ABSTRACT

Titanium dioxide (TiO$_2$) is one of the most widely studied transition metal oxides with interesting optical, electrical and magnetic properties. Such properties can be harnessed for suitable applications in the field of photocatalysis, photovoltaics, solar cells, etc. From decade on, doped TiO$_2$ nanomaterials is gaining immense importance as they have fascinating optical properties with tuned band gap and electronic structure, with properties better than their native pristine forms. Nevertheless, doping is known to induce magnetic moment in this otherwise non magnetic TiO$_2$ making it a promising material for spin based electronic devices, such as magneto-optical and spintronic devices.

The work undertaken in this thesis is a study of the optical and magnetic properties of pure and metal ion doped TiO$_2$ nanoparticles. The main objective is to explore the defect and dopant mediated tuning of structural, optical and magnetic properties of TiO$_2$ based semiconductor nanoparticles synthesized by sol-gel method. The approach was to investigate the local structure, absorption and luminescence spectra and magnetic properties of TiO$_2$ in the pristine as well as in doped form. The dopants selected for the study are cobalt, manganese, chromium, cerium and neodymium.

Chapter 1 is an introductory chapter that highlights the fundamental properties of TiO$_2$ including its crystal structure, electronic structure, types of defects present and the formation of the different phases. Moreover, optical and magnetic properties of pristine and doped TiO$_2$ have also been discussed in a broader aspect. Few areas of applications are also mentioned based on its different physical properties.

In Chapter 2 we have discussed the sol-gel preparation method of pure and doped TiO$_2$ nanoparticles. We carried out detail structural, morphological, valence state of dopants and its coordination environment in TiO$_2$ with the help of X-ray diffraction (XRD), transmission electron microscopy (TEM), Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and electron paramagnetic resonance (EPR) spectroscopy respectively.
Phase transformation of nanoscale anatase TiO$_2$ to bulk rutile TiO$_2$ is initiated by different factors including annealing temperature, size of anatase nanocrystallite, structural defects, etc. In the process of the phase transformation from anatase to rutile, the physical properties of TiO$_2$ also changes drastically and structural defects, particularly oxygen vacancies play a prominent part in this whole process. It is observed that high concentration of oxygen vacancies not only reduce the wide band gap of anatase TiO$_2$ but also induce ferromagnetic moment in otherwise non magnetic TiO$_2$. These results are discussed in Chapter 3.

Cobalt serves as an active dopant element because of its magnetic and optically active nature. In Chapter 4 we have reported that cobalt forms intermediate d-states in the band gap of TiO$_2$ and extend the absorption edge from UV to visible region. Steady state and time resolved photoluminescence measurement verifies the long lifetime of the charge carriers in the doped TiO$_2$. In contrast to the usual expectation that incorporation of ferromagnetic cobalt in TiO$_2$ may induce ferromagnetic signal, we have observed only paramagnetism in the as prepared cobalt doped TiO$_2$ nanoparticles. Ferromagnetism is observed only when the doped samples are vacuum annealed. Annealing in vacuum generate large numbers of oxygen vacancies which couple with the magnetic impurities to impart ferromagnetism.

Chapter 5 details some interesting optical and magnetic results of Mn doped TiO$_2$ nanoparticles. Mn$^{2+}$ shows several absorptions peaks extending from 370 to 700 nm in the framework of TiO$_2$. The band gap of TiO$_2$ reduces to 2.03 eV and the reduction in band gap is associated with band gap renormalization effect (BGR) that involves hybridization of the Mn $d$-state with the conduction band of host. PL analysis has been done to correlate the role of various factors such as defects, band structure and carrier mobility with the luminescence process of Mn doped TiO$_2$. Mn doped TiO$_2$ exhibit magnetic properties at low applied magnetic field and paramagnetism at high field. The ferromagnetic contribution appears due to the interaction of Mn$^{2+}$ via oxygen vacancies and the paramagnetic part is possibly due to the formation of Mn$_3$O$_4$ phase.

In Chapter 6 we have discussed the modification of local structure of TiO$_2$ and non linear variation of lattice constant depending on the substitutional or interstitial position of Cr$^{3+}$. A spin forbidden Fano type antiresonance absorption peak appears at
735 nm. The corresponding Fano emission peak emerges at 688 nm. Room temperature ferromagnetism was observed in entire Cr doped TiO$_2$ systems and oxygen vacancy mediated exchange interaction of Cr$^{3+}$ ions is suggested to explain the observed ferromagnetism in the system.

Chapter 7 discusses the individual and codoping effect of Ce, Nd and Ce-Nd on the optical, photocatalytic and magnetic properties of TiO$_2$. Ce-Nd codoped TiO$_2$ exhibit visible absorption peaks in the range from 400-900 nm. Ce-Nd codoping shows better efficiency in the separation of charge carriers than individual doping. We have discussed that Ce-Nd codoping leads to maximum degradation of methyl orange dye under visible light as compared to individual doped one. One of the important aspects of this chapter is the observation of room temperature ferromagnetism in TiO$_2$ on doping these rare earth ions. Codoped TiO$_2$ exhibits highest magnetization than the individual doped one.

Chapter 8 summarizes the results discussed above and also gives emphasis on the possible areas for the extension of these works.