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Structures and properties of transition-metal-doped TiO_2 nanorods

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ABSTRACT

Titanium dioxide (TiO_2) doped with magnetic elements is a promising candidate for the applications of spintronic devices. In this work, we have successfully synthesized rutile TiO_2 nanorods doped with a variety of transition metals (Co, Ni, Mn and Fe) through a molten salt method. XRD and Raman results indicate the effective incorporation of dopant ions into TiO_2 lattice. SEM and TEM images demonstrate that most of the samples are grown along the c-axis with the shape of nanorods except 1%Fe-doped sample. The M-H loops indicate that all the samples exhibit weak room temperature ferromagnetism. Whereas, in undoped TiO_2, diamagnetic and ferromagnetic signals are detected at room temperature and the coexistence of the paramagnetic phase is found at 5 K. It is evident that the incorporation of various dopants such as Co, Ni, Mn or Fe into TiO_2 nanostructures gives rise to paramagnetism instead of enhancing the ferromagnetic ordering.

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1. Introduction

Titanium dioxide (TiO_2) has been extensively studied in the past decades because of its excellent properties for photocatalyst and a wide variety of optoelectronic applications [1–4]. Moreover, doping with transition metal elements can modify the magnetic properties of the semiconductor host to produce the diluted magnetic semiconductor (DMS). DMS is an ideal material for spintronic devices [5–7]. Co-doped TiO_2 is the first oxide-based DMS that has a Curie temperature above room temperature [8,9]. In fact, most research on DMS had been focused on thin films [10–12]. One-dimensional (1D) materials have also attracted much attention recently owing to their superior physical properties over the best thin film and bulk counterparts, which may associate with the quantum size effect. However, producing the massive 1D nanostructural materials with the desired physical properties is still a serious challenge [13–16].

Most of the researches on TiO_2 nanostructures have been concentrated on the properties of anatase nanoparticles [17–19]. Recently, Liu et al. have demonstrated that massive transition-metal-doped rutile TiO_2 nanowires can be produced with molten salt flux technique [20]. Subsequently, optical and electrical properties of these samples were well-studied. However, the report on the magnetic properties of these TiO_2 samples is very limited. In this work, we intend to fill this gap by preparing the rutile TiO_2 nanorods doped with different transition metal elements using a similar molten salt method and investigating their microstructures and magnetic properties.

2. Experimental details

Rutile TiO_2 nanorods were synthesized using a molten salt method. The powder mixture composed of TiO_2 P25 powders, NaCl and Na_2HPO_4 with a ratio of 1:4:1 was used as the reactant. The powder precursors were ground using an alumina mortar and placed into a sealed alumina crucible with a subsequent heating in a tube furnace at 825 °C for 8 h. The products were then washed several times using DI water in order to remove NaCl and other impurities. A centrifuge was used to separate the powder products and NaCl solution. The powder products were dried in an oven at 90 °C for 6 h. The transition-metal-doped samples were prepared by adding 1 at% $Co(NO_3)_2$, $Ni(NO_3)_2$, $Mn(NO_3)_2 \cdot 4H_2O$ or $Fe(NO_3)_3 \cdot 9H_2O$ individually into the powder mixture.

The phase of TiO_2 nanorods was characterized by X-ray diffractometery (XRD, PANalytical Xpert Multipurpose X-ray Diffraction System) with Cu Kα radiation. The sample morphologies and crystal structures were examined by scanning electron microscopy (SEM, FEI Nova NanoSEM 230) and transmission electron microscopy (TEM, Philips CM200), respectively. The TEM samples were prepared by dipping the small amount of powders into ethanol, then ultrasonic for a few minutes to disperse the nanorods. The final step is using pipette to drop the ethanol solution contained

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with the nanorods onto the TEM copper grid for a few times, and then leave it dry naturally. The diameters of the nanorods were measured using the SEM software (xT Microscope Control software). The lengths and diameters of the nanorods were the average value measured from at least 20 nanorods. Raman spectroscopy (Renishaw inVia Raman Microscope equipped with a 514 nm Argon ion laser and fitted with a diffraction grating of 1800 lines/mm) was used for determining the crystalline phase and bonding characteristics of TiO_2. X-ray photoelectron spectroscopy (XPS, ThermoScientific ESCALAB 250i X-ray Photoelectron Spectrometer) was used for the analysis of chemical bonding and element composition. Superconducting quantum interference device (SQUID, Quantum design-XL-7) was used to measure the magnetic properties of the samples.

3. Results and discussion

XRD spectra of the TiO_2 nanorods (Fig. 1a) show that all the samples exhibit the rutile phase. The rutile (110) peaks shift towards lower angle for the samples with the addition of transition metal elements (Fig. 1b), indicating the incorporation of transition metal ions in the TiO_2 matrix. The radii of transition metal ions are all larger than the radius of Ti^{4+}. The incorporation of transition metal ions tends to increase the lattice parameters of TiO_2 and the peak shift increases with the ionic radii of the dopants [21]. It is also found that an intermediate phase of $Na_4TiP_2O_9$, which is formed by the reaction between TiO_2 and Na_2HPO_4 and assists the growth of nanorods, is detected in all the samples.

Raman spectroscopy was carried out to confirm the phase identification of TiO_2 nanorods as well as to investigate the defects in the materials as shown in Fig. 1c. The E_g mode of the undoped TiO_2 nanorods at 444 cm^{-1} is due to the out-plane vibration mode of the oxygen [22]. The A_{1g} mode at 607 cm^{-1} is responsible for the Ti-O stretching vibration [22]. The peak at 677 cm^{-1} observed in the undoped TiO_2 sample is shifted to $\sim$690 cm^{-1} due to the addition of transition metals. The peak at 678 cm^{-1} or 690 cm^{-1} is corresponding to the peak 668 cm^{-1} after a large shift owing to defects, non-stoichiometry or size distribution [23,24]. This peak could be interpreted as Ti-O-Ti crystal phonons, in which it might not be assigned to either the anatase or rutile TiO_2 Raman spectra [23]. It was also reported that this peak may be induced by the change of particle size [25]. A significant shift of this peak observed in our samples may be attributed to the lattice disordering induced by the doping. The presence of transition metal ions affects the Ti-O-Ti bonds in the lattice, which also lowers the peak intensity. In 1% Fe-doped sample, this peak is nearly absent, which indicates that it may also be particle-size-dependent because the morphology of Fe-doped sample is nanoparticle instead of one-dimensional nanorods, as shown in Fig. 2.

Most of the samples are grown into nanorods with the diameter of 100 – 200 nm and the length of 3–5 μm (see the insets in Fig. 2a–d) except for the 1% Fe-doped sample (Fig. 2e) which consists of nanoparticles. Such an exceptional growth behaviour may be related to the solubility of iron nitrate nonahydrate and TiO_2 in NaCl solution. It is believed that the dopant of Fe may suppress the formation of $Na_4TiP_2O_9$ thus affect the nanorod growth. TEM micrographs shown in Fig. 2 indicate that all the nanorods are grown along the c-axis, which has been reported due to the direction of c-axis having the lowest liquid-solid interfacial energy [20]. Fig. 2e shows the selected area electron diffraction (SAED) pattern of a 1% Mn-doped TiO_2 nanorod along the [110] zone axis. It confirms the single crystalline structure and the inset shows the growth direction of a nanorod. Similar growth features are found in other samples except for the Fe-doped TiO_2.

XPS is carried out to investigate the effects of doping on the chemical bonding in TiO_2. Fig. 3a shows the XPS spectra of Ti 2p core levels. For the undoped TiO_2, the separation of $2p_{3/2}$ and $2p_{1/2}$ is 5.75 eV, which confirms that the valance of Ti is 4+. As the presence of different transition metal ions in TiO_2, the Ti $2p_{3/2}$ peak is shifted towards lower binding energy and the separation increases to 5.82 eV. These results suggest that Ti element exists in the form of Ti^{3+} instead of Ti^{4+}, and also imply an increase of oxygen vacancy due to the incorporation of transition metal ions in TiO_2 lattice.

Two peaks associated with $2p_{3/2}$ and $2p_{1/2}$ in Co 2p core levels are separated by 15.8 eV, as shown in Fig. 3b, suggesting that the valence state of Co ion is 2+. In a Ni 2p spectrum (Fig. 3c), the separation of Ni $2p_{3/2}$ and Ni $2p_{1/2}$ peaks is 17.5 eV, implying the existence of Ni^{2+} [26]. The Mn 2p spectrum (Fig. 3d) peaked at 641.4 eV and 653.4 eV is consistent with the spectrum of Mn_2O_3. A broad peak of Mn $2p_{2/3}$ implies that Mn ions may exist in both the valance state of 2+ and 3+ [27]. Fe $2p_{3/2}$ and Fe $2p_{1/2}$ peaks (Fig. 3e) are centred at 710.9 eV and 724.4 eV, respectively, which is in agreement with Fe_2O_3 [27]. It had been reported that the binding energy of Fe^{3+} and Fe^{2+} are 710.9 eV and 709.4 eV,

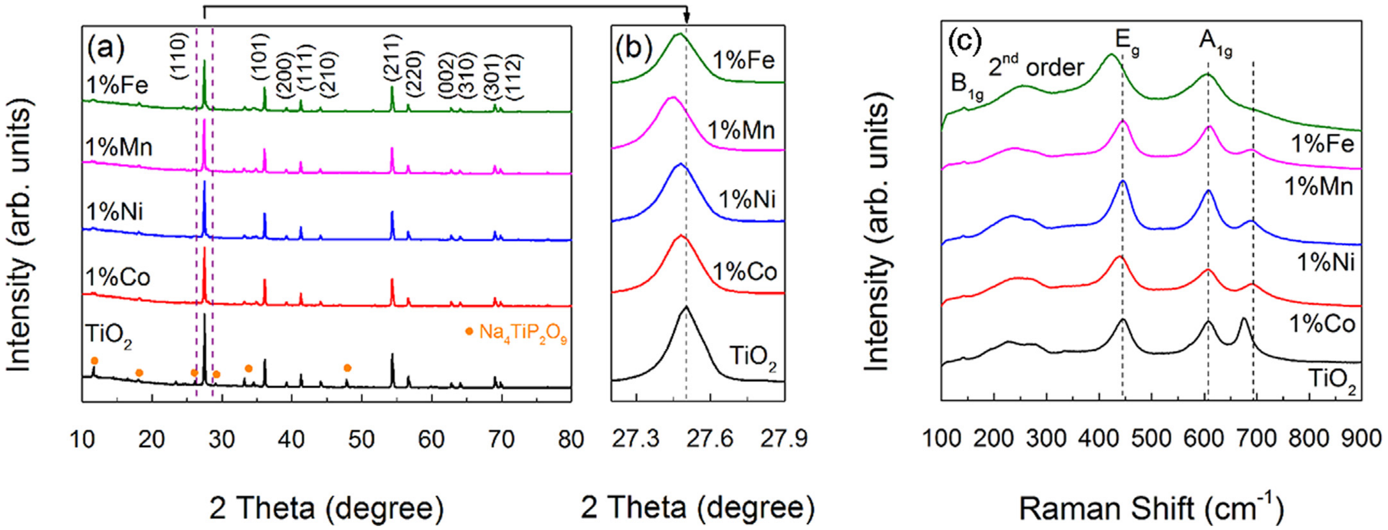

Fig. 1. (a) XRD spectra of rutile TiO_2 nanorods doped with different transition metal elements (orange circle: $Na_4TiP_2O_9$). (b) The narrow scale of (110) peak. (c) Raman spectra of TiO_2 nanorods doped with various transition metal elements. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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