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Sol–Gel Synthesis and Magnetic Studies of Titanium Dioxide Doped with 10% M (M=Fe, Mn and Ni)

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TiO₂ nanocrystals doped with 1%, 5% and 10% Co/TiO₂ and 10% M (M = Fe, Mn and Ni) were prepared by the sol-gel technique and characterized using X-ray diffraction and SQUID. The as-prepared samples are found to be paramagnetic at room temperature, with the magnetic susceptibility following the Curie–Weiss law in the investigated range of 2–370 K. However, transformation from paramagnetism to room-temperature ferromagnetism (RTFM) for the 5% Co/TiO₂ was observed by hydrogenating the sample at 573 K while the 1% sample remained paramagnetic. As the percentage of Co was increased from 5% to 10% the Curie temperature increased from 390 K to 470 K determined via extrapolation. Transformation from paramagnetism to room-temperature ferromagnetism to room-temperature ferromagnetism (RTFM) was also observed by hydrogenation of 10% Fe/TiO₂ at 573 K for 6 h. X-ray diffraction of the hydrogenated sample shows only single phase TiO₂ structure suggesting that the observed RTFM may be intrinsic but magnetic studies may suggest the possibility of Fe nanoparticles.

KEY WORDS: Magnetism; nanoparticle; titanate; sol-gel.

INTRODUCTION

Nanoparticles often can display properties that differ from their bulk counter part. In particular, titanate nanoparticles have been extensively studied for applications in photocatalysis, optical coatings, and opto-electronic devices [1-7]. The properties of the titanate nanoparticles can be further tuned by

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adding dopants to the lattice. Literature has shown that transition metal doped titanium dioxide can be produced in a variety of ways including pulse laser deposition, sputtering, molecular-beam epitaxy, and sol–gel techniques. Typically, sol–gel methods are often employed since it offers the advantages of crystallinity, small particle size and high purity [8–11].

Currently, room-temperature ferromagnetism (RTFM) in Co-doped TiO₂ has attracted significant attention, but the cause of the RTFM has been under debate [12–17]. One explanation is that undetected Co particles, because of their high Curie temperature of bulk Co ($T_c \approx 1388$ K), could readily account for the observations [18, 19]. Another report states that Co atoms substitute in place of the Ti atoms within the lattice and the exchange interaction between the substituted n-type carriers induces ferromagnetism [20, 21]. Lastly, ferromagnetism could be achieved by Co atoms occupying the interstitial positions in the lattice [22].

Recently we have shown that 10% Co/TiO₂ prepared by sol-gel synthesis is paramagnetic at room temperature, with the magnetic susceptibility following Curie–Weiss law (Table I) [23, 24]. However, by controlled hydrogenation of this sample at 573 K, the paramagnetic 10% Co/TiO₂ is transformed to a ferromagnet (Table II) with the Curie-temperature $T_c \approx 470$ K. This transformation occurs without any observable change in the crystal structure as revealed by X-ray diffraction. We have also shown that increasing the time of hydrogenation from 1 to 6 h increases the remanence. XPS and TEM studies of the hydrogenated sample failed to detect the presence of any Co nanoparticles.

We have extended this study to encompass other transition metals, such as Fe-, Mn- and Ni-doped TiO₂. It has already been suggested by Park and co-workers that these metals when doped into TiO_2 may be suitable for spintronic applications [25, 26]. Our present work focuses on the synthesis and characterization of various metal doped TiO_2 nano-crystalline powder prepared by a simple sol–gel route.

Sample	χο	С	θ
1% Co/TiO ₂ Hydrogenated 3 h Hydrogenated 6 h 5% Co/TiO ₂ 10% Co/TiO ₂	$7.8 \times 10^{-6} 6.4 \times 10^{-6} 5.4 \times 10^{-6} 7.9 \times 10^{-6} 1.5 \times 10^{-6} $	$2.5 \times 10^{-4} 2.5 \times 10^{-4} 2.5 \times 10^{-4} 1.2 \times 10^{-3} 2.6 \times 10^{-3}$	1.8 1.5 0.6 4.0 9.8

Table I. Temperature Variation of χ Fit the Curie–Weiss Law for the 1%, 5% and 10% Co/TiO_2 Samples

Sample	Temp (K)	Hydrogenated (h)	$M_{\rm r}~({\rm emu/g})$	$H_{\rm c}$ (Oe)
5% Co/TiO ₂	5	3	0.056	201
		6	0.008	51
	300	3	0.006	21
		6	0.003	44
10% Co/TiO ₂	5	3	0.53	220
		6	0.80	354
	300	3	0.35	184
		6	0.50	222

Table II. Temperature Variation of the Remanence and the Coercivity Data for 5% and 10% Co/TiO₂ Hydrogenated for 3 and 6 h at 5 K and 300 K

EXPERIMENTAL

Samples of 10% M-doped TiO₂ (where M = Fe, Mn and Ni) were prepared by mixing (reacting) 10 ml of titanium isopropoxide (Aldrich) with the appropriate amount of the corresponding metal nitrate (specifically $Co(NO_3)_2$, $Fe(NO_3)_3$, $Mn(NO_3)_2$ and $Ni(NO_3)_2$ (Aldrich), in 25 ml of ethanol (Aldrich). The solution was dried in an oven and the powder obtained was placed into a furnace quenched at 723, 743, and 723 K for Fe, Mn, and Ni, respectively, for 5 min. Parts of these powders were used for magnetic measurements and the remaining used for 3 and 6 h of hydrogenation carried out at 573 K. The hydrogen reduction set-up consisted of a tubular furnace kept inside a continuously vented hood. The samples, contained in an open glass boat, were placed inside the tubular furnace and H₂ gas was passed over the sample at 573 K with the help of a gas flow control unit.

X-ray diffraction (XRD) patterns of the powder sample were measured at room temperature with a Rigaku Diffractometer (DMAX-B) and CuK_{α} radiation ($\lambda = 1.5418$ Å). The samples were mounted on a silicon plate for X-ray measurements. Temperature and magnetic field variations of the magnetization M of the samples were then measured using a commercial SQUID (superconducting quantum interference device) magnetometer (Quantum Design). These results are presented below.

RESULTS AND DISCUSSION

Figure 1 shows a representative XRD pattern for the Co/TiO₂ samples (specifically 5% Co) both as-prepared and hydrogenated at 573 K for 3 and 6 h. It is evident that the XRD patterns show an excellent match with anatase (PDF 21-1272) without any impurity peaks indicating Co is well dispersed within the TiO₂ lattice. Figure 2 is a representation (specifically



Fig. 1. X-ray diffraction patterns of the as-prepared (0 h) sample of 5% Co/TiO₂ and the sample hydrogenated for 3 and 6 h at 573 K. The expected line positions for the anatase phase are shown.



Fig. 2. Temperature dependence of the magnetic susceptibility (χ) of the as-prepared sample of 1% Co/TiO₂. The solid line is fit to the equation shown. The magnetic field applied was 500 Oe.

1% Co/TiO₂) of the temperature dependence of χ for the as-prepared samples (prior to hydrogenation) fit to the Curie–Weiss law: $\chi = \chi_0 + C/(T-\theta)$. This dependence is similar to the one reported for 10% Co/TiO₂ [23]. From the Curie-constant $C = 2.5 \times 10^{-4}$ (emu-K/gOe) ($C = N\mu^2/3k_B$ with N being the number of magnetic ions/g, $k_B =$ Boltzmann constant and $\mu =$ magnetic moment), $\mu(Co^{2+}) = 4.0 \ \mu_B$ is obtained. This magnitude of μ is consistent with the high spin state of Co²⁺, assuming that Co²⁺ substitutes for Ti⁴⁺ in the anatase unit cell for 1% cobalt doping with the balance of the charge compensated for by O₂. After hydrogenation at 573 K up to 6 h, the sample retains its paramagnetic behavior with a similar $\mu(Co^{2+})$. The results are presented in Table I. It is significant to note that the Curie-constant remains unchanged even when the sample is hydrogenated for 6 h.

The as-prepared sample of 5% Co/TiO₂ displays paramagnetic behavior similar to the observed results for 1% Co/TiO₂ with (Table I) and also gives $\mu = 4.0 \mu_B$. However, after hydrogenation for 3 h at 573 K, the sample displays RTFM as indicated by χ vs. *T* (Fig. 3) and M vs. H (Fig. 4) plots. The absence of a peak in χ for the zero-field cooled (ZFC)



Fig. 3. Temperature variation of the magnetic susceptibility of the 5% Co/TiO₂ hydrogenated at 573 K for 3 h under ZFC and FC conditions.



Fig. 4. M vs. H variation of 5% Co/TiO₂ hydrogenated for 3 h measured at 300 K (a) and an expanded view (b).

cases, which is a signature of the blocking temperature ($T_{\rm B}$) for cobalt as reported recently for the thin films of Co/TiO₂ prepared by sputtering [15], provides additional assurance for the absence of Co nanoparticles in our samples. The reported *T*B values of Co nanoparticles of different sizes are: $T_{\rm B} \simeq 20$ K (3 nm), $T_{\rm B} \simeq 50$ K (6 nm), $T_{\rm B} \simeq 100$ K (8 nm) and $T_{\rm B} \simeq 260$ K (11 nm) [27, 28]. Again, it is significant to note that hydrogenation does not appear to affect the crystal structure since no significant differences are observed in the XRD patterns of the four samples. From the widths of the XRD lines, the average particle size of the anatase phase is $\simeq 10(\pm 2)$ nm, without any major changes upon hydrogenation. The temperature variation of the magnetic susceptibility and the magnetization are also indicative of RTFM for the sample hydrogenated for 6 h. The temperature variation of the remanence and the coercivity data for the 3-and 6-h samples are shown in Table II. The significantly lower values are attributed to lower percentage of Co doped in the sample [9].

For the 6-h sample, Fig. 5 shows the temperature variation of the remanence M_r (M at H=0) and coercivity H_c (H at M=0) from 5 K to 350 K. Measurements for temperatures higher than 350 K could not be made due to experimental limitations. These variations of M_r and H_c vs. T illustrate a $T_c \approx 390$ K determined from extrapolating the M_r and H_c data to zero which is significantly lower than the T_c observed for the 10% sample (470 K) also attributed directly to the lower percentage of doped Co [23]. Although the extrapolations of Fig. 5 show a similar T_c obtained from the M_r and H_c data, the extrapolations are clearly very approximate since M_r and H_c are often non-linear approaching T_c . The primary effect of increasing the hydrogenation time from 1 to 6 h demonstrates an increase in M_r and H_c for the 10% sample. However, the 5% Co doped sample, when hydrogenated for 6 h shows more temperature dependence.

XRD of the as-prepared powders confirm the anatase form of TiO₂, with only a trace amount of the rutile and/or brookite phases in the asprepared samples as shown in Fig. 6a. This is significant since other methods at similar percentages do not show a single phase of TiO₂ exclusive of the dopant. Optimization of the temperature used for calcination is critical since deviations lower or higher, from the above stated temperatures, resulted in the appearance of either amorphous or rutile phases correspondingly. From the widths of the XRD lines, the average particle size of the anatase phase is $\approx 10(2)$ nm, without any major changes on hydrogenation.

The results of the hydrogenation are shown in Fig. 6b and c. Figure 6 illustrates that Fe is doped into the TiO_2 lattice upon calcination and remains doped within the lattice after hydrogenation. Adversely, Mn is doped within the lattice when hydrogenated for 3 h, but MnO₂ is present after hydrogenating for 6 h. Metallic Ni is also detected after hydrogenation in both the



Fig. 5. Temperature variation of (a) remanence (M_r) and (b) coercivity (H_c) of the sample hydrogenated 6 h at 573 K. The dotted lines are extrapolations, indicating T_c 390 K where M_r and H_c approaches zero.

3- and 6-h samples. Alteration of the temperature and duration of hydrogenation experiment has yet to be successful in producing a single phase.

Figure 7 (specifically 10% Fe/TiO₂) is representative of the temperature variation of χ for the as-prepared 10% M/TiO₂ prior to hydrogenation where the solid line is fit to the Curie–Weiss law with the calculated values of μ for the as-prepared 10% Fe, Mn and Ni (prior to hydrogenation) shown in Table III.

Our previous report has shown that 10%Co/TiO₂ after hydrogenation at 573 K, acquires RTFM. This was confirmed by measuring χ vs. *T* for the 6-h sample under ZFC and field-cooled (FC) conditions. The absence of a peak in χ for the ZFC cases, which is a signature for the blocking temperature $T_{\rm B}$ for Co as reported recently for the thin films of Co/TiO₂ prepared by sputtering [15], provides additional assurance for the absence of Co



Fig. 6. XRD showing 10% Fe/TiO₂ as-prepared (a) and hydrogenated for 3 h (b) and 6 h (c).



Fig. 7. Temperature dependence of the magnetic susceptibility of the as-prepared 10% Fe/ TiO_2 . The solid line is fit to the equation shown.

nanoparticles in our samples. However, hydrogenation of 10% Ni/TiO₂ resulted in the presence of metallic Ni in the XRD pattern. This was also confirmed by measuring χ vs. *T* under ZFC which displayed a blocking temperature at 21 K attributed directly to the presence of metallic Ni.

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Sample	χο	С	θ	$\mu/\mu_{\mathbf{B}}$
10% Co/TiO ₂ 10% Fe/TiO ₂ 10% Mn/TiO ₂ 10% Ni/TiO ₂	$\begin{array}{c} 1.4 \times 10^{-6} \\ 8.7 \times 10^{-6} \\ 6.7 \times 10^{-6} \\ 1.0 \times 10^{-4} \end{array}$	$\begin{array}{c} 2.6\!\times\!10^{-3} \\ 2.0\!\times\!10^{-3} \\ 1.0\!\times\!10^{-3} \\ 1.5\!\times\!10^{-3} \end{array}$	-9.8 -4.2 -1.5 -4.9	4.1 3.6 2.5 3.2
Hydrogenated 3 h 10% Fe/TiO ₂ 10% Mn/TiO ₂	3.0×10^{-5} 3.4×10^{-5}	2.0×10^{-3} 1.1×10^{-3}	-4.1 -3.2	3.6 2.7

Table III. Temperature Variation of χ Fit the Curie–Weiss Law for the 10% Co-, Fe-, Mn-, Ni-doped TiO₂ Samples



Fig. 8. XRD showing 10% Mn/TiO₂ as-prepared (a) and hydrogenated for 3 h (b) and 6 h (c).

Table IV. Temperature Variation of the Remanence and the Coercivity Data 10% Co-, Fe-, Mn-doped TiO₂ Hydrogenated for 6 h at 300 K

Sample	$M_{\rm r}~({\rm emu}/{\rm g})$	$H_{\rm c}$ (Oe)	
10% Co/TiO ₂	0.50	222	
10% Fe/TiO ₂	0.05	301	
10% Mn/TiO ₂	0.08	51	



Fig. 9. Temperature variation of the magnetic susceptibility of 10% Fe/TiO₂ hydrogenated for 6 h under ZFC and FC conditions.



Fig. 10. *M* vs. *H* variation of 10% Fe/TiO₂ at 300 K. The inset shows an expanded view.

The results of measuring χ vs. *T* for Mn can be summarized as follows. While the XRD patterns of hydrogenated 10% Mn confirmed that metallic Mn was not present in the 3-h hydrogenated sample, χ vs. *T* measurements showed only paramagnetic behavior similar to the as-prepared sample (Table III). The data was fit to the Curie–Weiss law and the calculated magnetic moment of 2.9 for the 3-h hydrogenated sample showed little deviation from the as-prepared sample. However, the magnitude of this value is significantly lower than the reported value of 5.9 for Mn^{2+} . The χ vs. *T* measurements for the 6-h hydrogenated sample exhibited significantly higher χ values which did not follow the Curie–Weiss behavior observed for the as-prepared and 3-h hydrogenated samples. The *M* vs *H* data indicates RTFM which may arise from the presence of MnO_2 as observed in the XRD indicated in Fig. 8. The remanence (M_r) and coercivity (H_c) observed at 300 K are reported in Table IV.

This magnetic moment calculated for 10% Fe/TiO₂ hydrogenated for 3 h was 4.0. This value is also comparable to the as-prepared sample, but again is significantly lower than the accepted value of 5.4. Conversely, χ vs. T measured for 10% Fe hydrogenated for 6 h resulted in ferromagnetic behavior as shown in Fig. 9. The presence of a peak in χ for the ZFC cases at 350 K is signature for the blocking temperature, $T_{\rm B}$, for Fe. Literature has shown that the $T_{\rm B}$ values of Fe nanoparticles of different sizes are $T_{\rm B} \approx 230$ K (5 nm), $T_{\rm B} \approx 150$ K (4 nm) and $T_{\rm B} \approx 120$ K (3 nm) [26]. The hysteresis loop observed at room temperature is indicative of ferromagnetism (Fig. 10). The values of $M_{\rm r}$ and $H_{\rm c}$ are also reported in Table IV.

CONCLUSIONS

In summary, we have reported the synthesis of 10% M-doped TiO₂ powders successfully prepared via sol–gel synthesis and controlled calcinations. XRD for M-doped TiO₂ indicates the formation of a single phase compound without any impurity which is paramagnetic. Theoretically, it has been suggested that oxygen holes are essential to provide the exchange coupling between the doped ions, leading to intrinsic RTFM [29]. This indeed was the motivation for our hydrogenation experiments, since H₂ is likely to extract oxygen from the sample thus producing oxygen holes. For 10% Co- and Fe-doped TiO₂ we have shown that hydrogen reduction is necessary to convert the magnetic nature from paramagnetic to ferromagnetic.

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