ABSTRACT

Nanocrystalline transition metal oxides are of considerable interest owing to their potential applications in a range of processes. These are expected to be the key materials for further applications in the field of science and technology. Among various semiconductors TiO$_2$ has been a focus of attention because of its excellent properties such as high activity, good stability and non-toxicity. It has been widely used in the fields of renewable energy and ecological environmental protection. However, as a wide band gap semiconductor TiO$_2$ can show optical absorption and photocatalytic activity only under UV irradiation. Scientists and industrial communists tangled in photocatalytic research are in constant endeavor to intensify the spectral sensitivity of TiO$_2$ based photocatalyst to visible region. Doping opens up the possibility of changing the electronic structure of TiO$_2$ with properties better than undoped TiO$_2$. Nonetheless, doping is also known to have an immense effect on fueling magnetism in this otherwise non-magnetic TiO$_2$. Tunable ferromagnetism attainable in DMS is one of the leading areas of semiconductor spintronics. Diluted magnetic semiconductors (DMS) represent a synergetic collaboration between charge based semiconductors and spin based magnetism [1]. The discovery of room temperature ferromagnetism in Co-doped anatase TiO$_2$ has led to intense experimental and theoretical research in the field of doped titanium oxides [2]. Non-Magnetic metal oxide exhibiting room temperature ferromagnetism is a surprising phenomena arising at the nanoregime. Santara.et.al [3] observed ferromagnetism in undoped TiO$_2$ nanoribbons. The observed magnetism was corroborated to the existence of oxygen vacancies.

The first systematic study on the role of metal ion dopant in quantum size TiO$_2$ was performed by measuring the photoreactivities and the charge carrier recombination dynamics [4]. Although this study was a pioneer work in the research of metal ion doped TiO$_2$, the photoreactivity experiments were carried out under UV light which means that the prepared nanoparticles was not visible light responsive. Many endeavors were made to extend the absorption of metal ion doped TiO$_2$ to visible region after this pioneering work [5,6]. More recently TiO$_2$ doped with lanthanide ions has also provoked great interests [7,8]. Lanthanide ions are known for their stability to form complexes with various Lewis bases. They have special electronic structure of $4f^{n}5d^{m}$. (n
being the number of electrons) that leads to different optical properties and dissimilar catalytic capacity [9]. Choi.et.al [10] reported the mechanism of Gd doping using density functional theory and addressed the structural benefits of electrodes in accommodating the Gd dopants and their consequences on the photocatalytic degradation. Density functional theory is an extraordinarily valuable method to analyze and throw light on the doping process and its effect on the electronic structure.

The main scope of the thesis is to study the defects and dopant mediated changes in the optical, photocatalytic and magnetic properties of TiO$_2$ nanoparticles prepared by sol-gel method. In our work we have chosen Ni$^{2+}$, Mn$^{2+}$ as the transition metal ion dopants and Gd$^{3+}$, Er$^{3+}$ as the rare-earth metal ion dopants. These dopant ions are chosen as they are expected to introduce their respective d or f shell in the TiO$_2$ matrix, inducing photoactive transition in the visible region, thereby throwing light on the use of material as potential photocatalytic candidate on one hand and modulating the magnetic nature of non-magnetic TiO$_2$ on the other hand. In the thesis theoretical computation based on density functional theory (DFT) has been carried out for Mn and Gd doped TiO$_2$ nanoparticles to establish the presence of these states. The results obtained from the partial density of states are correlated with the visible light photocatalytic degradation of phenol.

In Chapter 1 the photocatalytic reaction mechanism using TiO$_2$ as a photocatalyst has been thoroughly discussed. The Density functional theory has been highlighted. Further, the magnetic properties of undoped and doped TiO$_2$ has been emphasized in a broader aspect. Lastly, few areas of applications of TiO$_2$ are mentioned based on its different properties.

In Chapter 2 preparation method of pure and doped TiO$_2$ nanoparticles employing sol-gel method has been discussed. The detailed, structural, morphological and valence state of the dopant ion and its co-ordination environment in TiO$_2$ are analyzed using X-ray diffraction, Raman spectroscopy, transmission electron microscope (TEM), X-ray photoelectron spectroscopy (XPS) respectively.

Although doping in the semiconductor nanostructures is an important method of tuning the electronic structure and obtaining superior properties. But researchers are also in the search of improving the photocatalytic activity of TiO$_2$ nanoparticles without adding impurities. Recently the anatase-rutile mixture is found to have a magical effect on the charge transfer process. [11]. In chapter 3 the optical and photocatalytic activity of mixed phase TiO$_2$ under visible light illumination has been broadly discussed. A
detailed analysis on the emissivity and carrier lifetime have been carried out using steady state and time resolved photoluminescence spectra. Due to the synergistic effect of mixed anatase and rutile phases, mixed phase nanocrystalline titania are found to exhibit superior photocatalytic activity.

Chapter 4 reports some interesting optical and magnetic properties of Ni$^{2+}$ doped TiO$_2$ nanoparticles. Ni doping introduces $d$ states in the band gap of TiO$_2$ and shifts the optical response from UV to visible region. A remarkable red shift of the absorption edge is observed with increasing nickel content. The photocatalytic activity is significantly increased after doping. Room temperature ferromagnetism is observed in the entire doped nanoparticles and oxygen vacancy mediated exchange interaction is proposed to explain the observed ferromagnetism.

Mn$^{2+}$ serves as an active dopant because of its magnetic and optically active nature. In Chapter 5 based on the studies of lattice strain, Raman spectra and Urbach parameter Mn doping is found to introduce some strong lattice distortion. The changes in the property are attributed to the introduction of Mn 3$d$ states. The presence of these states have been identified using DFT study. The chapter than moves on discussing the magnetic nature of Mn doped TiO$_2$ nanoparticles at room temperature as well as at 10 K. A comparative study on the magnetic behavior of the highest doped sample has been carried out under both aerobic and anaerobic atmosphere. It is surmised that although oxygen vacancies are generated due to doping, the numbers are insufficient in comparison to the vacuum annealed sample to bring any ferromagnetic ordering.

Chapter 6 discusses the enhanced photocatalytic activity of Gd doped TiO$_2$ nanoparticles due to formation of Gd 4$f$ energy levels in the band gap of TiO$_2$. The PDOS analysis based on DFT study clearly shows the Gd 4$f$ state, that is more prominent near Fermi level whereas Ti and O have lesser impact. The other states of Gd i.e., $s$, $p$ and $d$ has almost no contribution in comparison to the $f$ state. Hence $f$ state of Gd is the key factor to tune the optical property and increase the photocatalytic efficiency of TiO$_2$ nanoparticles. In contrast to the usual belief that incorporation of ferromagnetic Gd may induce ferromagnetic signal, we have observed paramagnetism at room temperature as well as at 10 K. To the best of our knowledge there are no reports on magnetism in Gd doped TiO$_2$ nanoparticles.

Erbium, a member of the lanthanide rare earth series possess 11 electrons in the 4$f$ shell. Er doped TiO$_2$ nanocrystals are mainly used for optical applications [12]. Chapter 7 reports detailed study on the optical and magnetic properties of Er doped
TiO$_2$ nanoparticles. Compared to undoped TiO$_2$ the emission intensity of the doped TiO$_2$ samples is noticeably enhanced, suggesting that the host matrix not only functions as an ideal host for well dispersed and highly accommodated concentration of Er$^{3+}$ but also as a good sensitizer for proficient absorption of light and transfer of energy to Er$^{3+}$ ions. One of the important finding of this chapter is the analysis of magnetic nature of the sample which has not been reported so far. The results clearly suggest absence of any ferromagnetic interaction. There is persistence of antiferromagnetic ordering and it gets stronger at 0.07 mol. The antiferromagnetic nature is ascribed to the super exchange interaction of Er$^{3+}$ via O.$^2$.  

Chapter 8 summarizes the results discussed above and highlights the probable areas for the expansion of these works. 

**Bibliography:**


