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Electronic structure and room temperature ferromagnetism of C doped TiO_2

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ABSTRACT

C-doped TiO_2 nanoparticles were successfully synthesized using a simple hydrothermal synthesis method. After this preparation, a portion of the samples were annealed separately in air on the one hand, and in argon on the other, and another portion remained untreated. The results of X-ray diffraction show that the untreated samples primarily display anatase and rutile structures. However, after annealing, the samples displayed the rutile structure only. The Ti *K*-edge and *L*-edge Near Edge X-ray Absorption Fine Structure analyses clearly show that C atoms were successfully incorporated into the TiO_2 host lattice. All doped samples exhibit ferromagnetism at room temperature. The saturation magnetization (Ms) and coercive fields (Hc) tend to decrease after the samples are annealed in argon and in air. The maximum Ms of the untreated samples was approximately 0.038 emu/g.

1. Introduction

Titanium dioxide (TiO_2) has attracted widespread attention due to its potential application in the field of photoconductors, dielectric materials, and photocatalysts [1–3]. The various transition metals doped TiO_2 also shows magnetic properties and becomes one of the widely studied Dilute Magnetic Semiconductors (DMS) [4–6]. Transition-metal doped TiO_2 is a promising candidate for spintronic application due to its excellent optical properties, strong magnetization, and high *Tc*. However, a number of reports indicate that the ferromagnetic properties of these materials may be affected by the precipitation of magnetic clusters or by secondary magnetic phases [7,8]. As a consequence, the origin of room temperature ferromagnetism (RTFM) in transition-metal doped TiO_2 has remained a popular and controversial topic over the last few years. Recently, TiO_2 doped with nonmagnetic elements such as C and N, has attracted wide attention since doping with these nonmagnetic elements may avoid the possible influence of extrinsic ferromagnetism stemming from the formation of magnetic secondary phases [9–11].

Wang et al. [12] studied the origin of observed RTFM in TiO_2 doped with light elements using both experimental and theoretical electronic structure investigation. They found that light element doping not only creates more oxygen vacancies but also introduces new density of states near the fermi level. The importance of additional in-gap states other than oxygen vacancies has been further proved by experimental and theoretical electronic structure investigation in N-doped TiO_2 [13]. It indicates that electronic structure investigation is crucial in exploring the origins of RTFM in C-doped TiO_2. Therefore, further studies seeking to clarify the *p*–*d* hybridization in valence and conduction bands are necessary for the aforementioned TiO_2 systems. In this work, pure phase C-doped rutile TiO_2 nanoparticles were synthesized using a simple hydrothermal synthesis method and were then annealed in different environments. The structural, magnetic, and morphological properties were investigated and compared. It was found that C-doped TiO_2 exhibits RTFM and its magnetic properties decrease after being treated in both air and in Ar environments. Near edge X-ray absorption fine structure (NEXAFS) analysis was performed to clarify the mechanism which induced the RTFM in C-doped TiO_2.

2. Experimental

C-doped TiO_2 was prepared using the low temperature hydrothermal method. In general, 0.3 g TiC powder was added to a

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solution of 14 ml absolute ethyl alcohol and 3 ml deionized water. To this was added 3 ml nitric acid (65%) and the solution was stirred for 20 min. The mixture was then transferred to a Telfon-lined autoclave with an inner volume of 35 ml and heated to 160 °C for 6 h in an oven. After washing several times in deionized water and then being dried at 80 °C, a gray powder was obtained. The gray powder, as prepared, was separated into three parts, one of which was put into a quartz tube furnace and was annealed at 700 °C in an Ar (99.999% pure) ambient at a flow rate of 200 sccm for 2 h. The second portion of gray powder was annealed in air with all conditions being the same as the above. The third portion of the powder was left untreated.

The crystal structure and the morphology of the samples was examined using X-ray powder diffractometry (XRD, Mac Science M18XHF22-SRA) and transmission electron microscopy (TEM, Hitachi-600), respectively. A vibration sample magnetometer (VSM, Lakeshore 7404) was used to measure the magnetization of the samples. Ti *K*-edge near edge X-ray absorption fine structure (NEXAFS) data was collected at 4B7A and 4B9B beamline of Beijing Synchrotron Radiation Facility (BSRF) with the total electron yield method. The Ti *K*-edge NEXAFS spectra were normalized by removing the background at the pre-edge region using Athena [14], and the Ti *L*-edge spectra were normalized and baseline corrected using WinXAS [15].

3. Results and discussion

The XRD patterns for the C-doped and annealed samples in different environments are shown in Fig. 1(a). Except for the two diffraction peaks, which are marked as A(101) and A(200) in the as-prepared C-doped TiO_2, the powder patterns in all samples are in good agreement with standard tetragonal TiO_2 rutile (JCPDF file no. 78-1508) structure. The other two diffraction peaks in the as-prepared samples matched well with standard anatase (JCPDF file no. 71-1166) structure. None of the samples show redundant carbon or other impurity phases. This indicates that for C-doped TiO_2, the reaction using the hydrothermal method is easier to bring to completion than when using the solid state reaction method [12]. After annealing in air and in Ar, the mixed phase changes into a single TiO_2-rutile phase.

XRD patterns of C-doped samples in Fig. 1(a) reveals that no trace of TiC or any other secondary phases could be observed. The corresponding XRD patterns for the (110) peak are shown in Fig. 1 (b). Compared with the as-prepared C-doped TiO_2, the peaks of the Ar annealed samples shift toward higher 2 theta, and the peaks of air annealed samples shift toward lower 2 theta. There are two possible explanations for these spectral changes: (a) a change of the lattice constant of the annealed samples, and/or (b) the change in the concentration of C impurities and oxygen vacancies in the host lattice. The latter explanation is theoretically supported by N- and C-doped TiO_2 [16] and will be further validated by Ti *K*-edge and *L*-edge NEXAFS in the following section.

TEM micrographs of the as-prepared C-doped TiO_2 samples are consist of unhomogeneous crystallites with size distribution in range of tens of nanometers (Fig. 2(a)). The annealed samples show crystallites which like an as-prepared one and the annealing does not influence the size of nanoparticles. Fig. 2(b), (c) and (d) shows high resolution transmission electron microscopy (HRTEM) images of as-prepared, Ar and air annealed nanoparticles. The parts Fig. 2(e), (g) and (i) are the fast Fourier transform (FFT) images of region A in Fig. 2(b), region C in Fig. 2 (c) and region F in Fig. 2(d). The Fig. 2(f), (h), and (j) are the amplification of region B, D and E in Fig. 2(b), (c) and (d), respectively. Comparing the HRTEM images of as-prepared, air and Ar annealed nanoparticles, the crystallization of samples becomes better after annealing in Ar and in air environment. It was further proved the increased intensity of all diffraction peaks in Fig. 1(a) after annealing in Ar and in air condition.

Fig. 3 depicts the room temperature magnetization versus magnetic field (*M*–*H*) curves of as-prepared, air and Ar annealed C-doped TiO_2 nanoparticles. Pure TiO_2 is well known as a paramagnetic at room temperature. However, the C-doped TiO_2 nanoparticles exhibited clear *M*–*H* hysteresis loop, which indicated the existence of strong RTFM. The inset in Fig. 3 demonstrates the value of the saturation magnetization (*Ms*) and coercivity (*Hc*). At the room temperature, the value of 3.18×10^{-3} emu/g is the maximum for the *Ms* of the as prepared C-doped TiO_2 nanoparticles. However, the *Ms* are 0.71×10^{-3} emu/g and 0.59×10^{-3} emu/g for Ar annealed and air annealed nanoparticles, respectively. Surprisingly, the *Ms* values almost four times decrease with annealing in air and in Ar atmosphere. The origin of RTFM in nonmagnetic element doped TiO_2 has been attributed to the exchange interaction between the oxygen vacancies and valence electrons of cation [17]. The decreased magnetization in air annealed nanoparticles was explained by the decreasing of the oxygen vacancies through the annealing process. If it was the case, it will contradict with the Ar annealed samples because the oxygen vacancies should not decease in same amount with different annealing environment (the saturation magnetization was decreased to same level after annealing in different environment). It implies that except the oxygen vacancies, the doped C impurities also play a crucial role in RTFM in C-doped TiO_2. As a consequence, in order to investigate the influence of C impurities on electronic

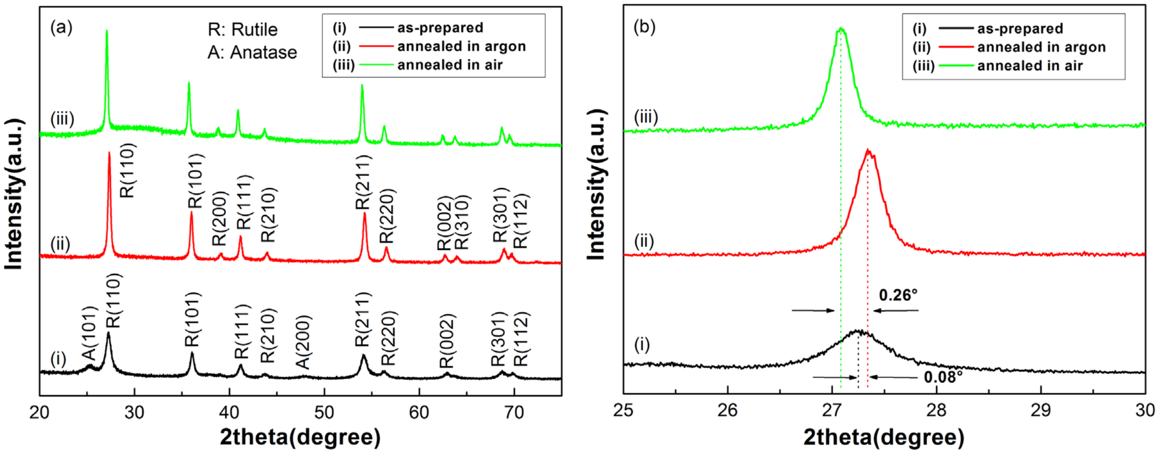

Fig. 1. (a) X-ray diffraction patterns of as-prepared, Ar and air annealed C-doped TiO_2 samples; (b) The enlarged 2 theta from 25 to 30.