Structural and magnetic study of undoped and cobalt doped TiO₂ nanoparticles

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The present study investigates the influence of cobalt doping on the structural and magnetic properties of TiO₂ nanoparticles prepared by a simple wet chemical method. The single phase anatase structure of Co-doped TiO₂ nanoparticles was confirmed by X-ray powder diffraction. A morphological study using scanning electron microscopy and transmission electron microscopy indicates the formation of TiO₂ nanoparticles of sizes 6–10 nm. The high resolution TEM image shows clear lattice fringes indicating the highly crystalline nature of the nanoparticles which was further analysed by selected area electron diffraction pattern which indicates a polycrystalline nature of anatase TiO₂. The shifting and broadening of the most intense E₂ (1) mode in micro-Raman study of Co-doped TiO₂ nanoparticles and XPS spectra indicate the incorporation of Co in TiO₂. Magnetic measurement shows ferromagnetic behavior at room temperature in undoped TiO₂ which has originated due to the presence of oxygen vacancies which are intrinsic in nature. But the M–H curve of Co-doped TiO₂ shows the coexistence of ferromagnetic and paramagnetic phases with enhanced magnetization. The enhancement in magnetization has arisen due to Co doping and the paramagnetism may be due to the presence of some undetected clusters of oxides of cobalt.

1. Introduction

Dilute magnetic semiconductors (DMS)1 formed by doping a sizable amount of transition metal into a semiconductor have been of great interest to researchers due to their possible applications in spintronics2 devices like spin light-emitting diodes (spin-LEDs), spin field effect transistors (spin-FETs) and spin qubits for quantum computers and spin-based memory devices like MRAM3–5 in which both the spin and the charge of the electrons can be used. One of the major challenges for semiconductor spintronics devices is the injection and transport of spin polarized charge carriers. The realization of such DMS is still a widely discussed issue due to the questionable magnetic behavior of the material. For data storage and other device applications ferromagnetism (FM) at room temperature (RT) is one of essential requirements. Although successful doping could be achieved in Mn based III-V semiconductors, but their curie temperature was found unsuitable for practical device applications.7,8 Since then a large number of efforts has been carried out to find the possibility of FM at RT in III-V based DMS such as GaN, GaSb, InAs8–12 and oxide-based DMS such as ZnO, TiO₂, SnO₂, In₂O₃ etc.13–24.

Nanosized titanium dioxide (TiO₂) materials have attracted considerable attention due to its modified electronic and optical properties which provide extensive applications in photo-catalysis, sensors, solar cells, spintronics, energy storage, waste water management, as well as for self-cleaning surfaces.25–30 It can also be used as an antibacterial agent because of strong oxidation activity and superhydrophilicity.31 However due to its wide band gap (3.0–3.2 eV) its activity is limited to near-ultraviolet region. Doping TiO₂ with transition metals tunes the electronic structure and shifts the light absorption region from UV to visible light as well as it gives FM at RT which can be of potential use in spintronics devices. After the experimental report by Matsumoto32 about FM at RT in Co-doped TiO₂ thin films, much effort has been focussed on TiO₂ as a host material for magnetic ion doping. Subsequently, extensive research has been carried out on Co-doped TiO₂ thin films which were grown by different growth techniques like pulsed laser deposition, laser molecular beam epitaxy (LMBE), combinatorial LMBE, sputtering, metal organic chemical vapour deposition as well as sol–gel technique.33–39 FM at RT has been observed by many groups in Co-doped TiO₂ anatase and rutile phases.34,40,41 However the origin of FM in these materials has been of controversial nature like whether the FM arises due to substitution of magnetic ions on the host lattice sites or due to formation of secondary phases of dopant ions. Recently FM
Raman scattering study was carried out with 633 nm line of preparation of Co-doped TiO2 nanoparticles. The same procedure and it should not arise due to magnetic clusters formed due to spintronics application requires that FM should be intrinsic oxygen vacancy induced lattice distortion created FM. The *q* moment mediated by defects in doped nanoparticles. Hong et al. and Yoon et al. have claimed that FM in TiO2 thin films has been caused by oxygen vacancies while Kim et al. reported oxygen vacancy induced lattice distortion created FM. The spintronics application requires that FM should be intrinsic and it should not arise due to magnetic clusters formed due to transition metal doping. Few studies have been done on Co-doped TiO2 nanoparticles (NPs) in contrast to thin films. In this study, undoped and Co-doped anatase TiO2 NPs have been prepared by a simple cost effective chemical route whose structural, morphological and magnetic properties have been studied.

2. Experimental details

Synthesis of un-doped and Co-doped (3 at%, 5 at%, 7 at%) TiO2 NPs were carried out using titanium diisopropoxide bis(acetylacetone) (C16H30O4Ti) as the starting materials. For the synthesis of un-doped TiO2 NPs, precursor and distilled water were taken to prepare a 1 molar solution to which drop of conc. HNO3 was added to maintain the pH of the solution. Then the solution was kept on a magnetic stirrer for duration of 40 minutes. After 40 minutes the solution was heated at a temperature of 50 °C to evaporate the water present in the sample. Once it is completely dried it was crushed into uniform powders using a mortar and pestle. At last the powder was kept inside the heated oven for calcinations for 2 h at 400 °C. For preparation of Co-doped TiO2 nanoparticles the same procedure was followed as in the case of pure TiO2 along with the addition of requisite amount of cobalt chloride in different concentrations (3%, 5%, and 7%).

3. Results and discussion

The morphology of the TiO2 powder was studied by SEM and TEM. Fig. 1 shows SEM images (a–d) of un-doped and Co-doped TiO2 samples. Spherical shaped nanoparticles can be seen from un-doped sample while agglomeration of particle making big clusters can be seen in Co-doped samples. The small particles are agglomerated and bound to the spherical shape due to the doping of Co. To further elucidate the size and structure of these particles TEM was carried out.

Fig. 2(a–c) show the TEM images taken on un-doped and Co-doped (3% and 5%) TiO2 powder while Fig. 2(d–f) indicate the HRTEM images and 2(g–i) show the SAED pattern taken on undoped, 3% and 5% Co-doped TiO2 NPs. TEM images show almost spherical shaped particles with uniform size distribution. Particle size found out from TEM image is in the range 6–15 nm which is in good agreement with the crystallite size obtained from XRD (discussed later). HRTEM show clear lattice fringes with *d*-spacing of 0.37 nm in undoped, 0.365 nm in 3% and 0.36 nm in 5% doped samples which corresponds (101) plane of tetragonal anatase phase of TiO2 indicating the preferable crystal growth plane is (101) which is also the highest intense peak in XRD. Image J software was used to find out the *d*-spacing from HRTEM Images. The SAED patterns taken on un-doped and Co-doped samples show clear distinct rings corresponding to different planes of tetragonal anatase TiO2 structures. The rings obtained in the SAED pattern indicate the formation of polycrystalline anatase TiO2 NPs. The planes corresponding to different rings have been found out by calculating the *d*-spacing using Image-J software which is in agreement with the planes obtained in XRD and those planes correspond to tetragonal anatase phase of TiO2.

The structural parameters and phase purity were studied using powder X-ray diffraction and Full-proof software. The XRD patterns of undoped and Co-doped TiO2 powder with varying dopant concentrations from 3% to 7% are shown in Fig. 3a. All the samples are found to crystallize in single anatase phase with a space group *I4*/*ami* (JCPDS 78-2486) without any rutile peak or peaks related to metallic cobalt or cobalt oxide confirming that anatase phase is not disturbed upon Co doping in TiO2. The most intense peak (101) (shown in Fig. 3b) shows a slight shifting of the peak position towards higher angle as
well as change in FWHM indicating change in local structure
around Ti\(^{4+}\) after Co doping. This shift in peak position
and change in FWHM with cobalt doping (Fig. 3b) indicate
the incorporation of Co in TiO\(_2\). The particle size of
undoped and Co-doped TiO\(_2\) NPs determined from XRD
pattern using Scherer’s equation was found out to be 7 nm
and 6–11 nm respectively which matches well with the
particle size obtained from TEM data. The change in
d-spacing calculated for (101) peak from undoped to 3%, 5%
and 7% doped samples are 0.0019 nm, 0.0036 and 0.0040
nm respectively. As the change in
d-spacing is not that
prominent this means that a very few
percentage of Co has taken part in
substituting Ti\(^{4+}\) and others
may have gone to interstitial site or in grain boundary or on
the surface. As the ionic charge of Ti (+4) and Co (+2) are
different, dopant substitution leads to creation of oxygen
crystallinity and disorder induced due to dopant
incorporation in the host lattice, the presence of defects,
etc. According to factor group analysis, anatase TiO\(_2\) having
tetragonal structure has six Raman active modes (\(A_{1g} + 2B_{1g} + 3E_g\)).
Ohsaka\(^\text{33}\) studied Raman spectrum of an anatase single crystal,
who investigated that the six allowed modes of anatase crystal
appear at 144 cm\(^{-1}\) (\(E_g\)), 197 cm\(^{-1}\) (\(E_g\)), 399 cm\(^{-1}\) (\(B_{1g}\)), 513 cm\(^{-1}\)
(A1g), 519 cm⁻¹, and 639 cm⁻¹ (Eg). Fang et al. showed that Eg peak appears due to O–Ti–O symmetric stretching vibration in TiO₂, B1g appears due to O–Ti–O symmetric bending vibration and A1g appears due to O–Ti–O anti-symmetric bending vibration.

Non-stoichiometry created due to oxygen vacancy and phonon confinement effect strongly affects the Raman spectrum producing shifting and broadening of some spectral peaks. Fig. 4 shows the micro-Raman spectra of undoped and Co-doped TiO₂ samples taken at room temperature in the range 80–800 cm⁻¹. The spectrum of a standard powder sample taken from Sigma Aldrich is also given for comparison. The Raman lines at 142, 390, 511, 637 cm⁻¹ can be assigned as Eg, B1g, A1g, or B1g and Eg modes of anatase phase respectively, the presence of which confirms that our samples belong to tetragonal anatase phase of TiO₂. Four Raman modes have appeared and no mode corresponding to Rutile phase has been observed. In our study the most intense Eg (1) Raman mode at 142 cm⁻¹ shows blue shift with doping and maximum blue shift is in 5% Co-doped sample. All the observed peaks show broadening and weakening of intensity as compared to undoped sample. The shifting of the position and broadening of the Raman peak has been explained due to phonon confinement effect due to nanoscale size of the crystallites.

From XRD and TEM analysis crystallite size has been observed to be very small (6–15 nm). Also Raman signal of TiO₂...
is very sensitive to the vibrational mode of oxygen ions in the Ti–O bond. The presence of oxygen vacancy strongly influences the vibration of Ti–O which makes an effect on the intensity, position, and width of Raman signal. In our study it is observed that the $E_g$ (1) peak has broadened as well as the intensity has decreased with increase in doping concentration while the intensity of other peaks has become almost negligible. The broadening of $E_g$ (1) peak seen from the increase in FWHM with increase in Co concentration is indicated as an inset in the right Fig. 4. The shifting and broadening of the main $E_g$ (1) Raman mode has been interpreted due to the nonstoichiometry in TiO$_2$ lattice due to oxygen vacancies or disorder induced defects and phonon confinement effects. The crystallite size in the nanoscale range may affect the frequency shifting and broadening of Raman peaks due to the phonon confinement. The sudden reduction in scattering intensity in Co doped samples may be due to the breakdown of long-range translational crystal symmetry caused by the incorporated defects. The oxygen vacancies are introduced due to Co doping, which may be the reason for the observed weakening of the Raman signals.

To further check the possibility of secondary phases, oxygen deficiency and oxidation states of Ti and Co in the near-surface region, XPS was carried out on undoped TiO$_2$ and 7% Co-doped TiO$_2$ samples at room temperature. The survey spectra of XPS are shown in the Fig. 5(i). Evidently, all the peaks can be ascribed to the elements Ti, C and O in undoped TiO$_2$ while one extra peak of Co in addition to these peaks has appeared in 7% Co:TiO$_2$ which is in good agreement with our expectation. The high-resolution spectra of Ti 2p and Co 2p were recorded and shown in the Fig. 5(ii). Fig. 5(ii)(a and b) shows deconvoluted XPS spectra of Ti 2p of undoped and 7% Co-doped TiO$_2$ samples. The peak of Ti 2p$_{3/2}$ for both the samples located at 459.49 eV corresponds to Ti$^{4+}$. The broadening of Ti 2p$_{3/2}$ obtained for both the samples at low binding energy could be ascribed to the appearance of Ti$^{3+}$ or Ti$^{2+}$, however, after deconvolution, the Ti 2p$_{3/2}$ spectrum can be separated into two peaks which corresponds to Ti$^{4+}$ and Ti$^{3+}$. Furthermore, the Co peak appeared in 7% Co:TiO$_2$ can be deconvoluted into two peaks one at 781.94 eV which corresponds to Co 2p$_{3/2}$ and other at 797.6 eV corresponds to Co 2p$_{1/2}$ in Co 2p spectra (Fig. 5(ii)(c)). The separation of Co 2p peak into 2p$_{3/2}$ and 2p$_{1/2}$

![Fig. 3](a) XRD pattern of undoped and Co-doped TiO$_2$, (b) expanded region of (101) peak of figure (a) around 20–30 degrees, (c) Rietveld refinement data of 3% Co-TiO$_2$, (d) Rietveld refinement data of 5% Co-TiO$_2$, (e) Rietveld refinement data of 7% Co-TiO$_2$.

![Table 1](Rietveld refinement of powder XRD data of undoped and Co-doped TiO$_2$ (T1: undoped TiO$_2$, T3: 3% Co-TiO$_2$, T4: 5% Co-TiO$_2$, T5: 7% Co-TiO$_2$)

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indicates that the valence state of Co is 2+. The spin–orbit splitting in our samples is approximately 16 eV. Broadening of the Raman modes and XPS data strongly supports the incorporation of Co$^{2+}$ at the expense of Ti atoms in the host which creates oxygen vacancy. Confirmation of the presence of Ti$^{3+}$ and Co$^{2+}$ in the XPS analysis indicates that undoped and Co-doped samples possess certain amount of oxygen vacancies which corroborates the Raman spectra data.

To get information about the magnetic behavior of the undoped and Co-doped TiO$_2$ powders, field dependent magnetization ($M$–$H$) measurements were carried out at 300 K with field varying from $-90$ kOe to $+90$ kOe. The $M$–$H$ curves measured at 300 K show ferromagnetic behaviour (FM) of undoped TiO$_2$ NPs which is shown in Fig. 6. However, the $M$–$H$ curves of doped (3%, 5% and 10%) samples show paramagnetic (PM) type behaviour along with some FM ordering which is attested by the presence of hysteretic nature at lower field region (shown as the inset of each figures). There is an increase in magnetic moment (emu g$^{-1}$) with an increase in concentration of cobalt, and the saturation magnetization is not observed up to the maximum applied field of 90 kOe, as shown in Fig. 7. The magnetization values observed at 90 kOe are 0.013, 0.037, 0.330 and 0.636 emu g$^{-1}$ for undoped, 3%, 5%, 7% Co-doped TiO$_2$ nanoparticles respectively. Although square like hysteric

**Fig. 4** Left: Raman spectra of standard, undoped and Co-doped TiO$_2$, right: expanded region of Raman spectra taken around 80–200 cm$^{-1}$ (Inset showing the variation of FWHM with Co concentration).

**Fig. 5** (i) XPS survey spectra (a) TiO$_2$ (b) 7% Co-doped TiO$_2$. (ii) XPS: high resolution scan (a) Ti 2p of TiO$_2$ (b) Ti 2p of 7% Co-doped TiO$_2$ (c) Co 2p of 7% Co-doped TiO$_2$. 

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behaviour has been obtained in undoped sample, the saturation could not be obtained even with the application of 90 kOe field which indicates the presence of paramagnetic (PM) kind of behaviour along with the FM. The presence of FM in undoped TiO$_2$ suggests that Co doping is not only the origin of FM. The origin of weak FM in undoped TiO$_2$ may be intrinsic i.e. due to presence of defects and/or oxygen vacancies which has been extensively reported. The oxygen vacancies at the surface of the nanoparticles may have introduced exchange interactions between localized electron spin moments which might have induced FM in undoped TiO$_2$. The PM kind of behaviour may have originated due to the formation of the clusters of oxides of Co, however, the same could not be detected in the XRD. It is to be noted that XRD plots of Co doped samples don’t show any kind of impurity phases and this may be due to the lower detection limit of the instrument. It can be observed that the coercivity ($H_c$) of doped samples is larger than that of undoped one (11 Oe), it is highest (170 Oe) in 3% doped sample, then decreased to 124 Oe for 5% and 54 Oe in 7% doped sample. The $M_r$ value for undoped sample is $1.854 \times 10^{-4}$ emu g$^{-1}$ while for doped samples it is $2.8 \times 10^{-4}$, $1.0 \times 10^{-3}$ and $5.29 \times 10^{-4}$ for 3%, 5% and 7% doped samples respectively. Surprisingly, both $H_c$ and $M_r$ values have been increased with Co doping but the trend is different. There is decrease in $H_c$ with increase in Co concentration while the $M_r$ value is highest in 5% doped samples. This can be explained on the basis of two types of interaction forces. The most prominent interaction among the clusters is the inter-particle dipole interaction. In addition, there also exists presence of inter-particle exchange interactions. Using Monte-Carlo (MC) simulations, Kechrakos and Trohidou et al. have investigated the role of inter-particle dipole and exchange interactions in determining the coercivity and remanence of the magnetization. The remanence increases due to the effect of weak exchange forces which favour ferromagnetic alignment of the moments. Dipolar interaction on the other hand produce a suppression of the remanence with concentration. The concentration dependence of remanence is determined by the competition between two types of interactions and a crossover occurs when the strength is comparable and in our case it may have happened at 5% concentration after which the remanence is decreased. It is also explained that when both types of interactions are present, the coercivity decreases with concentration for all values of exchange strength.

From this it can be inferred that magnetism in Co-doped samples is mainly due to Co doping. But in this study oxygen vacancies play an important role in enhancing the magnetism. From XRD and XPS no secondary phases of either Co metal or Co oxide related phases have been detected and both XPS and Raman spectra indicate presence of more oxygen vacancies in doped samples. The enhancement in the magnetic moment (as can be seen from Fig. 7) may be due to exchange interaction forces. The most prominent interaction among the clusters is the inter-particle dipole interaction. In addition, there also exists presence of inter-particle exchange interactions. Using Monte-Carlo (MC) simulations, Kechrakos and Trohidou et al. have investigated the role of inter-particle dipole and exchange interactions in determining the coercivity and remanence of the magnetization. The remanence increases due to the effect of weak exchange forces which favour ferromagnetic alignment of the moments. Dipolar interaction on the other hand produce a suppression of the remanence with concentration. The concentration dependence of remanence is determined by the competition between two types of interactions and a crossover occurs when the strength is comparable and in our case it may have happened at 5% concentration after which the remanence is decreased. It is also explained that when both types of interactions are present, the coercivity decreases with concentration for all values of exchange strength.

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Fig. 6 $M$–$H$ plots taken at 300 K for all the samples of undoped and Co-doped TiO$_2$ NPs. Insets in all the figures show expanded region at low field.
between sp-bond electrons or holes and the d-electron spins localized at the magnetic ions, superexchange between complexes (oxygen vacancies + magnetic impurities) which are stabilized by the electron transfer from vacancies to impurities and magnetic polaron formed by trapped electrons in oxygen vacancies and magnetic ions around it. Thus we can make a conclusion that oxygen vacancies play an important role for FM ordering and the doping enhances the FM ordering. The observed magnetism is purely intrinsic property in undoped and both extrinsic and intrinsic properties account for the magnetism in Co-doped TiO₂ nanoparticles.

4. Conclusion

Influence of cobalt doping on the structural and magnetic properties of TiO₂ nanoparticles prepared by a simple wet chemical method was investigated. The structural analyses showed that the synthesized samples were in anatase phase with slight deviation in lattice variation which were due to Co doping. The morphological study by scanning electron microscope and transmission electron microscope indicate the formation of nanoparticles of sizes 6–10 nm. High resolution TEM image shows clear lattice fringes indicating highly crystalline nature of the nanoparticles which was further analysed by selected area electron diffraction pattern which indicates polycrystalline nature of anatase TiO₂. The shifting and broadening of most intense E₂ (1) mode in micro-Raman study of Co-doped TiO₂ nanoparticles indicate the incorporation of Co in TiO₂. Presence of oxygen vacancies in undoped and Co-doped TiO₂ samples is evident from the X-ray photoelectron spectra and Raman spectra analysis. The magnetic measurement shows ferromagnetic behavior at room temperature in undoped TiO₂ which has originated due to the presence of oxygen vacancies which is intrinsic in nature. But M–H curve of Co-doped TiO₂ shows coexistence of ferromagnetic and paramagnetic phases.

The ferromagnetism has arisen due to oxygen vacancies and the enhancement in magnetism is due to Co doping and the paramagnetism may be due to presence of some undetected clusters of oxides of cobalt.

Conflict of interest

There are no conflicts of interest to declare.

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