Effect of annealing temperature on magnetic properties of pure TiO_2 nanoparticles

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We report the magnetism of pure TiO_2 nanoparticles, which were prepared by sol-gel method with the postannealing in air at different temperatures without any ferromagnetic dopant. The results of X-ray diffraction and Raman spectra show that the samples change from anatase phase to rutile phase with the increasing of annealing temperatures from 450 °C to 800 °C. Magnetization measurement indicates that the TiO_2 nanoparticles annealed at 450, and 550 °C exhibit the weak ferromagnetism at 5 K, and at 800 °C exhibit the diamagnetism which is due to the decreasing surface defects with the increasing of annealing temperature. In addition, the mechanism of magnetic transition measured at different temperature is also discussed.

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1. Introduction

Diluted magnetic semiconductors (DMS) have recently attracted a great deal of attention due to their potential applications in spintronic devices which utilize both the charge and the spin of electrons to create new functionalities beyond conventional semiconductors [1, 2].

Recently, the ferromagnetic properties obtained by doping 3d transition metal ions into TiO_2 attracted wide attention due to its potential applications in spintronics [3-6]. Although a lot of results have been reported, the origin of ferromagnetism (FM) in transition-metal-doped TiO_2 has not been fully understood. When different groups try to give various explanations for the FM, an unexpected FM was found in the undoped HfO_2 materials [7, 8]. These findings challenge our understanding of magnetism in these systems, because neither cations nor anions have unpaired d or f electrons. Generally, the candidate defects responsible for the unexpected ferromagnetism must fulfill three conditions: (1) the defects should prefer a spin-polarized ground state with a nonzero magnetic moment; (2) the low formation energy of the defects is required to achieve a high defect concentration; (3) the exchange interactions between the defects should be ferromagnetic energetically. Following this, FM was observed in undoped wide band gap semiconductor nanoparticles and thin films, such as TiO_2, ZnO, SnO_2, In_2O_3, CeO_2, CuO and so on [9-14]. These reports created great excitement in this new phenomenon, also known as d^0 magnetism.

Among the various oxides, TiO_2 is a well-known band gap semiconductor with potential applications in catalysts, dye-based solar cells, and chemical sensors [15-18]. Magnetic properties of undoped TiO_2 have been widely studied. However, despite of numerous studies, the origin of the ferromagnetism in undoped TiO_2 remains unclear. Therefore, exploring the unexpected ferromagnetism in the un-doped TiO_2 is desirable.

In this work, we prepared nanoparticles with different annealing temperatures. This study will allow us to investigate the role of different phase in tailoring FM in the undoped TiO_2 system. To the best of our knowledge, a little of experimental results report the different kinds of magnetic characteristic for pure TiO_2. In this paper, the possible origin of magnetic is also discussed. Therefore, undoped semiconductor oxides provide an excellent direction to suitably investigate the origin of intrinsic FM in DMS systems.

2. Experimental details

The samples were prepared using Tetra-n-butyl titanate as initial precursors. Tetra-n-butyl titanate was mixed with the ethanol, distilled water and hydrochloric acid and stirred for 3 h at room temperature. The solution was aged for 1 day and dried at 70°C for 60 h. Then the samples were annealed at 450, 550, 800 °C for 1 h in air. Powders were obtained by grinding using an agate mortar.

X-ray diffraction (XRD) patterns of the nanoparticles were recorded using a Rigaku D/Max-IIIC (Cu Kα radiation). Raman spectra were measured at room temperature using the 514.5 nm of an Ar^+ laser as the exciting light source (JY-HR800). Variable-temperature

magnetization measurements under a magnetic field of 2000 Oe and under both zero-field-cooled (ZFC) and field-cooled (FC) conditions were performed on a Quantum Design SQUID MPMS XL-7 (SQUID) at temperatures ranging from 300 K down to 5K. The dc hysteresis loops were collected on the same SQUID in magnetic field from 50000 to -50000 Oe at 5 and 300 K, respectively.

3. Results and discussions

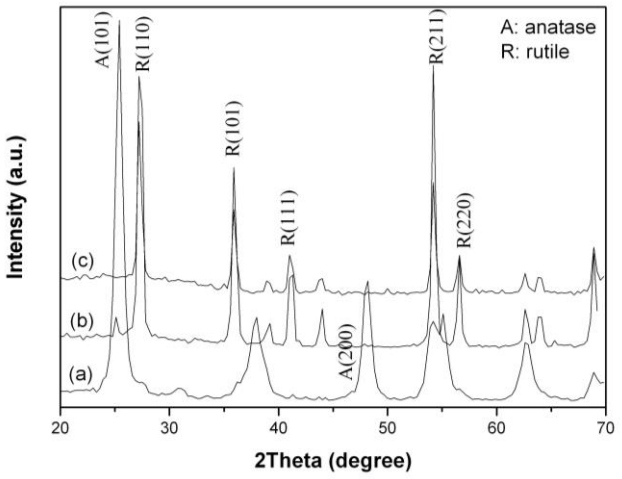

Fig. 1. XRD pattern of TiO_2 nanoparticles annealed at 450, 550, and 800 °C.

Fig. 1 shows XRD patterns of the samples of TiO_2 prepared at different annealing temperatures. All diffraction peaks are indexed to the anatase or rutile phase of TiO_2 with no evidence of the presence of secondary phase. The crystal structure of TiO_2 sample annealed under 450 °C is anatase (2θ=25.3°, 37.9°, 48.1°, 54.3°, 55.1°, and 62.7°). With further annealing, the peaks for rutile phase appear while that for anatase phase attenuate, this clearly indicates the phase transformation from anatase to rutile. The crystal structure completely transforms to rutile (2θ=27.4°) at 800 °C. The anatase-rutile transformation process can be observed more clearly from Raman spectra. Furthermore, the crystallite sizes of the samples are determined from the half-width of peaks by using Scherrer's formula. The crystallite sizes for different annealing temperature from 450 °C to 800 °C are estimated as 12.9, 22.0, and 25.5 nm, respectively. The crystallite sizes of anatase and rutile phases increase with the increase of annealing temperature.

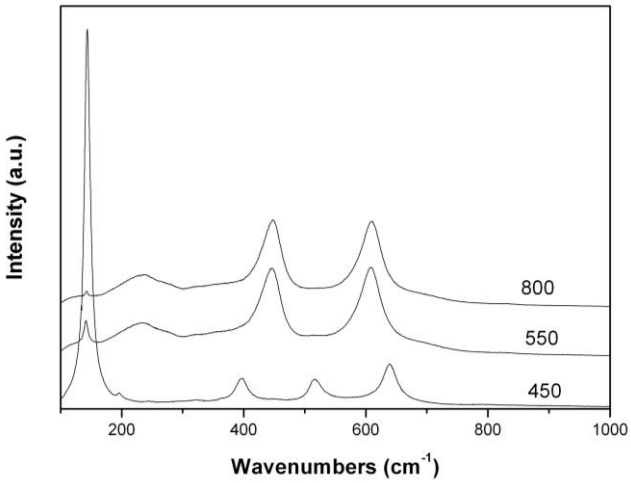

Fig. 2. Raman spectra of TiO_2 nanoparticles annealed at 450, 550, and 800 °C.

Raman spectroscopy can be used properly to examine the surface structure of TiO_2 samples. Iida and Li both claim that this method is more sensitive to nanometer sized crystals than X-rays [19, 20]. It is well known that TiO_2 has three natural phases: anatase, rutile, and brookite. Anatase is tetragonal (D_{4h}^{19}) with two formula units per unit cell and six Raman active modes ($A_{1g} + 2B_{1g} + 3E_g$), whereas rutile (tetragonal, D_{4h}^{19}) has two units and four Raman active modes ($A_{1g} + B_{1g} + B_{2g} + E_g$). Brookite is orthorhombic (D_{2h}^{15}), has eight formula units per unit cell and shows Raman active modes ($9A_{1g} + 9B_{1g} + 9B_{2g} + 9B_{3g}$) [21].

The Raman spectra of TiO_2 samples are displayed in Fig. 2. The three bands at 639, 197, and 144 cm^{-1} are assigned to the E_g modes and the band at 399 cm^{-1} to the B_{1g} mode of the TiO_2 anatase. The band at 516 cm^{-1} is a double of A_{1g} and B_{1g} modes of TiO_2 anatase. This result confirms that the crystal structure of TiO_2 sample annealed under 450 °C is anatase. For sample annealed at 800 °C, only the signal shows the Raman spectrum of the rutile phase with a band at around 235 cm^{-1} due to multiphonon scattering and two bands at 447 cm^{-1} (E_g mode) and 612 cm^{-1} (A_{1g} mode). The crystal structure of TiO_2 sample annealed under 550 °C is mixed of anatase and rutile. The Raman results are consistent with XRD analysis.

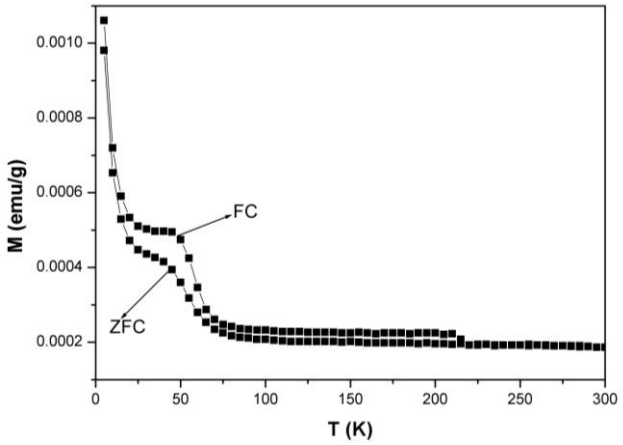

Fig. 3. ZFC and FC curves of sample annealed at 550 °C under a magnetic field of 2000 Oe.

The temperature dependence of magnetization is shown in Fig. 3 for TiO_2 annealed at 550 °C. The figure shows a plot of zero-field-cooled (ZFC) and field-cooled (FC) magnetization measurements performed on the materials by applying a field of 2000 Oe. The drastic increase of the magnetization below 50 K with decreasing temperature can be attributed to the strong paramagnetism in TiO_2, and the clear separation between the FC and ZFC curves indicates the weak ferromagnetism in TiO_2. At around 220 K, the magnetization decreases rapidly with increasing temperature, and also the FC and ZFC curves start to coincide. Thus the Curie temperature Tc is around 220 K.

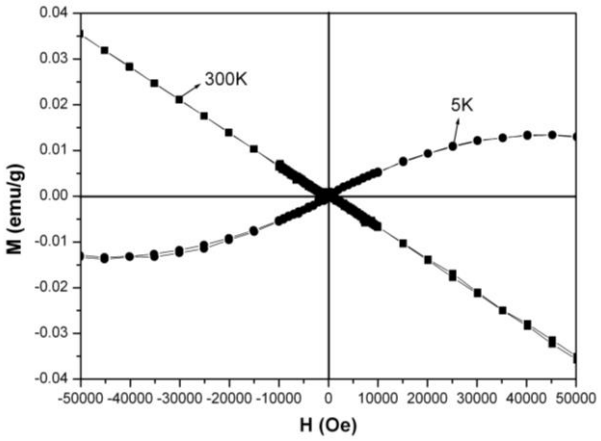

Fig. 4. M-H curves of TiO_2 annealed at 450 °C measured at 5 K and 300 K.

Fig. 4 shows the magnetization (M) versus applied magnetic field (H) curves of TiO_2 nanoparticles annealed at 450 °C measured at 5 K and 300 K. The magnetic hysteresis curve at 5 K clearly shows a weak ferromagnetic behavior and the linear M–H curve with negative slope at 300 K indicates the diamagnetism in TiO_2 at room temperature. Xu et al has been reported that the paramagnetic/ferromagnetic to diamagnetic transition is due to the competition between the paramagnetism/ferromagnetism from the defects and the diamagnetism from the bulk ZnO [22]. This mechanism is also suitable for the TiO_2 nanoparticles.

As shown in Fig. 5, the M-H curves measured by SQUID at 5K for the TiO_2 nanoparticles annealed at different temperatures. The hysteresis loops indicate that the samples annealed at 450 and 550 °C clearly have weak ferromagnetic properties and the samples annealed at 800 °C have diamagnetic properties. It can be seen that the magnetization decreases with the annealing temperature increasing.

Some other groups have reported the ferromagnetism in undoped semiconducting and insulating oxides. And they explained that the origin of ferromagnetism in these samples is due to defects [23, 24]. Hong et al [25] reported that annealing ferromagnetic TiO_2 (with anatase structure) in an oxygen atmosphere for a few hours could reduce its magnetic moment enormously. It was possible to turn from a ferromagnetic state to a diamagnetic state by further increasing the duration of annealing. This evidence implies that the magnetism in TiO_2 is quite strongly related to the existence of oxygen vacancies.

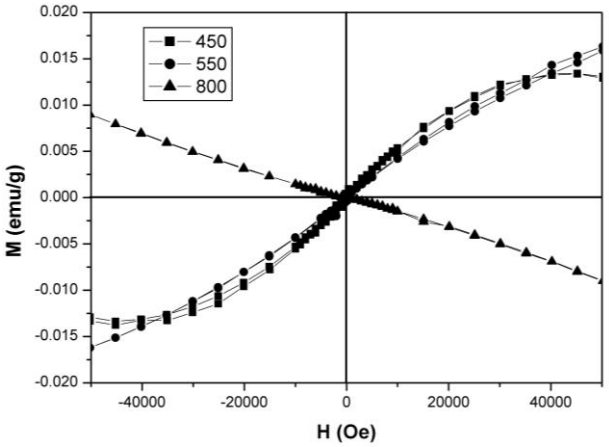

Fig. 5. M-H curves of TiO_2 annealed at 450, 550, and 800 °C measured at 5 K.

As we know, heat treatment could provide thermal energy and then the crystal lattice reformation happens to form higher quality crystal and larger size of the particles, but this process decreases the surface defects, which can explain the magnetization decreasing with the increase of annealing temperature. These evidences clearly prove that the magnetism of undoped TiO_2 nanoparticles in our case really originates from oxygen vacancies locating at the surface of nanoparticles, which are due to the losing of oxygen. According to the principle, the oxygen atoms at the surface escape from the bondage of the chemical bond because of heating, then the unpaired electrons show the abnormal spin phenomenon, which causes the magnetism.

We suggest that the unpaired electron spins on the surfaces of the particles are responsible for the ferromagnetism in TiO_2 nanoparticles.

4. Conclusions

In conclusion, we have successfully prepared the TiO_2 nanoparticles by sol-gel synthesis method with postannealing in air. XRD pattern and Raman spectra show that the synthesized TiO_2 nanoparticles change from anatase to rutile phase with the annealing increasing from 450 °C to 800 °C. The ferromagnetism decreases with the increase of the annealing temperature. These results indicate that oxygen vacancies at the surface of the nanoparticles are likely to be responsible for the ferromagnetism.

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References

[1] C. Thum, V. M. Axt, Phys. Rev. B **85**, 165203 (2012).
[2] T. Dietl, Nat. Mater. **9**, 965 (2010).
[3] J. Y. Yang, Y. L. Han, L. He, R. F. Dou, C. M. Xiong, J. C. Nie, Appl. Phys. Lett. **100**, 202409 (2012).
[4] V. R. Singh, K. Ishigami, V. K. Verma, G. Shibata, Y. Yamazaki, T. Kataoka, A. Fujimori, F. H. Chang, D. J. Huang, H. J. Lin, C. T. Chen, Y. Yamada, T. Fukumura, M. Kawasaki, **100**, 242404 (2012).
[5] S. K. Patel, N. S. Gajbhiye, S. K. Date, J. Allo. Comp. **509**, S427 (2011).
[6] B. Santara, B. Pal, P. K. Giri, J. Appl. Phys. **110**, 114322 (2011).
[7] M. Venkatesan, C. B. Fitzgerald, J. M. Coey, Nature **430**, 630 (2004).
[8] J. M. Coey, M. Venkatesan, P. Stamenov, C. B. Fitzgerald, L. S. Dorneles, Phys. Rev. B **72**, 024450 (2005).
[9] L. Zhang, S. H. Ge, Y. L. Zuo, B. M. Zhang, L. Xi, J. Phys. Chem. C **114**, 7541 (2010).
[10] D. Q. Gao, J. Y. Li, Z. X. Li, Z. H. Zhang, J. Zhang, H. G. Shi, D. S. Xue, J. Phys. Chem. C **114**, 11703 (2010).
[11] X. L. Lin, S. S. Yan, M. W. Zhao, S. J. Hu, C. Han, Y. X. Chen, G. L. Liu, Y. Y. Dai, L. M. Mei, Phys. Lett. A **375**, 638 (2011).
[12] M. Naeem, S. Qaseem, I. Ahmad, M. Maqbool, J. Nanopart. Res. **14**, 808 (2012).
[13] M. A. Anwar, S. Kumar, F. Ahmad, N. Arshi, G. S. Kil, D. W. Park, J. Chang, B. H. Koo, Mater. Lett. **65**, 3098 (2011).
[14] R. K. Singhal, S. Kumar, P. Kumari, Y. T. Xing, E. Saitovitch, Appl. Phys. Lett. **98**, 092510 (2011).
[15] H. F. Lin, L. P. Li, M. L. Zhao, X. S. Huang, X. M. Chen, G. S. Li, R. C. Yu, J. Am. Chem. Soc. **134**, 8328 (2012).
[16] K. Zhuang, J. Qiu, F. S. Tang, B. L. Xu, Y. N. Fan, Phys. Chem. Chem. Phys. **13**, 4463 (2011).
[17] Y. Z. Zhang, L. H. Wu, E. Q. Xie, H. G. Duan, W. H. Han, J. G. Zhao, J. Power Sources **189**, 1256 (2009).
[18] M. G. Manera, G. Montagna, E. F. Vila, L. G. García, J. R. Valencia, A. R. Elipe, A. Cebollada, J. M. Martin, A. G. Martin, G. Armelles, R. Rella, J. Mater. Chem. **21**, 16049 (2011).
[19] Y. Iida, M. Furukawa, T. Aoki, T. Sakai, Appl. Spectrosc. **52**, 673 (1998).
[20] M. J. Li, Z. C. Feng, G. Xiong, P. L. Ying, Q. Xin, C. Li, J. Phys. Chem. B **105**, 8107 (2001).
[21] P. P. Lottici, D. Bersani, M. Braghini, A. montenero, J. Mater. Sci. **28**, 177 (1993).
[22] Q. Y. Xu, S. Q. Zhou, H. Schmidt, J. Allo. Comp. **487**, 665 (2009).
[23] D. Q. Gao, G. J. Yang, J. Y. Li, J. Zhang, J. L. Zhang, D. S. Xue, J. Phys. Chem. C **114**, 18347 (2010).
[24] M. Naeem, S. Qaseem, I. Ahmad, M. Maqbool, J. Nanopart. Res. **14**, 808 (2012).
[25] N. H. Hong, J. Sakai, N. Poirot, V. Brize, Phys. Rev. B **73**, 132404 (2006).

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