Chapter 4

Making optically and magnetically active Co doped TiO$_2$ nanoparticles

In Chapter 2, we discussed the synthesis procedure of Co doped TiO$_2$ nanoparticles with varying concentrations of cobalt and carried out its structural and morphological study with the help of X-ray diffraction, TEM, etc. XRD confirmed the anatase phase of TiO$_2$ without any impurity peaks. Cobalt is predominantly in the +2 valence state as confirmed with X-ray photoelectron spectroscopy (XPS). In this chapter we will mostly concern about the changes in the optical absorption and luminescence properties of TiO$_2$ nanoparticles on incorporation of different percentage of cobalt. Similarly, the dependence of the magnetic properties on cobalt and on oxygen vacancy will be discussed.

4.1 Absorption and luminescence properties of cobalt doped TiO$_2$ nanoparticle

4.1.1 UV-vis absorption study

Doping effect of cobalt on the band structure and therefore on the optical absorption of TiO$_2$ is understood from the diffuse reflectance spectra (DRS) of the samples. The DRS spectra of pristine (0.0 %), 2.0 % and 4.0 % cobalt doped TiO$_2$ are displayed in Figure 4.1 (a). The K-M equation is given by $F(R) = (1-R)^2/2R$, where $R$ is the reflectance of the samples and $F(R)$ is the absorbance [1]. The obtained absorption spectra are shown in Figure 4.1 (b). Both pristine and doped TiO$_2$ exhibits an absorption peak in between 320-350 nm. This peak is due to the transition of electrons from valence band to the conduction band. The absorption edge of doped TiO$_2$ is shifted towards visible region and two extra peaks appear in between 375–505 nm and at around 609 nm. These peaks are the result of the $d$-$d$ electronic transition of Co$^{2+}$ in the crystalline environment of TiO$_2$ [2]. The peak in between 375–505 nm is due to the $^4T_{1g}$ to $^4T_{1g}(P)$ electronic transition and the peak at 609 nm is due to the
transition of electrons from $^4T_{1g}$ to $^4A_{2g}$ state. In anatase TiO$_2$, each Ti$^{4+}$ is surrounded by six oxygen ions in an octahedral co-ordination, forming TiO$_6$ octahedra. When Co$^{2+}$ substitutes Ti$^{4+}$, it forms bond with six oxygen ions. According to crystal field theory, the electrons in the $d$-orbital of Co$^{2+}$ will undergo repulsion by the electrons of the surrounding oxygen ions. This results in the splitting of the $d$-orbital of Co$^{2+}$ into ground and several excited $d$-states. When light interacts with the ground state $d$-electrons, the electrons absorb light and are excited to the upper lying $d$-states showing the aforementioned $d$-$d$ absorption peaks.

![Figure 4.1](image)

**Figure 4.1** Pristine and cobalt doped TiO$_2$ nanoparticles with their (a) reflectance and (b) Kubelka-Munk absorption spectra. Compared to pristine one doped TiO$_2$ exhibit two absorptions in the visible region, related to Co$^{2+}$ $d$-$d$ electronic transition.

These types of electronic transitions will be shown by Co$^{2+}$ when it is in the octahedral or pseudo octahedral coordination. Thus, absorption spectroscopy can be taken as a tool to investigate the interaction of the dopant with the host and to find whether the dopant has undergone into the TiO$_2$ lattice or not. Depending on the coordination environment (octahedral, tetrahedral, etc.) the $d$-$d$ transition probability of these dopants will be different. From the characteristic absorption peaks of Co$^{2+}$, it is clear that dopant creates $d$-electronic states and shifts the absorption edge of TiO$_2$ from UV to visible region. Thus, doping of cobalt may influence the band gap of the samples and to understand this we determined band gap of both pure and doped samples. The variation in the indirect band gap of TiO$_2$ with Co$^{2+}$ concentration is shown in Figure 4.2 (a). The band gap of the material is calculated by extrapolating $[F(R)hv]^{1/2}$ vs. $hv$ at $[F(R)hv]^{1/2}$=0. Quantum confinement effect prevails in pristine
TiO$_2$ nanoparticles and hence the band gap of this sample is enlarged by 0.05 eV than that of bulk anatase TiO$_2$ (3.2 eV). However, the band gap of TiO$_2$ is reduced to 2.86 eV and 2.55 eV and on incorporation of 2.0 % and 4.0 % of cobalt. This reduction in the band gap, after doping, is illustrated as a line diagram in Figure 4.2 (b). The band gap narrowing is occurring owing to the $sp$-$d$ exchange interaction of the Co$^{2+}$ $d$-orbital with the $sp$ electrons of the TiO$_2$ lattice [3,4].

![Figure 4.2 Band gap determination of pure and doped TiO$_2$](image)

4.1.2 Doping effect on the emission intensity of pristine TiO$_2$

Photoluminescence measurement of the samples is performed to understand the doping effect on the carrier recombination process. In order to obtain the emission spectra, the samples are excited at 320 nm and 395 nm respectively. Figure 4.3 (a) shows the emission spectra of the samples excited at 320 nm. Gaussian fitting is performed for one of the emission curves (correctness, $r^2$=0.99983) for clear observation of the position of different emission peaks. The emission spectra contains an UV emission peak at 392 nm, one violet emission peak at 429 nm, two blue emission peaks at 457 nm, 491 nm and one green emission peak at 535 nm respectively as seen in Figure 4.3 (a). The UV emission is considered as the band
edge emission of the host TiO$_2$. This peak appears due to phonon assisted indirect transition from edge ($X_{1b}$) of CB to the centre ($\Gamma_3$) of VB in the Brillouin zone [5]. The 429 nm peak can be ascribed to self trapped excitons (STE) localized on TiO$_6$ octahedra [6]. The STE originates by the interactions of CB electrons localized on Ti $3d$ orbital with holes present in O $2p$ orbital of TiO$_2$. Whether STE will be localized on TiO$_6$ or not depends on the compactness of the octahedra chain and also on the restriction on excitons transfer from one part of the chain to the other [7]. The peak at 457 nm and 535 nm are attributed to the colour centers associated with oxygen vacancies. These colour centers are referred as $F^+$ center (one trapped electron), $F$ center (two trapped electrons), and $F^{++}$ center (without any electrons) respectively [6,8]. The intense blue emission peak at 491 nm appear due to the electronic transition from Ti$^{3+}$ to oxygen anion in a TiO$_6^{2-}$ complex associated with oxygen vacancies [9]. We have observed a new emission peak at 598 nm, alongside 491 nm and 535 nm, on changing the excitation wavelength to 395 nm as shown in Figure 4.3 (b). This orange peak can be attributed to deep trap states [10].

![Figure 4.3 PL spectra at an excitation wavelength of (a) 320 nm (b) 395 nm respectively.](image)

From the observation of the PL spectra at the two excitations, it is understood that doping is neither introducing Co$^{2+}$ related emission peak nor is shifting the peak position. The mere effect of doping is to reduce the PL intensity. Lowering of emission intensity with dopant concentration infers generation of non radiative centers that suppresses the intense emissions of pure TiO$_2$. As shown in Figure 4.3 (a), the emission intensity of pure TiO$_2$ in the UV region is considerably less as compared to
that in the visible regions which is even less in the two doped samples. To understand this intensity variation, we have plotted $I_{\text{UV}}/I_{\text{defect(Blue)}}$ intensity ratio for all the samples, and found that the ratio decreases as we start from pristine to the two doped samples. This variation is shown in Figure 4.4 (a). This indicates that doping distorts the structure of the host and introduces defects near the conduction band minimum [12].

![Figure 4.4](image)

**Figure 4.4** Variation of PL emission intensity for (a) $I_{\text{UV}}/I_{\text{defect}}$ and (b) $I_{491}/I_{598}$ and $I_{491}/I_{535}$ vs. Co concentration

These defects are possibly responsible for the reduction in the intensity of the UV emission peak. For further understanding of the doping effect on the visible emission peaks, we have plotted $I_{491}/I_{535}$ and $I_{491}/I_{598}$ emission intensity ratio against Co$^{2+}$ concentration. This variation is shown in Figure 4.4 (b). This shows that the intensity ratio of $I_{491}/I_{535}$ and $I_{491}/I_{598}$ are nearly same for pure and 2.0 % Co, but decreases profoundly when the amount of cobalt is increased to 4.0 %. This declination in the emission intensity with doping may be due to non radiative recombination process associated with dopant concentration [13]. When the doping concentration is low, the interactions between ions are too weak to have effect on the energy levels of the dopants. However, at high dopant concentration the distance between ions or between ions and defects decreases, thus allowing energy transfer from one ion to another. In this process, the transferred energy may also be captured by impurities or defects, enhancing nonradiative relaxation and hence reduction in the visible emission intensity ratio [14-16].

In our case the intensity ratio is not varied much between pure and 2.0 %
cobalt, since ion centers are not close enough. But, when dopant concentration has a value of 4.0%, the intensity ratio is completely quenched. This indicates that at high loading of cobalt, the coupling among ions or among ions and defects are enhanced. The strong interaction increases the number of emission quenching centers, and hence result in the reduction of the PL intensity. Photoluminescence excitation (PLE) spectra were taken to differentiate the excitation behavior of doped and pristine samples (Figure 4.5). PLE was recorded monitoring the 598 nm emission peak. The two samples show one strong excitation at 398 nm. This is the band edge excitation peak.

![Photoluminescence excitation spectra of pristine and cobalt doped TiO$_2$ nanoparticles monitored at the emission wavelength of 598 nm.](image)

**Figure 4.5** Photoluminescence excitation spectra of pristine and cobalt doped TiO$_2$ nanoparticles monitored at the emission wavelength of 598 nm.

The whole excitation spectra of pure and doped samples are deconvoluted into five peaks with Gaussian fitting function. The excitation peaks ranging from 400 to 550 nm are attributed to surface oxygen vacancies [17]. The PLE spectrum of doped TiO$_2$ contains two peaks at 441 nm and 459 nm which are otherwise absent in the pure sample. The 459 nm peak can be associated with $d-d$ transition of Co$^{2+}$ from $^{4}T_{1g}$
4. The 441 nm band in the excitation spectra was assigned to trapped holes [18].

4.1.3 Doping effect on the recombination time of charge carriers

Time dependent PL decay curves for pure and 4.0 % cobalt are shown in Figure 4.6. The decay was measured monitoring 491 nm emission wavelength. The curves were fitted bi-exponentially, using the following equation [3,19].

\[ y = y_0 + \alpha_1 \exp\left(\frac{-t}{\tau_1}\right) + \alpha_2 \exp\left(\frac{-t}{\tau_2}\right) \]  

(4.1)

Where \( y_0 \) is the baseline correction factor, \( \tau_1 \) and \( \tau_2 \) are decay constants and \( \alpha_1 \) and \( \alpha_2 \) are pre-exponential factor. For pure TiO\(_2\), the values of \( \tau_1 \) and \( \tau_2 \) are 1.16 and 0.634 ns and \( \alpha_1 \) and \( \alpha_2 \) are 5066.7 and 19548.06 respectively. The values of \( \tau_1 \) and \( \tau_2 \) for cobalt doped TiO\(_2\) are 1.802 and 0.854 ns respectively and values of \( \alpha_1 \) and \( \alpha_2 \) are 439.6 and 16724.85. The mean lifetimes (\( \tau_m \)) are calculated by using the equation 2.

\[ \tau_m = \frac{\sum_{i=1}^{n} \alpha_i \tau_i^2}{\sum_{i=1}^{n} \alpha_i \tau_i} \]  

(4.2)

The values are coming out to be 0.90 ns for cobalt doped TiO\(_2\) and 0.80 ns for TiO\(_2\). Thus, the lifetime of the carriers in the doped TiO\(_2\) is longer as compared to pristine TiO\(_2\). Since electron and holes are confined within a small volume of TiO\(_2\), the extent of overlapping of their wave function is more leading to faster recombination [20]. But, inclusions of dopant states in the band gap of TiO\(_2\) hinder the efficient recombination of the charge carriers and thus give them longer lifetime [3]. In pristine TiO\(_2\) the electrons from conduction band relax in the shallow or deep trap states. Usually, trapping is a non radiative process and shallow traps have shorter lifetime than deep traps [21]. In our results the relatively faster component in TiO\(_2\) is due to the relaxation of electrons on shallow trap levels such as Ti\(^{3+}\) or surface trap states. The trapping probability in case of doped one is higher than pristine one because in addition to oxygen related defects, Co\(^{2+}\) \( d \) states are also introduced in the mid band gap. In pristine TiO\(_2\), the electrons first relax in the shallow trap states and then
directly transits to the valence band to recombine with the valence band holes. Doping, however, introduces $d$-states nearby oxygen and $\text{Ti}^{3+}$ related trap centers. Therefore, in doped $\text{TiO}_2$ the electrons take a longer path, comprising of oxygen defects, $\text{Ti}^{3+}$ and $d$-states of dopant, before they undergo recombination with the holes. Hence, a prolonged carrier lifetime can be expected in the 4.0 % cobalt doped $\text{TiO}_2$ than that in the pure one which contains less number of trap centers.

**Figure 4.6** Fluorescence decay curves of pristine and cobalt doped $\text{TiO}_2$ nanoparticles monitored at the emission wavelength of 491 nm

### 4.2 Ferromagnetism in cobalt doped $\text{TiO}_2$ nanoparticles

Cobalt is ferromagnetic and hence incorporation of this metal into $\text{TiO}_2$ may induce ferromagnetic ordering while preserving its semiconducting properties. However, reports on ferromagnetism in pristine $\text{TiO}_2$ evoked confusion on the necessity of magnetic impurities to get magnetism. The magnetism in pristine $\text{TiO}_2$ is mainly assigned to oxygen vacancies. In order to understand the nature of magnetism (due to magnetic impurities or defects), we have annealed the samples both in vacuum and air. The vacuum annealed samples exhibit room temperature hysteresis at an applied field of 15 kOe as shown in Figure 4.7 (a-c). The saturation magnetization ($M_s$) the doped samples with 7.5 %, 9.5 % and 10.5 mol % cobalt are 0.088 emu/g, 0.1266 emu/g and 0.1200 emu/g, while the coercivity ($H_c$) are 110 Oe, 225 Oe and
228 Oe respectively. The remittance \( (M_r) \) of the respective samples are 0.00327 emu/g, 0.0162 emu/g and 0.0163 emu/g. The variation of \( M_s \) with Co is shown in Figure 4.7 (d).

![M-H curve at 300 K](image)

**Figure 4.7** M-H curve at 300 K for the vacuum annealed samples for (a) 7.5 % (b) 9.5% and (c) 10.5 % Cobalt doped sample at an applied magnetic field of 15 kOe. Fig (d) shows variation of \( M_s \) with Co concentration.

When the doping concentration is low, the magnetic cations are situated apart and the total magnetization comes from isolated Co\(^{2+}\) ions. But, at higher dopant concentration, the nearest Co\(^{2+}\) ions are paired up and antiferromagnetic superexchange interactions become prominent among those ions. Due to this interaction the magnetic spins on the nearest Co\(^{2+}\) ions are antiferromagnetically aligned, leading to reduced average moment per magnetic dopant ions and hence reduction in the total magnetization [22-23]. The reduced magnetic moment of the samples indicate that only spin magnetic moment contribute to total magnetization, as orbital moment is completely quenched due to crystal field and antiferromagnetic coupling effects of Co\(^{2+}\) [24]. As the size of the host semiconductor is small, all the added Co\(^{3+}\) may not have gone to substitutional Ti\(^{3+}\) position. Some of the dopant...
atoms may be located in the interstitial position of TiO$_2$ or most possibly on the surface, leading to surface spin disorder and hence canted moment on the surface [25].

The $M-H$ plot of air annealed TiO$_2$ with 7.5 % and 9.5 % cobalt is shown in Figure 4.8 (a-b). The $M-H$ plot is a linear line showing the behavior of paramagnetism. The disappearance of ferromagnetism on air annealing puts a question on the intrinsic nature of magnetism in the doped nanoparticles. Air annealing leads to oxidation of any Co ions present on the surface. Therefore, the surface magnetism coming from ferromagnetic impurities dominates the intrinsic magnetism coming from few Co$^{2+}$ sitting on the lattice site. Therefore, the surface magnetism coming from ferromagnetic impurities dominates the intrinsic magnetism coming from few Co$^{2+}$ sitting on the lattice site. In the vacuum annealed samples, large numbers of defects, particularly oxygen vacancies are generated on the lattice site, surface and on the grain boundary.

![Figure 4.8](image)

**Figure 4.8** Room temperature $M-H$ curves for (a) 7.5 and (b) 9.5 mol % Co doped TiO$_2$ in air annealing condition. Both the sample shows linear M-H behaviour characteristic of paramagnetism.

For each Co$^{2+}$ (75 pm) substituting Ti$^{4+}$ (61 pm), oxygen vacancies are created for charge neutrality. In a theoretical report, it has been suggested that oxygen vacancy formation is energetically more favorable near the impurity ion than that of host Ti$^{4+}$ ion [26]. In contrast, air annealing removes many of the paramagnetic oxygen vacancy centers and oxidize the surface bound Co metal traces to antiferromagnetic Co$_3$O$_4$. Furthermore, the antiferromagnetic interactions of Co$^{3+}$ ions, mediated by oxygen ions, may also result in the loss of ferromagnetism. If there would be more
number of $\text{Co}^{2+}$ on $\text{Ti}^{4+}$ sites, we could expect ferromagnetic ordering in the samples inspite of air annealing. But the dopant content at the substitutional position is very less because of which instead of ferromagnetic ordering, antiferromagnetic interactions become predominant.

To explain the intrinsic or extrinsic nature of magnetism in the samples, temperature dependent magnetic ($M$-$T$) measurements are performed for the samples. Figure 4.9 (a-b) displays the zero field cooling (ZFC) and field cooling (FC) $M$-$T$ curves for 7.5 and 9.5 mol % vacuum annealed samples. At first the sample is cooled down from 300 K to 24 K without applying any magnetic field and then at an applied field of 500 Oe, the magnetization is measured on heating the sample back to 300 K. This results in ZFC curve. The sample is again cooled down from room temperature (RT) to 24 K without removing the field and then magnetization is measured while increasing the temperature to RT. This gives FC curve.

**Figure 4.9** ZFC and FC $M$-$T$ curves of (a) 7.5 mol % and (b) 9.5 mol % Co concentration. Both the curves show a Blocking temperature in the ZFC curves. The temperature range is from 24-300 K.

The ZFC curve shows a blocking moment at 37.9 K ($T_B$), which indicates the presence of superparamagnetic phase in the material. Presence of blocking temperature suggests that nanosized Co clusters or aggregates are present in the interstitial or may be on some regions on the surface. The ZFC and FC curves bifurcate on approaching the blocking temperature, and below blocking moment the two curves completely separate and magnetization increases for FC curve. Below blocking temperature, ferromagnetism occurs and above it superparamagnetism persists. As the concentration is increased to 9.5 %, the blocking temperature shifts to
41 K as displayed in Figure 4.9 (b). Increase in the dopant content increases the interaction between dipole moment of the magnetic dopant ions. This enhances the resistance to thermal agitations and shifts the blocking temperature $T_B$ to higher temperature. The magnetization is also higher for this sample than that of 7.5 %.

The temperature dependent inverse susceptibility ($1/\chi$) curves for 7.5 and 9.5 mol % sample are shown in the inset of Figure 4.9 (a-b) respectively. For both the doped samples we have fitted the high temperature regime of 258-300K in $1/\chi(T)$ plot of the FC branch using the Curie-Weiss (CW) law

$$\chi = \frac{C}{T-\theta_CW}$$

(4.3)

Where $\chi$ is the magnetic susceptibility, $C$ is the Curie constant and $\theta_{CW}$ is the Curie-Weiss temperature and $T$ is the absolute temperature. After linear fitting the high temperature regime and extrapolating the line, the value of $\theta_{CW}$ comes out to be +130 K and +165 K respectively for 7.5 % and 9.5 % samples. The positive value of $\theta_{CW}$ indicates presence of ferromagnetic interactions. The $M-T$ curve, along with the inverse susceptibility, for air annealed 9.5 % Co doped TiO$_2$ is shown in Figure 4.10. In this sample also, the high temperature regime is linear fitted following Curie-Weiss law and on extrapolation the value of $\theta_{CW}$ comes out to be $\sim$ –16 K. The negative value suggests that interactions between dopant ions in presence of oxygen are antiferromagnetic. The peak point in ZFC curve at 41.4 K is very close to the Neel temperature of Co$_3$O$_4$ [27]. Co$_3$O$_4$ has a spinel structure with Co$^{2+}$ ions in tetrahedral (T) and Co$^{3+}$ in octahedral (O) position. Since Co$^{3+}$ ions in (O) positions do not contribute any magnetic moment due to 3d crystal splitting of the ions, only Co$^{2+}$ undergoes weak T-T antiferromagnetic interactions and contribute to magnetism. In our experiments, it was found that vacuum annealing leads to the formation of oxygen vacancy. These oxygen vacancies may contribute to the ferromagnetic ordering in the samples. A bound magnetic polaron (BMP) theory may be adopted to explain the ferromagnetic interaction of dopants mediated by oxygen vacancies [28]. According to this theory, the oxygen vacancies form hydrogenic type orbital overlapping the nearest dopant ions to yield BMP. The exchange coupling between two Co$^{2+}$ ions through oxygen vacancy (Co$^{2+}$-O$_{vacancy}$-Co$^{2+}$) in the BMP induces ferromagnetism. A subcategory of BMP is $F$-centre exchange mechanism (FCE) in which dopants
interacts via trapped oxygen vacancy [29]. Therefore, BMP or FCE mechanism may be operative in our vacuum annealed samples, because of which we are getting ferromagnetic ordering. On the other hand, in the air annealed samples these vacancies are filled up and in that case Co\(^{2+}\) in presence of oxygen ions undergo Co\(^{2+}\)-O\(^{-}\)-Co\(^{2+}\) superexchange interactions leading to antiferromagnetic ordering and reduce magnetization.

![Magnetization curve](image)

**Figure 4.10** Temperature dependent magnetization curve for Co 9.5 \% air annealed sample. Inset of figure shows inverses susceptibility curve with a negative $\theta$ value.

### 4.3 Conclusion

We can summarize the results in the following points

1. Doping shifts the absorption onset to visible region and lowers the band gap. The decrease in emission intensity on doping indicates lower recombination rate and hence enhanced photoactive response. The lowering in UV to visible intensity ratio, after each doping, confirms degradation of structural quality. This was also confirmed by X-ray diffraction. The decrease in intensity ratio of visible emission peaks after doping is due to quenching effect of dopant concentration. Doping of cobalt increases the lifetime of photogenerated carriers by introducing trap states associated with d-states of cobalt, where increase in relaxation time of conduction electrons is observed.
before it undergoes recombination. The increased lifetime indicates the availability of charge carriers for photocatalysis.

2. Oxygen vacancy is mainly responsible for the observed ferromagnetism as ferromagnetism completely vanishes when the sample is annealed in air. Increase in Co concentration leads to increase in superexchange interactions among dopant ions for which even in vacuum annealed sample, decrease in magnetization is found when concentration is increased to 10.5 mol%. Those Co$^{2+}$ ions which could not substitute Ti$^{4+}$ on lattice site, remains as Co clusters giving blocking magnetic moment. Air annealing oxidizes Co impurities to its stable oxide resulting in antiferromagnetic coupling. Thus, Both oxygen vacancy and optimal doping concentration are necessary for getting room temperature ferromagnetism. Increase in the concentration of magnetic impurities and presence of oxygen prevent ferromagnetic interactions. This result in the surface magnetism due to antiferromagnetic Co$_3$O$_4$ dominant over the ferromagnetism interaction due to substitution of Co$^{2+}$ on lattice Ti$^{4+}$ site.

References


[22] White, M.A., et al. Colloidal nanocrystals wurtzite Zn$_{1-x}$Co$_x$O (0≤x≤1):


