Oxygen vacancy-mediated enhanced ferromagnetism in undoped and Fe-doped TiO$_2$ nanoribbons

This content has been downloaded from IOPscience. Please scroll down to see the full text.

(http://iopscience.iop.org/0022-3727/47/23/235304)

View the table of contents for this issue, or go to the journal homepage for more

Download details:

IP Address: 133.30.106.11
This content was downloaded on 14/05/2014 at 05:32

Please note that terms and conditions apply.
Oxygen vacancy-mediated enhanced ferromagnetism in undoped and Fe-doped TiO$_2$ nanoribbons

Batakrushna Santara$^{1}$, P K Giri$^{1,2}$, Soumen Dhara$^{3}$, Kenji Imakita$^{3}$ and Minoru Fujii$^{3}$

$^1$ Department of Physics, Indian Institute of Technology Guwahati, Guwahati-781039, India  
$^2$ Centre for Nanotechnology, Indian Institute of Technology Guwahati, Guwahati-781039, India  
$^3$ Department of Electrical and Electronic Engineering, Graduate School of Engineering, Kobe University, Kobe 657-8501, Japan

E-mail: giri@iitg.ernet.in

Received 28 January 2014, revised 2 April 2014  
Accepted for publication 10 April 2014  
Published 13 May 2014

Abstract

We have investigated the structural, optical and ferromagnetic properties of undoped and Fe-doped TiO$_2$ nanoribbons (NRbs) grown by a solvothermal method. A strong room temperature ferromagnetism (RTFM) is observed in both undoped and Fe-doped TiO$_2$ NRbs. Fe-doped TiO$_2$ NRbs exhibited a $\sim$4.8-fold enhancement in RTFM as compared to the undoped NRbs grown under similar conditions. However, the RTFM decreases at higher Fe concentration, possibly due to antiferromagnetic ordering between nearby Fe$^{3+}$ ions caused by a super exchange interaction. X-ray diffraction patterns reveal the pure TiO$_2$(B) phase, the TiO$_2$(B)–anatase mixed phase and the anatase–rutile mixed phase of the TiO$_2$ structure. Field emission scanning electron microscopy and transmission electron microscopy observations reveal NRbs with uniform pore distribution and nanopits formed on the surface for both undoped and Fe-doped NRbs. These samples exhibit strong visible photoluminescence associated with oxygen vacancies and the ferromagnetic hysteresis loop, both of which are strongly enhanced after vacuum annealing. Optical absorption, electron spin resonance and x-ray photoelectron spectroscopic analyses are performed to elucidate the origin of RTFM. The observed RTFM in undoped and Fe-doped TiO$_2$ NRbs is qualitatively explained through a model involving bound magnetic polarons, which include an electron locally trapped by an oxygen vacancy with the trapped electron occupying an orbital overlapping with the unpaired electron (3d$^5$) of a Ti$^{3+}$ ion and/or the unpaired electron (3d$^5$) of a Fe$^{3+}$ ion. The development of TiO$_2$ NRbs with tunable optical and magnetic properties constitutes an important step towards realizing improved magneto-optical and spintronic devices from novel TiO$_2$ nanostructures.

Keywords: TiO$_2$ nanostructures, ferromagnetism, photoluminescence

(Some figures may appear in colour only in the online journal)

1. Introduction

Diluted magnetic semiconductors (DMSs), where transition metal (TM) atoms are introduced into the cationic sites of the semiconducting host lattice and in particular undoped ferromagnetic oxides, have been at the forefront of research due to their potential use in future spintronic and magneto-optic devices [1–3]. The discovery of ferromagnetism (FM) in Co-doped TiO$_2$ with a Curie temperature ($T_C$) exceeding 300 K [3] has played a crucial role in expanding the field of DMS to oxides, leading to a rapid development of new materials and phenomena arising from a synergy of semiconductor physics and strongly correlated systems. As a result, intensive attention has been focused on DMS such as TM-doped ZnO [4, 5], SnO$_2$ [6, 7], In$_2$O$_3$ [8] and TiO$_2$ [9] due to the realization of room temperature ferromagnetism (RTFM) in these systems.
Among various oxide-based DMSs, TiO\textsubscript{2} has drawn extensive research interest because it is an excellent photo-catalyst for water splitting, and possesses a high solubility limit of dopant magnetic ions and good optical transmission in the visible and near-infrared (NIR) region, making it a suitable candidate for magneto-optic devices as well. However, in spite of several studies reported in TiO\textsubscript{2}-based DMSs, there is no clear agreement about the nature and origin of the observed FM in the diluted magnetic oxide doped with a low percentage of 3d cations. It is being currently debated whether the observed FM in oxide DMS is connected with TM doping or whether it might be solely related to intrinsic defects. In particular, some reports suggested segregation and the formation of secondary phases or metallic clusters as the origin of the FM signal [10, 11], while the most recent results strongly support the intrinsic nature of FM mediated by carriers or defects [9, 12, 13]. These controversial results among research groups suggest that the magnetic properties of DMS materials are critically dependent on the fabrication, growth procedure, doping agents and processing conditions. Different synthesis methods may result in different defect concentrations, structures and surface morphologies, affecting the magnetic properties. Compared to other methods of preparation, the solvothermal method is very simple, has a low cost, and one can easily tune the surface as well as bulk defects by controlling the growth temperature, reaction duration, doping concentrations, etc. In particular, the solvothermal method is an effective method of doping, because the dopant ion precursor distributes uniformly in a high-pressure reaction chamber under continuous stirring throughout the synthesis process, depending upon the solvent used, the pH concentration and the solubility limit of the doping agent in the mixed precursor solution.

Interestingly, some of the outstanding reports revealed no evidence of FM ordering of the active doped metal in Co, Mn-doped ZnO systems [14–16] and Fe-doped TiO\textsubscript{2} (Fe:TiO\textsubscript{2}) systems [17, 18]. Using \textit{ab initio} electronic structure calculation, Pandey and Choudhary [19] argued that an oxygen vacancy (O\textsubscript{v}) leads to electron doping in the TiO\textsubscript{2} system, but does not induce an appreciable magnetic moment. On the other hand, using density functional theory calculation, Chen et al [20] proposed that O\textsubscript{v} plays the important role in determining the FM in Fe-doped rutile TiO\textsubscript{2}. More recently, Hoa and Huyen [21] reported enhanced FM in undoped TiO\textsubscript{2} nanowire as compared to Ni-doped TiO\textsubscript{2} nanowire. Furthermore, RTFM has been observed in a wide range of undoped oxides such as TiO\textsubscript{2} [22–24], HfO\textsubscript{2} [25], In\textsubscript{2}O\textsubscript{3} [22], SnO\textsubscript{2} [26] and ZnO [27]. These reports help to address the controversies about the issues related to the role of defects in FM ordering. In fact, Sundaresan and Rao suggested FM as a universal feature of inorganic nanoparticles where FM was confined to the surface of the nanoparticles [28]. However, unambiguous determination of the nature of defects responsible for the observed FM remains a considerable challenge to researchers. It is unclear whether O\textsubscript{v} or Ti vacancy defects contribute to the magnetic moments, since both titanium and oxygen vacancies were proposed to be responsible for the FM in undoped TiO\textsubscript{2}. On the other hand, theoretical [29] studies indicated that cation vacancies and divacancies are ferromagnetically coupled. Interestingly, more and more theoretical and experimental [30, 31] evidence shows that the magnetic ordering of undoped TiO\textsubscript{2} is strongly related to O\textsubscript{v} and thus it was thought to be the source of RTFM in undoped semiconducting oxides. Therefore, it is important to understand the presence of specific defect types and their role towards the FM. In fact, this will provide the key for interpreting the theoretical predictions and experimental data correctly.

At present, most of the reported FM in undoped and doped TiO\textsubscript{2} systems has been for thin films [12, 28, 30–32] and nanoparticles [28] while their undoped bulk counterparts are diamagnetic or paramagnetic. This implies that spatial dimensionality might play an important role in the FM ordering. Compared to thin films and nanoparticles, the exploitation of 1D TiO\textsubscript{2} nanostructures such as nanowires, nanorods and nanoribbons (NRbs) with a high surface area make it easier to engineer a high availability of defect sites for trapping electrons and may favor FM ordering, thus making them an ideal candidate for the realization of intrinsic enhanced RTFM. Moreover, 1D nanostructures are favoured compared to nanoparticles in terms of electron transport, storage and information processing that can enhance the performance of spintronic devices at the nanoscale for practical applications. Although many reports on RTFM in undoped and TM-doped TiO\textsubscript{2} thin films and nanoparticles are available in the literature [12, 28, 30–32], there is little information about undoped and doped 1D nanostructures [23, 33]. In our previous report [34], we observed RTFM in undoped TiO\textsubscript{2} NRbs and the FM was enhanced after vacuum annealing which suggested that O\textsubscript{v} defects were the source of magnetism in undoped TiO\textsubscript{2}. The earlier results motivated us to examine the individual and combined effect of TM doping and oxygen vacancy defects and clarify the controversial issues related to long-range FM ordering in TM-doped TiO\textsubscript{2} systems. Moreover, a clear demonstration by correlating the magnetism between dopant concentration and O\textsubscript{v} defects in the host semiconducting oxide lattice is crucial and needs thorough investigation. Our present attempt in this study is to enhance the magnetic moments by Fe doping into the TiO\textsubscript{2} matrix and gain a better understanding of the origin of observed FM in the doped 1D TiO\textsubscript{2} system.

Here, we grow undoped and Fe-doped TiO\textsubscript{2} nanoporous NRbs using an ethylene glycol mediated solvothermal method, and studied the effect of doping concentrations and calcination temperatures on the optical and magnetic properties. We investigate the origin of RTFM in the undoped and Fe-doped TiO\textsubscript{2} NRbs. The high surface area and higher concentration of surface defects, such as oxygen vacancies, expected in these nanoporous NRbs could ultimately lead to enhanced FM ordering and strong FM even at RT. It will be demonstrated that a large concentration of oxygen vacancies with high thermal stability indeed results in RTFM in undoped TiO\textsubscript{2} systems. Moreover, when TiO\textsubscript{2} is doped with a low concentration of Fe, its properties are modified. For example, additional oxygen vacancy defects are expected due to the substitution of Ti\textsuperscript{4+} by Fe\textsuperscript{3+} in the TiO\textsubscript{2} lattice and thus, formation of the Fe\textsuperscript{3+}–O\textsubscript{v} defect complex, resulting in enhanced FM in doped TiO\textsubscript{2} NRbs compared to undoped NRbs. However, we observed that a
higher concentration of Fe doping leads to a decrease in FM that may be due to the Fe$^{3+}$–Fe$^{3+}$ antiferromagnetic ordering in the absence of O$_6$ in between two nearby Fe atoms. This result highlights that TM ions in the presence/absence of O$_6$ in the host TiO$_2$ still play a major role in deciding the DMS properties. The primary aim of this work is to figure out the precise role and impact of O$_6$ defects and Fe dopant on the observed RTFM in our Fe$^{3+}$:TiO$_2$ NRbs, and supported this with structural and optical measurements.

2. Experimental details

2.1. Growth and processing of undoped/doped TiO$_2$ NRbs

The details of the synthesis procedure for the undoped TiO$_2$ NRbs were reported in our previous study [34]. Briefly, 0.275 g of anatase TiO$_2$ powder was mixed with 60 ml of 10 M NaOH in mixed solvent (DI water/ethylene glycol : 1 : 1) and stirred for 1 h to produce a milky solution. Next, the mixed solution was transferred into a Teflon-lined autoclave (Berghof, BR-100). During the growth process, the temperature inside the autoclave was monitored and maintained at 180 °C under autogenous pressure and constant magnetic stirring at 250 rpm for 24 h. The formed precipitates were obtained by centrifugation and washed several times with DI water. Subsequently, the products underwent ultrasonic treatment with 0.1 M HCl until the pH was ~7 and finally the precipitates were calcined at different temperatures in the range of 500–900 °C for 5 h in air. For Fe-doped samples, Fe$_2$O$_3$ (Loba Chemie) was used as a precursor with an appropriate quantity (0.1 and 0.2 at. %) and mixed with anatase TiO$_2$ precursor, ground for 10 min in a ceramic mortar, then mixed with the alkaline 10 M NaOH mixed solvent. A similar growth procedure was followed as for the undoped samples. For convenience of discussion, the undoped TiO$_2$ NRbs samples are categorized as the ‘A’ series and after calcinations at 500 and 900 °C are named as A500 and A900, respectively. The 0.1% Fe-doped samples are termed the ‘B’ series and after calcination at 500, 700 and 900 °C are named B500, B700 and B900, respectively. The sample B500 after vacuum annealing at 300 °C under 1.2 × 10$^{-2}$ mbar pressure for 2 h is named B500V. Similarly, 0.2% Fe-doped samples are termed as C500, C700 and C900 after calcination at 500 °C, 700 °C and 900 °C, respectively.

2.2. Characterization techniques

The crystal structures of the obtained samples are characterized by x-ray diffraction (XRD) (Rigaku RINT 2500 TTRAX-III, Cu Kα radiation). Morphologies of the samples were studied by field emission scanning electron microscopy (FE-SEM; Sigma, Zeiss). The energy dispersive x-ray (EDX) spectrum was studied with the help of an x-ray detector (Oxford Instruments, UK) attached with a scanning electron microscope (SEM; LEO 1430VP). The high-magnification surface morphologies and structures of the samples were studied by transmission electron microscopy (TEM), high-resolution TEM (HRTEM) and selected area electron diffraction (SAED) pattern (JEOL-JEM 2010 operated at 200 kV). Specimens for HRTEM investigations were prepared by dispersing powder particles in ethanol and drop casting on a carbon-coated copper grid of 400 meshes (Pacific Grid, USA). The UV-vis absorption spectroscopy measurements were recorded using a commercial spectrophotometer (PerkinElmer UV win Lab). The steady state photoluminescence (PL) spectrum was recorded at RT using a 405 nm diode laser (Coherent, Cube) excitation with a cooled charge coupled device (Princeton Instruments, PIXIS 100B) detector. The powder samples were put onto a conductive carbon tape (black) for the PL measurements. Each spectrum was corrected for the detector response as a function of wavelength after background subtraction. X-ray photoelectron spectroscopy (XPS) measurements were carried out with a PHI X-Tool automated photoelectron spectrometer (ULVAC-PHI, Inc.) using Al Kα x-ray beam (1486.6 eV) with a beam current of 5 mA. Carbon 1s spectrum was used for the calibration of the XPS spectra recorded for various samples. Electron spin resonance (ESR) measurements were taken with a JEOL (JES-FA200) instrument operating in the X band. The magnetic properties of the samples were measured using a Lakeshore (Model no. 7410) vibrating sample magnetometer (VSM).

3. Results and discussion

3.1. Structural characterization

The XRD patterns of the solvothermally synthesized undoped and Fe-doped TiO$_2$ nanostructures after different calcinations are shown in figure 1. All the peaks correspond to the TiO$_2$(B) phase for samples A500 and B500; however, the diffraction peaks of doped sample (B500) are shifted to a lower angle by ~0.06° for the (1 1 0) at 24.91° as compared to the undoped sample (A500). The inset in figure 1(a) shows the enlarged view of the (1 1 0) peak of the TiO$_2$(B) phase, showing the lower angle peak shift in the doped sample. This lower angle shift in the doped sample provides a clue regarding the occupation of mostly Fe$^{3+}$ ions at the substitutional sites of Ti$^{4+}$ in the TiO$_2$ host lattice. Note that for a coordination number of 6 (octahedral), high-spin Fe$^{3+}$ (0.79 Å) has slightly larger ionic radii than Ti$^{4+}$ ions (0.75 Å), so Fe$^{3+}$ can more easily substitute Ti$^{4+}$ in the TiO$_2$ lattice and the corresponding lattice expansion (the lower 2θ value) is expected. Patel et al [35] reported the incorporation of high-spin Fe$^{3+}$ and occupation of the Ti$^{4+}$ site in TiO$_2$ using Mössbauer spectroscopy. Note that the step size was 0.01° for the XRD measurement. So, we believe that the shift of ~0.06° is meaningful and may be due to the substitution of Ti$^{4+}$ by the Fe$^{3+}$ ion. The large concentration of oxygen vacancies in the doped sample may also have some contribution to the lattice expansion, as it is reported theoretically [36, 37] that the Ti–Ti and Ti–O bonds are relaxed due to the missing O atom. The nearest-neighbour Ti atoms move outwards from the vacancy to strengthen the bonding with the rest of the neighbouring O lattice, while the next-nearest-neighbour O atoms move slightly inwards due to the absence of electrostatic repulsion by the missing O atom. The outward relaxation is greater than the inward relaxation; as a result lattice expansion is possible. We
Figure 1. Comparison of XRD patterns for different samples: (a) A500, B500 and C500; (b) B500, B700 and B900. The inset in (a) shows the magnified view of the corresponding (1 1 0) Bragg peak of TiO2(B), indicating a shift in peak position for A500 and B500 samples.

observed the mixed TiO2(B)–anatase phase for C500 with a mostly anatase structure, and a pure TiO2(B) phase for B500, indicating that dopant concentrations play an important role in the formation of different phases of TiO2. Figure 1(b) shows the phase transformation of 0.1% Fe-doped samples with different calcination temperatures. The XRD patterns of sample B700 reveal the pure anatase phase, whereas B900 reveals a mixed anatase–rutile phase with a mostly anatase structure. Note that no segregated phases such as Fe–Ti oxides (FeTiO3(JCPDS: 79–1838), Fe3TiO5(JCPDS: 73-1898)), iron oxides (Fe2O3(JCPDS: 79-1741), Fe3O4(JCPDS: 85-1436)) and metallic clusters (JCPDS: 85-1410) are found within the XRD detection limit.

3.2. Morphological studies

The morphologies of the as-synthesized nanostructures observed by FESEM are shown in figure 2. The FESEM image of sample A500 (figure 2(a)) shows long and straight NRbs of TiO2. Figures 2(b)–(d) show the FESEM image of Fe-doped samples, i.e. B500, B700 and C500, respectively. These samples show the well-defined 1D NRbs without any sign of an impurity cluster, indicating that all the precursor anatase TiO2 and Fe2O3 were uniformly mixed and distributed throughout the solvent and formed a uniform aqueous mixed solution. They then underwent the solvothermal reaction inside the high-pressure reaction chamber and formed doped 1D NRbs. The EDX spectrum of NRbs (B500) is shown in figure 2(e), which shows only Ti, O and Fe elements, indicating that no other contamination element was introduced into the Fe : TiO2 during the sample preparation.

Figures 3(a)–(f) show the TEM images of as-grown samples A500, B500 and C500, respectively. All the samples show the complete formation of 1D NRb morphology to be consistent with the FESEM images. The nanobrick-like structures are attached on the surface of the NRbs making them porous structures. Besides the surface, the HRTEM image in figure 3(e) shows that nanobricks are also observed at the edges of the NRbs in some cases. The details of the formation of these nanoporous NRbs were demonstrated in our previous reports [34, 38]. These surface morphologies are not affected by Fe doping, indicating that Fe is successfully incorporated into the TiO2 lattice crystal, thus eliminating any impurity and Fe metal clusters forming from the morphological point of view. The insets in figures 3(a), (c) and (e) show the SAED patterns of the corresponding NRbs. The SAED patterns demonstrate a single crystalline nature and clearly indicate the monoclinic structure of the TiO2(B) phase of as-grown samples, fully consistent with the XRD results. Figure 3(b) shows the HRTEM lattice fringe of A500 with d-spacing of 3.55 Å corresponding to the (1 1 0) plane of the TiO2(B) phase. The HRTEM lattice fringe of B500 with d-spacing of 3.55 Å and 3.07 Å corresponds to the (1 1 0) and (0 0 2) plane of the TiO2(B) phase, respectively (figure 3(d)). Figure 3(f) shows the lattice fringe of C500 with d-spacing of 2.62 Å corresponding to the (1 1 0) plane of the anatase TiO2 phase. These nanoporous NRbs with nanobrick-like structures on the surface arise due to the defects in TiO2 and this plays a crucial role in tuning the electrical, optical and magnetic properties of the nanostructures. Note that the precursor TiO2 powder did not show any trace of FM, despite the presence of a large concentration of oxygen vacancies as evidenced by a strong visible PL band. Thus, the surface morphology strongly influences the surface defects as a result of different surface areas and seems to be able to tune the RTFM.

3.3. Optical absorption and PL studies

Light absorption characteristics of the solvothermally synthesized 1D TiO2 NRbs and the precursor TiO2 are shown in figure 4. All the as-synthesized samples exhibit a red shift of the absorption edge and considerable absorption in the visible violet region. With the increase in doping concentration, the band gap is slightly decreased (figure 4(a)). According to the energy band structure of TiO2, the valence band top and the conduction band bottom correspond to mainly O 2p and Ti 3d
Figure 2. FESEM images of the morphology of TiO$_2$ NRs: (a) A500, (b) B500, (c) B700, and (d) C500. (e) The EDX spectrum of B500, indicating Ti, O and Fe elements.

states, respectively. The optical absorption of around 380 nm for undoped TiO$_2$ is solely due to the band-to-band (O 2p $\rightarrow$ Ti 3d) transition, while the slight red shift in Fe:TiO$_2$ NRs can be explained as being mainly due to sp–d exchange interactions between the band electrons and the localized d-electrons of the Fe$^{3+}$ ions substituting Ti$^{4+}$ cations. The s–d and p–d exchange interactions give rise to downward shifting of the conduction band edge and an upward shifting of the valence
band edge, leading to a band gap narrowing. The indirect band gap of all samples was determined from the linear fit to the linear portion of the $(\alpha h\nu)^{1/2}$ versus $h\nu$ plot (insets of figure 4). The calculated band gap of undoped, 0.1 and 0.2% Fe-doped TiO$_2$ NRbs are 3.22 eV, 2.71 eV and 2.66 eV, respectively. The lowering of band gap energy for undoped NRbs synthesized by the solvothermal method was reported in our previous studies [34, 38], and is attributed to O$_6$ and Ti.
interstitial defects in TiO2 NRbs. So, it is not straightforward to identify the origin of the band gap narrowing in Fe:TiO2 NRbs from the absorption spectra only. Figure 4(b) shows the comparison of absorption spectra of B500 and B900. With an increase in calcination temperature, the band gap is decreased. Note that the B900 sample shows a Ti interstitial defect-related NIR PL in the PL spectra (discussed below) and this defect is responsible for the decrease in band gap [38]. The Ti interstitial concentration may partly be increased due to the structural transformation from the TiO2(B) phase to the mixed anatase–rutile phase. However, this is not very clear from our data. We believe that the Ti interstitial concentration mainly depends on the heat treatment in the presence of air, as it is confirmed from our previous study [38] that both anatase and rutile phases have Ti interstitial defects. The Ti interstitial peak intensity increased with higher temperature and calcinations. Since the higher calcinations give rise to the rutile phase, there may be some contribution from structural transformation.

Theoretical calculations suggest that a high vacancy concentration could induce a vacancy band of electronic states just below the conduction band [39]. Zuo et al [40] reported the presence of a mini band closely below the conduction band minimum, which is related to O	extsuperscript{·} associated with Ti	extsuperscript{3+} and is responsible for the band gap narrowing in TiO2. A similar observation related to O	extsuperscript{·}–induced band gap narrowing has been reported in a ZnO system [41]. Recently, Hoang et al [42] reported that the interaction between Ti	extsuperscript{3+} and N modified the band structure of TiO2 and is responsible for the enhancement in the water oxidation performance under visible light illumination. Note that the absorption edge of precursor TiO2 powder is at 380 nm; the red shift in the absorption edge in the as-synthesized NRbs may be due to the shallow trap states created by oxygen vacancies associated with Ti	extsuperscript{3+} and Fe	extsuperscript{3+} and/or sp–d exchange interactions between the band electrons and the localized d-electrons of the Fe	extsuperscript{3+} ions substituting Ti	extsuperscript{4+} cations, leading to band gap narrowing.

In order to confirm the nature of defects in undoped and doped TiO2, PL studies are performed. Figure 5(a) shows the RT PL spectra of samples A500, B500, B900 and B500V under identical conditions of measurement. The observed broad visible PL for all samples is primarily related to self-trapped excitons and O	extsuperscript{·}–related defect states in TiO2 [34, 36]. For a clearer understanding of the origin of the broad PL emission, the deconvolution of the peak was necessary. The broad emission peak of sample B500 is fitted properly with four Gaussian bands centred at 469.1 (peak 1), 519.2 (peak 2), 596.5 (peak 3) and 745.8 (peak 4) nm, as shown by the solid lines (blue curves) in figure 5(b). According to the literature, peak 1 may be ascribed to self-trapped excitons located at TiO	extsubscript{6} octahedra, while peak 2 and 3 are ascribed to O	extsuperscript{·}–related trap states. Peak 4 is attributed to the presence of hydroxyl (OH	extsuperscript{·}) species which may form an acceptor level just above the valence band [34]. After vacuum annealing (sample B500V), the visible PL intensity is increased, which is an indication that the visible PL may be due to the O	extsuperscript{·}–related defect trap states. Upon the loss of an O atom in the TiO2 lattice, the electron pair that remains trapped in the vacancy cavity leaves behind a pair of electrons, which gives rise to an F-centre, and one of the electrons in the F-centre tends to occupy the neighbouring Ti	extsuperscript{4+} ion and yield Ti	extsuperscript{3+}–centre and F	extsuperscript{−}–centre states within the band gap of the material [34]. Furthermore, the incorporation of Fe	extsuperscript{3+} into the substitutional site of Ti	extsuperscript{4+} creates additional oxygen vacancies for the charge neutrality in the host crystal lattice. Therefore, a large concentration of O	extsuperscript{·} is expected in our Fe-doped samples compared to undoped samples and this is observed from the enhancement of visible emissions for doped samples in the PL spectra. We observed that the visible PL decreased for the Fe-doped sample calcined at 900°C as compared to the sample calcined at 500°C. This is because of the dehydration of as-grown solvothermal products and creation of oxygen vacancies at lower calcination temperatures, and molecular O2 may not interact with the material at this stage. However, at a higher calcination temperature (900°C), molecular O2 interacts with the surface of the materials and starts filling oxygen vacancies. The NIR PL observed for the samples A500 and B900 is attributed to the Ti interstitial defects in TiO2 [36]. Note that the NIR PL is not observed for B500 and B500V, indicating
the absence or very low concentration of Ti interstitial defects below the detection limit. The Ti interstitial defect-related NIR PL evolved with higher growth temperatures and calcination temperatures; the corresponding mechanism was explained in our previous report [38]. So, we observed Ti interstitial defects in B900, which was calcined at 900 °C.

In order to gain a better understanding of broad visible PL, we studied the time-resolved photoluminescence (TRPL) measurements for B500, monitoring the emission at 550 nm with 405 nm laser excitation, and the data is shown in figure 5(c). The TRPL spectrum is fitted by a bi-exponential decay curve with time constant $t_1 = 0.4$ ns and $t_2 = 2.2$ ns. This result reveals that two defect states contributed to the emission at 550 nm, consistent with the steady state PL contribution of peak 2 and peak 3, and excluding the negligible contribution from peak 4.

3.4. XPS and ESR studies

XPS is a unique tool to investigate surface defects and chemical environment, because of its high sensitivity to surfaces. A more direct evidence of $O_v$-related surface defect states and incorporation of $Fe^{3+}$ in the TiO$_2$ matrix are further confirmed from XPS analyses. A comparison of the Ti 2p core-level spectra for samples B500, B500V and B500, C500 are shown in figures 6(a) and (b), respectively. The Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ core-level peak positions of samples B500, B500V and C500 are 458.2 eV, 458.1 eV, 458.5 eV and 464.1 eV, 463.9 eV, 464.4 eV, respectively. Interestingly, the Ti 2p peak shifts slightly to a lower binding energy in vacuum-annealed sample B500V as compared to B500, which can be attributed to the large concentration of $O_v$ in B500V [43]. The Ti 2p peaks of C500 are shifted to a higher binding energy compared to B500. Furthermore, an obvious broadening and shouldering of the Ti 2p$_{3/2}$ peak towards higher binding energy for sample C500 can be noted, which may be due to the effect of the large concentration of $Fe^{3+}$ in the interstitial and/or substitutional site in the TiO$_2$ crystal lattice. A lower binding energy shift for O 1s core-level peak is observed for B500V (figure 6(c)), while a higher binding energy shift is observed for C500 as compared to B500 (not shown). Note that we observed a higher binding energy shoulder in the O 1s spectra for both B500 and B500V. Such a shouldering may be attributed to the presence of $O_v$ (oxygen bound to carbon) and OH$^-$ species in TiO$_2$ nanostructures [34, 44]. In particular, the shouldering is enhanced for B500V, which implies that the $O_v$ concentration is dramatically increased after vacuum annealing; this ultimately increases the reactivity and binds more carbon and hydrogen as impurities. Finally, the Fe 2p core-level spectrum of C500 is shown in figure 6(d). The Fe 2p$_{3/2}$ and 2p$_{1/2}$ peaks are observed at 710.7 eV and 724.7 eV, respectively, which are the characteristic peaks of $Fe^{3+}$. This is significantly different from that of the metallic Fe, whose 2p$_{3/2}$ peak position is at 706.25 eV. Moreover, the broad satellite peak at around 717.5 eV is attributed to the $Fe^{3+}$ state. Thus, Fe doping and corresponding $Fe^{3+}$ states are confirmed in the doped samples.

ESR is an exceptionally powerful tool in detecting the spin polarized charge state of defective TiO$_2$ nanostructures. The ESR spectra of Fe$_2$O$_3$, A500, B500 and C500 are shown in figures 7(a)–(d), respectively. We observed the ESR signal with g-values 2.00 and 1.97 for A500, B500, B700 and C500, and these signals are assigned to single ionized $O_v$ ($F^+$) and Ti$^{3+}$, respectively [38, 40]. The ESR spectra reveal that $g = 2.22$ and 2.27 for B500 and C500, respectively, indicating the presence
of Fe$^{3+}$ in the TiO$_2$ lattice [45]. Note that the precursor Fe$_2$O$_3$ shows the ESR signal at $g = 2.11$ (figure 7(a)) and this is assigned to Fe$^{3+}$ in Fe$_2$O$_3$, which is different from the g-value of Fe$^{3+}$ in B500 and C500 samples. This eliminates the existence of Fe$_2$O$_3$-type clusters in our samples. If it exists, the g-value should be at 2.16–2.00 [46]. Inamdar et al [45] reported that a broad signal with $g = 2.20$ corresponds to ferromagnetic resonance (FMR) and was raised due to the FM exchange interaction between Fe$^{3+}$ ions in Fe-doped ZnO nanocrystals. Since the ESR signal is at $g = 2.22$ for B500 and it varies with Fe dopant concentration, this signal may be attributed to the FMR signal due to the FM exchange interaction between Fe$^{3+}$ and F$^+$ ions. More interestingly, we observed the ESR signal at $g = 4.77$ for samples A500, B500, B700 and C500 for the first time, and this signal is not observed in Fe$_2$O$_3$. Generally, the ESR signal with $g = 4.20$–4.29 is reported for Fe$^{3+}$ located in a strongly distorted rhombic environment [45, 47]. Hence, the observed g-value at 4.76 in our samples is not due to Fe species, because it is also observed in the undoped sample (A500) and more intense compared to doped samples. Therefore, we assigned this signal to the Ti$^{3+}$ in the distorted octahedral environment and it may possibly have originated due to the O$_2$ and contribute to the FMR due to the orbital overlapping of 3d$^1$ spin Ti$^{3+}$ and 1s$^1$ spin of F$^+$ within the O$_2$ cavity in the TiO$_2$ NRbs. Note that the broad ESR signal of Fe-doped TiO$_2$ NRbs consists of three overlapping signals and is clearly shown in figure 7(c) for the B700 sample. The g-values are obtained by differentiating the observed broad first order derivative ESR signal from all the samples. Thus, the ESR study proved very useful in identifying Fe$^{3+}$ in doped samples and O$_2$-related Ti$^{3+}$ and F$^+$ defects in both undoped and Fe-doped samples. The Ti$^{3+}$ defects are not observed in the XPS Ti 2p core-level spectra, but are observed in the ESR spectra, indicating that the Ti$^{3+}$ species present inside the bulk rather than on the surface of NRbs [40]. This plays a very crucial role in enhancing the stability of FM properties in the TiO$_2$ system.

### 3.5. Magnetic measurements

The magnetic properties of as-synthesized samples were investigated using VSM. The field-dependent magnetic (M-H) measurements are shown in figure 8. Figure 8(a) shows FM hysteresis loops for undoped samples A500 and A900. A900 shows a larger magnetic moment than A500. It has been reported that the oxygen vacancies induce lattice distortion in rutile TiO$_2$ and induce strong FM in undoped TiO$_2$ films due to charge redistribution [30]. The magnitude of the magnetic moment in the rutile phase was predicted to be about four times higher than that in anatase TiO$_2$ [30]. This is consistent with the observation of the higher magnetic moment seen in A900 with a mixed anatase–rutile phase
Figure 7. Room temperature ESR spectra for: (a) Fe₂O₃, (b) A500, (c) B500 and B700, and (d) C500.

as compared to A500 with a TiO₂(B) phase. Figure 8(b) shows the M-H loops of the 0.1% Fe-doped samples. The saturation magnetization systematically decreases with increasing calcination temperatures. This may be related to the different concentration of Oᵥ and the evolution of Ti interstitial defects. Note that the FM is enhanced ∼4.8-fold in Fe-doped sample B500 compared to the undoped A500 of the same TiO₂(B) phase. It is well known that the structure of TiO₂ is very sensitive to oxygen content and can be easily reduced under an oxygen-deficient environment. Therefore, the sample B500 was annealed at 300 °C under a moderate vacuum in order to induce a higher concentration of oxygen vacancies in the sample. Interestingly, the FM is significantly increased for the vacuum-annealed sample B500V as compared to B500 (see figure 8(b)). This clearly indicates that Oᵥ indeed plays a major role in inducing FM in the Fe-doped TiO₂ system. The M-H measurement of sample C500 (0.2% Fe-doped) is shown in figure 8(c). It is observed that the saturation magnetization decreases at a higher Fe concentration. These results underscore the active role of Oᵥ defects and Fe dopant in the observed RTFM. Such a strong RTFM in a 0.1% Fe-doped TiO₂ nanostructure may extend the development of spintronic devices which can be operated at RT. The magnetization parameters for the different samples are listed in table 1. Clearly, the 0.1% Fe-doped vacuum-annealed sample exhibits the highest $M_s$. Although PL measurement cannot provide quantitative analysis on the density of oxygen vacancies, following the earlier report [34], we expect the oxygen vacancy density to be $\sim 10^{16}$ cm$^{-3}$ for our samples. As per our earlier report [34], the density of vacancies is $\sim 5 \times 10^{15}$ cm$^{-3}$ for A900. However, more complimentary studies are required for a better quantification of the vacancy density.

3.6. Origin of strong FM

Despite many efforts, there is an incomplete understanding of the origin of RTFM in oxide-based DMS materials, and whether it is an extrinsic effect due to direct interaction between the local moments in magnetic impurity clusters or is indeed an intrinsic property caused by exchange coupling between the spin of the carriers and the local magnetic moments. Experimental results reported by various groups are quite controversial and in particular, the underlying origin of RTFM in TiO₂-based DMS is still debated. The possible reasons for the inconsistent results may have been raised due to the creation and distribution of the different concentration of defects and/or formation of secondary FM phases/metal clusters that are dependent on the growth methods and processing conditions of sample preparations. However, due to the fact that RTFM is
observed in the undoped TiO$_2$ system, it helps to partly resolve the controversies about the issues related to the role of defects in FM ordering in TiO$_2$ nanostructures [21, 22]. In our recent report [34], it was demonstrated that a large concentration of O$_v$ in TiO$_2$ NRbs with high thermal stability results in strong RTFM compared to those earlier reported in undoped/doped TiO$_2$ systems. In this work, we explore the role of oxygen vacancies and Fe dopant in the origin of enhanced FM in 0.1% Fe:TiO$_2$ compared to undoped TiO$_2$ and the mechanism of the decrease in magnetization for higher dopant concentrations; i.e., for 0.2% Fe:TiO$_2$ NRbs.

First, we address the origin of RTFM in our undoped TiO$_2$ NRbs. Kim et al [30] theoretically reported a weak FM moment in the Ti atom due to O$_v$ defects. Using *ab initio* electronic structure calculation, Pandey and Choudhary [19] argued that an O$_v$ leads to electron doping in the TiO$_2$ system, but does not induce an appreciable magnetic moment. In another theoretical study, Yang *et al* [49] reported antiferromagnetism in undoped TiO$_2$ which arises due to the antiferromagnetic ordering of two Ti$^{3+}$ ions close to the O$_v$ sites. They interpreted that the two electrons associated with O$_v$ will convert neighbouring Ti$^{4+}$ ions into two Ti$^{3+}$ ions which induce an equal local magnetic moment of 1 $\mu_B$ at these sites and results in net antiferromagnetism [49]. Coey *et al* [50] did not observe any FM signal in undoped TiO$_2$ films. However, most recent experimental results reported FM in undoped TiO$_2$ and they interpreted that the FM is due to the O$_v$ defects by using various experimental tools [23, 24, 34]. Thus, these controversial results among various groups suggest that magnetic properties of TiO$_2$ are highly dependent on the charge redistribution created by O$_v$. In particular, we observed a well-defined M-H hysteresis loop with saturation magnetization in undoped A500 and A900 samples, and these samples show a strong presence of O$_v$ defects as revealed from the PL studies. Therefore, it is thought to be the source of RTFM in our undoped TiO$_2$ NRbs. Under this condition, there could be a possibility of charge redistribution; for example, the presence of an O$_v$ on the surface of TiO$_2$ locally traps the electrons, forming an F-centre, and one of the electrons tends to occupy the nearby localized Ti 3d orbit and convert Ti$^{4+}$ ions to Ti$^{3+}$ ions, yielding an F$^+$-centre [34]. Note that our ESR results support the presence of Ti$^{3+}$ and F$^+$ defect species in the undoped A500 sample. The electrons in the F$^+$-centre localize and may form bound magnetic polarons (BMPs) by ordering the Ti$^{3+}$ (3d$^1$) electron spin neighbouring the oxygen vacancies, thereby gaining exchange energy. The s–d exchange interaction between the 1s$^1$ electron spin in the F$^+$-centre, which is localized in the vicinity of the 3d$^1$ electron spin of Ti$^{3+}$ ions within an orbit around the oxygen vacancies, favours long-range FM. The electrons in doubly occupied oxygen vacancies (F-centre) form a 1s$^2$ state, which only mediates a weak antiferromagnetic exchange [51]. Thus, the

---

**Table 1.** Magnetization parameters of the as-synthesized and vacuum-annealed samples: saturation magnetization ($M_s$), remanent magnetization ($M_r$) and coercive field ($H_c$) were determined from M-H loops.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>$M_s$ (emu g$^{-1}$)</th>
<th>$M_r$ (emu g$^{-1}$)</th>
<th>$H_c$ (kOe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A500</td>
<td>0.061</td>
<td>0.004</td>
<td>0.099</td>
</tr>
<tr>
<td>A900</td>
<td>0.109</td>
<td>0.007</td>
<td>0.087</td>
</tr>
<tr>
<td>B500</td>
<td>0.292</td>
<td>0.031</td>
<td>0.129</td>
</tr>
<tr>
<td>B700</td>
<td>0.253</td>
<td>0.021</td>
<td>0.09</td>
</tr>
<tr>
<td>B900</td>
<td>0.171</td>
<td>0.013</td>
<td>0.088</td>
</tr>
<tr>
<td>B500V</td>
<td>0.382</td>
<td>0.043</td>
<td>0.133</td>
</tr>
<tr>
<td>C500</td>
<td>0.075</td>
<td>0.008</td>
<td>0.134</td>
</tr>
</tbody>
</table>

---

**Figure 8.** Magnetic field versus magnetization (M-H) loop at room temperature showing comparison of hysteresis in samples: (a) A500 and A900; (b) B500, B700, B900 and B500V; (c) C500. The insets in each case show the M-H loop at low field near origin in a magnified scale. The inset in (c) (left panel) shows the comparison of visible PL data (oxygen vacancy-related) for B500 and C500.
formation of BMPs, which includes electrons locally trapped by oxygen vacancies, with the trapped electron in the $F^\text{−}$-centre occupying an orbital overlapping with the unpaired electron (3d$^1$) of Ti$^{3+}$, is proposed to explain the observed FM in our undoped TiO$_2$ NRbs.

The mechanism of FM in Fe-doped TiO$_2$ is rather complicated and several mechanisms have been proposed, such as double exchange and super exchange coupling [20], Ruderman-Kittel-Kasuya-Yoshida (RKKY) [52] and coupling of BMPs, which is formed with a localized hole/electron (usually induced by O$_v$ defects) and the Fe$^{3+}$ surrounding [13], etc. The dominant mechanism is still unclear, although one common feature in all these models is the vital role played by defects, carriers and/or their coupling. From the M-H measurements, it is found that the saturation magnetization of the 0.1% Fe-doped sample is enhanced ~4.8 times compared to the undoped sample, and the oxygen vacancies simultaneously increased in doped B500 as compared to undoped A500, as confirmed from the PL spectra. Furthermore, the magnitude of FM varies with different calcination temperatures for the same doping concentration (figure 8(b)). In order to understand the specific role of O$_v$ in Fe : TiO$_2$, we studied the M-H behaviour of the vacuum-annealed sample B500V and showed that oxygen vacancies indeed play a significant role in the observed FM. Our results point to the fact that the defects constitute the main ingredient in the observed FM in both undoped and doped TiO$_2$. This is quite reasonable because when Fe$^{3+}$ substitutes the Ti$^{4+}$ lattice sites, additional oxygen vacancies are expected for the charge neutrality in the host TiO$_2$ crystal. Since we observed FM in the undoped system and the lower magnetic moment in the 0.2% Fe-doped sample in contrast to the 0.1% doped sample, it strongly suggests that a simple carrier-mediated mechanism is not applicable to TiO$_2$-based DMS in this case. The O$_v$ defects introduced in the TiO$_2$ host lattice during the solvothermal growth and post-growth calcinations play a significant role in the FM ordering of 3d local spin, which are determined by the local atomic arrangement and local orbital overlapping and control the magnitude of the FM signal in Fe : TiO$_2$ nanostructures. Again, the question arises as to how the O$_v$ helps in the FM ordering in Fe : TiO$_2$ systems. Chen et al [20] predicted that O$_v$ enhances FM in the Fe : TiO$_2$ system in two different ways, either through a shallow impurity state of a nearest-neighbour Fe–O$_v$ complex or through the capture of vacancy electrons by the Fe atoms and subsequent enhancement of the FM double exchange. Coey et al [53] reported that an electron trapped in the O$_v$ defect level creates an F-centre. The exchange interaction between neighbouring magnetic ions mediated by the F-centre forms a AMP and the overlapping of such BMPs contributes to long-range FM ordering in doped nanocrystals. Based on this mechanism, several authors [13, 35] reported that when the defect concentration exceeds the percolation threshold, the electron associated with the oxygen vacancies overlaps with the 3d shells of many dopant ions to yield the BMPs. The coupling between the two Fe$^{3+}$ dopant spins through the O$_v$ with the trapped electron (Fe$^{3+}$−O$_v$−Fe$^{3+}$) leads to long-range FM ordering, and this is known as F-centre exchange coupling. However, if the one of the Fe$^{3+}$ is far away from the O$_v$, then another possible source of antiferromagnetic interaction may be the existence of oxygen vacancies with two trapped electrons having $1\text{s}^2$ configuration [51]. Therefore, we believe that the exchange interaction between 3d$^1$ spins of Fe$^{3+}$ and the $1\text{s}^1$ spin of the F$^\text{−}$-centre is most likely responsible for the observed enhanced FM in Fe : TiO$_2$ systems along with the exchange interaction between the 3d$^1$ electron spin of Ti$^{3+}$ and $1\text{s}^1$ spin of F$^\text{−}$, as in undoped systems. Theoretical studies suggest that oxygen vacancies can cause an obvious change in the band structure of the host oxides and make a significant contribution to FM. We observed that the absorption edges of as-synthesized NRbs are red shifted compared to the precursor TiO$_2$ powder, which may be due to sp-d exchange interactions between the band electrons and the localized d-electrons of the Fe$^{3+}$ ions substituting Ti$^{4+}$ cations and/or the s–d exchange interaction between F$^\text{−}$ and Ti$^{3+}$/Fe$^{3+}$, and favour the observed FM.

At a higher Fe concentration (0.2%), the FM is decreased. A similar feature was reported recently by Dodge et al [7] in an Fe-doped SnO$_2$ system. Chen et al [20] reported that the reduction of FM in a large concentration of Fe$^{3+}$ doping is possibly due to the antiferromagnetic ordering between two nearby Fe$^{3+}$ ions in the absence of O$_v$ by super exchange interaction. When the dopant concentration is high, Fe$^{3+}$ may reside in the interstitial position in host TiO$_2$ and most of the Fe$^{3+}$ spins exist in the isolated paramagnetic spin system or may interact antiferromagnetically by super exchange interaction between the two neighbouring Fe$^{3+}$ ions, which is responsible for the reduction of FM signals in the 0.2% Fe : TiO$_2$ sample. Our PL results show that the concentration of oxygen vacancies is considerably lower in C500 as compared to B500 (inset of figure 8(c)). Hence, a lower oxygen vacancy concentration is partly responsible for the lower saturation magnetization in C500. Note that the FM decreases with the calcination temperatures in the 0.1% Fe : TiO$_2$ system, which is the opposite of the case of the undoped system. This implies that the dopant concentrations, their distribution within the host lattice and the energy level of the dopant as well as the band gap of TiO$_2$ host may affect FM in Fe : TiO$_2$ systems. In the present case, a different concentration of overlapping of Fe$^{3+}$–F$^\text{−}$ and/or Ti$^{3+}$–F$^\text{−}$ complexes are expected and may enhance or reduce the overlapping of BMPs, which determine the magnitude of FM. The concentration of O$_v$ is considerably lower in B900 compared to that in B500, as confirmed from the PL spectra (figure 5(a)). Hence, the reduction of FM in the higher calcined sample (B900) is consistent with the above model. Another possible reason for the reduction of FM with calcinations in the 0.1% Fe : TiO$_2$ sample is the migration of Ti$^{3+}$ defects towards the surface to interact with atmospheric oxygen and convert to Ti$^{4+}$ interstitial defects during the course of calcinations in air at 900°C, and this may result in the reduction of BMPs. Note that the interstitial defect-related NIR PL was strong in B900 (figure 5(a)). Thus, the O$_v$-mediated FM interaction seems to be fully consistent with our results. The development of TiO$_2$ NRbs with strong intrinsic FM constitutes an important step towards realizing improved spintronic applications of this novel material in the macroscale.
4. Conclusions

We successfully synthesized the undoped and Fe-doped TiO$_2$ NRbs using a low-temperature solvothermal method and investigated the origin of RTFM in these novel systems using several experimental tools. Our studies revealed a one-to-one correlation of $O_v$ and RTFM in undoped and doped TiO$_2$ NRbs. The $O_v$-related enhanced visible PL emission after vacuum annealing of B500 correlated with the increased FM in B500V compared to B500, and indicated that $O_v$ plays a major role in the observed FM in Fe : TiO$_2$ systems. By comparing the $O_v$-related visible emission from PL spectra and saturation magnetization from M-H loops, we found that $O_v$ is mainly responsible for dictating the magnitude of FM in different samples. Since we observed the FM in undoped TiO$_2$ NRbs and there was no sign of impurity from XRD and HRTEM studies in Fe : TiO$_2$ samples, the controversy related to the Fe metal cluster and other secondary phases towards the FM in our Fe : TiO$_2$ system is eliminated. The ~4.8-fold enhanced saturation magnetization in 0.1% Fe : TiO$_2$ compared to undoped TiO$_2$ indicates that Fe$^{3+}$ also plays an important role in FM ordering in the presence of $O_v$ in Fe : TiO$_2$ systems. The observed RTFM is explained on the basis of BMPs whose formation is due to the s–d exchange interaction between Ti$^{3+}$-$F^-$ and Fe$^{3+}$-$F^-$ in the vicinity of $O_v$, and the overlapping of more BMPs results in enhanced FM. The FM decreases with the increase in Fe dopant concentration, which is attributed to the antiferromagnetic ordering caused by the super exchange interaction between two neighbouring Fe$^{3+}$ ions in the absence of $O_v$ and/or the isolated paramagnetic Fe$^{3+}$ located at the interstitial sites of host TiO$_2$. An optimal concentration of Fe doped into the nanocrystalline site of Ti$^{4+}$ and $O_v$ is the primary requirement for the enhanced FM in Fe : TiO$_2$ nanostructures. On the basis of our experimental findings, we conclude that both $O_v$ and Fe dopant and their charge distribution within the TiO$_2$ lattice play the pivotal role in increasing the FM ordering and enhancement of FM in Fe : TiO$_2$ nanostructures. These findings not only help us to gain better insight into the defect engineering of RTFM in undoped and Fe-doped TiO$_2$, but also constitute an important step for the development of practical nanospintronic devices that can be operated at room temperature.

Acknowledgments

This work was partly supported by JSPS invitation fellowship. We acknowledge the financial support from CSIR (Grant No 03(1270)/13/EMR-II) and BRNS (Grant No 2012/37 P1/BRNS) for carrying out part of this work. The Central Instruments Facility (CIF), IIT Guwahati is acknowledged for the HRTEM and FESEM facilities. The Central Instruments Facility (CIF), IIT Guwahati is acknowledged for the HRTEM and FESEM facilities. We acknowledge the financial support from CSIR (Grant No 03(1270)/13/EMR-II) and BRNS (Grant No 2012/37 P1/BRNS) for carrying out part of this work.

References

[21] Hoa N and Huyen D 2013 Comparative study of room temperature ferromagnetism in undoped and Ni-doped TiO$_2$...


[33] Patel S K S and Gajbihiye N S 2011 Intrinsic room-temperature ferromagnetism of V-doped TiO$_2$ (B) nanotubes synthesized by the hydrothermal method Solid State Commun. 151 1500–3

[34] Santara B, Giri P K, Imakuta K and Fujii M 2013 Evidence of oxygen vacancy induced room temperature ferromagnetism in solvothermally synthesized undoped TiO$_2$ nanoribbons Nanoscale 5 4767–88


[47] Duerr K et al 2010 Studies on an iron(iii)-peroxo porphyrin, Iron(iii)-peroxo or iron(ii)-superoxid Dalton Trans. 39 2049–56


