated as combination of integral
smooth functions outside the augmentation spheres plus contribution from radial
integration over augmentation spheres.

1.6.3. Plane Wave basis set

Density Functional theory thus provides a remarkably accurate method of simulating
materials quantum mechanically. Due to the cost effective factor, it has paved the way
to understand a plethora of materials which would have otherwise been out of reach of
quantum mechanical simulations.

In a real DFT calculations convergence criteria must be obtained with respect
to the number of k-points. It is usual to converge the wave functions in terms of a plane
wave energy cut off that determine the number of plane waves. The number of plane
wave require increases with the fine quality of the features of the wave functions. The
core wave functions of the atoms tends to oscillate rapidly and so they are unsuitable to
contribute to the expansion with plane waves. As the core electrons donot participate in
contributing to the physical properties of the solids they are typically removed. The core
electrons screen the nuclear potential and to recompense for their non appearance
pseudopotentials are used [40,41]. In Density functional theory, by comparing the total
energies of different atomic configurations the most energetically favored structure is
calculated. The allowed energy states are relaxed to lowest energy configuration and the
interatomic forces are calculated from the variation in total energy. Another important
feature is the spin polarization calculation used in DFT. The DFT calculations done in
the thesis uses Vienna Ab-initio Software Package (VASP). The package performs ab-
initio quantum mechanical molecular dynamics using pseudopotential and a plane wave
basis set. Both LDA/GGA functionals are available. VASP always needs minimum four
files:

- INCAR: that contains all settings of the programme parameters that we
wish to use.

- **KPOINTS**: contains all information regarding the k-point set.
- **POSCAR**: contains information regarding the geometry of our system.
- **POTCAR**: the information regarding the potentials functionals are contained in this file.

Due to the variation in electronic band structure a wide range of optical and electronic properties are observed in solid state materials. The atoms in a solid state materials are closely spaced together with the interatomic separation distance to form solid, the outer orbitals of the atom overlap and interact strongly with each other as a result of which electronic bands are formed [42]. The electronic states of a solid are determined by density of solids (DOS). In VASP spin polarization is not considered by default it has to be turned on for systems that contains magnetic spin. The spin polarised structure are found to be more stable than spin unpolarised. The concept of the density of states sprouts from the concept electronic band formation in solids. The density of states is defined as the number of electronic states or unit energy within a given interval.

The density of states function $D(\varepsilon)$ may be written in the form:

$$D(\varepsilon) = \sum_i \delta(\varepsilon - \varepsilon_i) \quad \text{------------------------------------------ (1.5)}$$

Calculation of the Density of States using VASP requires a fairly dense mesh of k-points in the Brillouin zone. A decomposition of the local states into state-resolved density of states gives the projected density of states (PDOS). The density of state analysis gives an idea of the trap states generated due to dopant incorporation [43].

In this thesis optical properties and photocatalytic activities of some transition and rare earth metal doped TiO$_2$ nanoparticles have been explored. Theoretical study based on DFT are carried out to identify the states generated due to doping.

1.7. **Diluted Magnetic Semiconductors.**

Dilute magnetic semiconductors have been the forefront of research due to their possible applications in nanomagnetics and spintronics for information storage, transport and processing. In DMS some fractions of atoms in a non-magnetic semiconductor is replaced by magnetic ions (Fig.1.3).
Fig.1.3: Schematic representation of a non-magnetic semiconductor (left) and a diluted magnetic semiconductor (right).

The emerging research area known as spintronics seeks to explore the properties and applications of established electronic devices by making use of spin of electrons in addition to their charge [44]. A different number of semiconductor oxides have been investigated to test the magnetic nature. Initially ferromagnetism has been reported for GaAs doped with Mn$^{2+}$ ions or InAs doped with Mn$^{2+}$ ions [45]. However they are disqualified for practical applications due to their high Curie temperature that was around 170 K and 35 K for (Ga, Mn)As and (In, Mn)As respectively [45,46]. Since than there has been a large incentive for developing new DMS materials that are ferromagnetic above room temperature. Matsumoto and his group was the first to successfully obtain room temperature ferromagnetism in Cobalt doped doped TiO$_2$ nanoparticles [47]. Although there are reports on the observation of ferromagnetism above room temperature, however the origin of magnetism in such systems is not fully understood. The magnetic properties of doped TiO$_2$ are strongly sensitive to preparation condition, morphology and presence of defects.

Bhattacharya et al [48]. synthesized Mn doped TiO$_2$ nanoparticles by one pot RAPET technique (reaction under autogenic pressure at elevated temperature) and
reported ferromagnetic behavior upto 1%. However, with the increase in dopant concentration upto 5 and 7% the system showed paramagnetic behavior. Peng et al [49] observed ferromagnetism in Mn doped TiO$_2$ nanoparticles prepared by a simple sol-gel method. Sellers and Seebauer reported room temperature ferromagnetism in Mn doped TiO$_2$ nanopillars prepared by atomic layer deposition method [50]. Thus, synthesis condition and morphology has a profound effect in modulating the magnetic property in TiO$_2$.

Presence of defects and annealing condition is also reported to affect the magnetism. Choudhury et.al [51] observed paramagnetism in air annealed Co doped TiO$_2$ nanoparticles while the same material exhibited ferromagnetism on calcination under vacuum. This contrasting nature of the magnetic property in the same system under two different annealing atmosphere is attributed to the formation of high density of oxygen defects under vacuum annealing [51].

Recently rare-earth doped DMS have caught up great interests because of their unique fluorescence properties and due to the high emission quantum yields. In transition metal magnetic moment arises from partially filled outermost 3$d$ electrons, whereas in rare earth ions magnetic moment arises from the inner 4$f$ incomplete sub-shell. Theoretical analysis have been carried out to explain the ferromagnetism in Gd doped GaN [52,53]. Dalpian and Wei reported that the direct coupling between the Gd atoms was antiferromagnetic in nature in Gd doped GaN [52]. The ferromagnetic phase was stabilized by the electrons due to the mixing of Gd$f$ with host $s$ states.

Thus it is surmised that introducing transition or rare earth ions in TiO$_2$ lattice result in partially filled $d$ or $f$ electron shells with unpaired electrons that couples ferromagnetically or anti ferromagnetically. Apart from the doped systems ferromagnetism has also been observed in oxide systems without adding impurities. Coey et al. [54] observed ferromagnetism in HfO$_2$ without adding impurity. They corroborated the observed magnetism to the presence of oxygen vacancies. Elfimov et al. [55, 56] demonstrated that Ca vacancies in CaO produce local magnetic moments and transform the non magnetic to half metallic ferromagnet. These discoveries introduce a new path to study ferromagnetism in undoped TiO$_2$. Hong et al. [57] and Yoon et al. [58] reported magnetism in TiO$_2$ thin films. They attributed these magnetism to the presence of oxygen vacancies that acts as n-type dopant.
1.8. Theoretical models for explaining ferromagnetism in DMS.

Two main theories are used for explaining ferromagnetism in oxide DMS- RRKY (Ruderman-Kittel-Kasuya-Yosida) interaction and Bound magnetic polaron (BMP) [59,60]. The RRKY model describes the magnetic interaction between a single localized magnetic ion and the delocalised conduction band electrons. As a result of this interaction the conduction electrons very close to the magnetic ion is magnetized and act as an effective field to induce polarization in the nearby magnetic ions with the polarization decaying in an oscillatory manner [61]. The oscillation mediates through either ferromagnetic or antiferromagnetic exchange coupling depending upon the separation between the magnetic ions.

The theory of bound magnetic polaron was given by Coey and his workers and is suitable for insulating systems where electrons are strongly localized [59]. In this model an electron trapped in an oxygen vacancy (F centre ) forms hydrogenic orbitals with radius $r_H = \varepsilon \left(\frac{m}{m^*}\right) a_B$, where $\varepsilon$ is the dielectric constant, $m$ is the electron mass , $m^*$ is the effective mass of the donor electron and $a_B$ is the Bohr radius. Formation of bound magnetic polaron is schematically shown in Fig.1.4.

![Fig.1.4: Schematic of bound magnetic polaron. The cations are represented by small circles, the unoccupied oxygen vacancies are represented by small circles.](image-url)
A Bound Magnetic Polaron is formed when the spin of the trapped electron couples effectively with the magnetic impurities within the hydrogenic radius. The oxygen defects in the BMP are responsible for the shallow donors and strongly stabilize the ferromagnetic state. When the neighboring polarons do not interact strongly a paramagnetic phase results. It is difficult to make any quantitative prediction about the distances, but the critical distance above which the exchange between two BMPs becomes ferromagnetic is typically of the order of a few Bohr radii [62, 63].

1.9. Applications of undoped and doped TiO$_2$ nanoparticles

TiO$_2$ is close to being an ideal photocatalyst and benchmark for photocatalysis activity. The single drawback is that it does not absorb visible light. The photocatalytic performance of pure TiO$_2$ can be enhanced by creating defects in the band gap of TiO$_2$. Oxygen deficient TiO$_2$ has been reported to have enhanced visible light activity [64, 65]. Apart from photocatalysis other most important application of TiO$_2$ is in dye sensitized solar cells. Ito et al. [66] demonstrated the methodical fabrication of TiO$_2$ electrodes that showed reproducible conversion efficiencies over 10%. Elsanousi et al. [67] fabricated highly ordered TiO$_2$ nanotube array by anodic oxidation on titanium foils and predicted significant photo-conversion efficiencies may be obtained by the front side illumination of DSSC when the length of the nanotube array is increased to several micrometers [67]. Hwang et al. [68] prepared DSSCs using four different anatase/rutile mixed phase (AR-3, AR-15, AR-20, and AR-23 denoted for the samples of 3%, 15%, 20%, and 23% rutile phase, respectively). They have reported photo conversion efficiency of 5.07% for AR-20. Some other applications of TiO$_2$ are in cosmetics [69], Li ion batteries [70].

The introduction of dopant ion is known to effect the electronic band edges or introduce impurity states in the band gap of the system. Choi et al. [71] presented a systematic study of metal ion doping of quantum sized TiO$_2$ for 21 metal ions and observed that the photoreactivity of TiO$_2$ is significantly increased in presence of these metal ions. Peng et al. [72] successfully prepared Chromium doped TiO$_2$ by sol-gel dip coating process and reported an enhancement in photocatalytic activity under visible light.

Rare earth doped TiO$_2$ is also reported to show good photocatalytic activity.
Stengl.et.al [73] reported enhanced photocatalytic degradation of orange II dye under UV and Visible light by doping rare earth ions in TiO$_2$. The increased photocatalytic activity was correlated to the higher adsorption and the 4f electronic transition of rare earth ions [73]. Choi.et.al [74] reported visible light driven photocatalytic activity of Gd doped TiO$_2$ nanoparticles. The high photocatalytic activity was attributed to the retarded recombination induced by the lower energy levels for Gd$^{3+}$ carriers.

Huang.et.al [75] evaluated the performance of DSSC using Zn doped TiO$_2$ nanoparticles and obtained an efficiency of 7.6% for 0.5 at%. The influence of F concentration in TiO$_2$ on performance of DSSCs was also investigated [76]. The highest efficiency obtained was about 11.3%. Well crystallized Nb doped TiO$_2$ nanoparticles prepared by a novel synthetic route has been used as photoanode of dye sensitized solar cells [77]. Some other applications of doped TiO$_2$ are in Li-ion batteries [78], gas sensing [79].

Spintronic technology in which data is processed based on electron spin rather than charge promises to transfigure the computing industry with smaller, faster and more efficient data storage and processing. Diluted magnetic semiconductor (DMS) is one of the key elements in spintronics. Spintronic technology has already been tested in mass storage components such as hard drives. The first spin based field effect transistor (spin FET) was first proposed by Datta and Das in 1990 [80]. A schematic of Datta-Das Spin FET is illustrated in Fig.1.5. In Datta-Das Spin FET the source and the drain are ferromagnets that act as injector and detector of the electron spin, the drain injects electrons with spin parallel to the transport direction. Lee.et.al [81] reported fabrication of Cobalt doped TiO$_2$ nanowire and the electric field effect transistor (FET) function of these nanowires.

Future nanotechnology is believed to be very much dependent on nanoscale material and devices. At this computer era spintronic devices finds extensive applications. Modern computers make use of spin valve in order to read and write data on their hard drive. Development of computer technology has been the initial driving force in spintronics. So it is very important to exploit and optimize the interesting properties exhibited by these nanomaterials.
1.10. **Objective of the thesis.**

The main objective of the thesis is to study the changes in the optical and magnetic properties of nanocrystalline titania by doping with some transition and rare-earth metal ions. Incorporation of these dopants changes the structural and electronic properties of the host lattice and imparts superior luminescent and magnetic properties. In our work we have chosen Ni and Mn as the transition metal ion dopants and Gd and Er as the rare-earth metal ion dopants. Modification in the structural and morphological property are studied with the help of X-ray Diffraction, Raman, Tem. Investigation of the optical property involves understanding the absorption, emission and carrier recombination behavior of the nanoparticles with the help of UV-Vis, Steady state and time resolved photoluminescence spectra. X-ray Photoelectron spectroscopy are employed to know the oxidation state of the dopant ions and also to understand the presence of oxygen vacancies created by the incorporation of these dopant ions. As doping of these transition and rare earth metal ions create their respective $d$ and $f$ states within the band gap of the host lattice , so computational techniques involving Density Functional theory is carried out to establish the presence of the $d$ and $f$ states. Now creation of these states is believed to effect the charge carrier recombination rate and shift the optical
response to the visible region. Both these properties are beneficial for the use of the material as a potential photocatalytic candidate. In our work the feasibility of the photocatalytic degradation of phenol was studied employing visible light.

Furthermore we have also studied the effect of these dopant ions (Mn, Ni, Gd, Er) in tuning the magnetic properties of undoped TiO$_2$ which is otherwise non-magnetic. In transition metal magnetic moment arises from partially filled outermost 3$d$ electrons, whereas in rare earth ions magnetic moment arises from the inner 4$f$ incomplete sub-shell. In transition metal ions the strength of the spin-orbital coupling is much smaller than the crystal field energy and hence, the orbital momentum is quenched and only spin moment contributes towards magnetism. In contrast in rare earth ions the 4$f$ electrons are shielded by the 5$d$6$s$ electrons and the strength of spin-orbital coupling is much greater than the crystal field energy. These 4$f$ electrons undergo indirect exchange interactions via 5$d$ or 6$s$ conduction electrons and yields high magnetic moment per atoms due to high orbital momentum.
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