Research Article

Influence of Sn Doping on Phase Transformation and Crystallite Growth of TiO_2 Nanocrystals

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Sn doped TiO_2 nanocrystals were synthesized via a single-step hydrothermal method and the influences of Sn doping on TiO_2 have been investigated. It is found that Sn doping not only facilitates the crystal transfer from anatase to rutile but also facilitates the morphology change from sphere to rod. The states of Sn were studied by XPS and the creation of oxygen vacancies by Sn doping is confirmed. Moreover, the HRTEM results suggest that Sn facilitates preferential growth of resulting nanocrystals along (110) axis, which results in the formation of rod-like rutile nanocrystals.

1. Introduction

In recent years, the applications of semiconductors in photocatalysis and other fields have attracted much interest [1, 2], and many semiconductor nanomaterials and their heterogeneous structures have been developed for their application in energy and environmental applications [3–5], for example, the investigations of TiO_2 on various organic pollutants photodegradation [6] due to its excellent photocatalytic activity, physical and chemical stability, and nontoxicity [7]. Because most of the solar energy is focused on the visible light, it is important to develop the visible-light-driven photocatalysts. However, TiO_2 is only sensitive to UV light because of its large band gap (3.2 eV). In order to efficiently use solar energy, many methods have been studied. An effective way is to introduce foreign ions into TiO_2 , including rare earth element doping [8], metals doping [9], and nonmetals doping [10, 11].

The property of TiO_2 can also be affected by foreign metal ions doping. It has been shown that the photocatalytic activity of the modified TiO_2 improves to different extents depending on different ion doping, such as Mn^{2+} [12], Zr^{4+} [13], and Fe^{3+} [14]. Moreover, the phase transformation behavior and structure of TiO_2 are also affected by foreign metal ions. For

example, Ag^+ [15], Mn^{2+} [16], and Cr^{3+} [17] are proved to promote phase transformation from anatase to rutile, while silicon ion doping strongly restrains the phase transformation [18] and lowers the phase transition temperature [19]. But, so far, no detailed study has been reported on the influence of Sn^{4+} doping on the phase transformation and structure of hydrothermal synthesis TiO_2 .

In our work, Sn doped TiO_2 nanocrystals were prepared by hydrothermal method. The existing states of Sn and its role in phase transformation as well as the morphology evolution were investigated. Sn facilitates the phase conversion from anatase to rutile and prefers the morphology evolution from spherical shape to nanorods.

2. Experimental Section

Sn doped TiO_2 nanoparticles were prepared by hydrothermal method. 2.9 mL acetic acid was added to 17 mL tetrabutyl titanate and stirred for 15 min. The mixture was then poured into 73 mL of water and vigorously stirred for 1 hour. After adding 1 mL concentrated nitric acid, the mixture was heated to 80°C and peptized for 75 min. Then the volume was adjusted with water to 80 mL. The mixture was kept in a

FIGURE 1: XRD patterns of TiO_2 samples prepared with different Sn doping ratios: (a) 0%, (b) 0.25%, (c) 0.50%, (d) 0.75%, and (e) 1.00%.

100 mL autoclave and heated at 200°C for 12 h. For Sn doped samples, appropriate volume of tin tetrachloride was added to distilled water in advance (the feed molar ratios of Sn/Ti were modulated as 0.25/100, 0.5/100, 0.75/100, and 1.0/100, resp.).

The powder XRD experiments were performed on Bruker D8 Advance X-ray diffractometer using monochromic $\text{Cu K}\alpha$ radiation ($\lambda = 0.15418\text{ nm}$). The scanning electron microscopy (SEM) images were recorded using S4700 Hitachi Ltd. The transmission electron microscopy (TEM) was performed with a Tecnai G2 20 transmission electron microscope of HongKong Co., Ltd. The X-ray photoelectron spectroscopy (XPS) experiments were carried out on Thermo ESCALAB 250 and the binding energies are calibrated by $\text{Cl } 1s$ photoelectron peak (284.6 eV).

3. Results and Discussion

The X-ray diffraction patterns of TiO_2 samples with different Sn doping ratios are shown in Figure 1. It can be seen that the undoped TiO_2 is mainly composed of anatase and weak diffraction peaks of rutile TiO_2 can also be found in the XRD pattern. With the addition of Sn, the samples undergo “reutilization” to give rutile as the predominant polymorph, and the conversion from anatase to rutile is completed on 0.75% and 1.0% Sn doped samples, which suggests that the doped Sn ions can promote the formation of rutile.

The TEM results in Figure 2 show that the particle shape changed from sphere (diameter of 10–20 nm) to rod (width of $\sim 20\text{ nm}$ and length of 100–200 nm) by Sn doping, which are consistent with SEM results (not shown here). The space between the lattice planes of Sn-free TiO_2 (Figure 2(a)) is 0.35 nm, which corresponds well to the d value of (101) plane for anatase. The lattice space of 0.33 nm displayed in Sn- TiO_2 samples (Figures 2(b)–2(e)) is equal to the d value of

(110) plane for rutile. Therefore, it is reasonable to conclude that the Sn-free TiO_2 spherical nanocrystals are mainly anatase structure and the Sn doped TiO_2 rod-like particles are rutile. As for our samples, with an increasing of Sn doping amount in TiO_2 , the content of the spherical anatase decreases and the rod-like rutile increases, illustrating that Sn doping facilitates the phase conversion from anatase to rutile, which is consistent with XRD. Furthermore, the HRTEM images reveal rod-like building units and nanocrystal growth along the [110] axis, indicating that the formation of the rod-like TiO_2 is the result of the preferential growth (PG) in crystallographic orientation favored by Sn incorporation. Since Ti (IV) and Sn (IV) ions have the similar ionic radii, it is reasonable to deduce that Sn ions substitute lattice Ti, which is confirmed by our subsequent experiment. The EDX spectrum in Figure 2(e) also confirms the existence of Sn in TiO_2 nanocrystals.

Figure 3 shows the XPS spectra of Sn doped TiO_2 sample with Sn/Ti atomic ratio of 1%. As for Ti $2p_{3/2}$ spectrum in Figure 3(a), the two peaks at 458.1 eV and 458.7 eV could be assigned to O–Ti–O and Ti–O–Sn, respectively. Due to the electronegativity of Sn (1.96) which is larger than Ti (1.54) [20], the substitution of Sn for Ti in the lattice leads to the shift of binding energy to a higher value.

As for O1s spectrum in Figure 3(b), the peak at 532.2 eV is attributed to surface hydroxyl oxygen atoms. The peak at 529.3 eV is the binding energy of O1s in Ti–O–Ti, while the occurrence of the peak at 530 eV is the result of Sn substitute for Ti leading to the positive shift. These observations all confirm the formation of Ti–O–Sn structure in the Sn doped TiO_2 , owing to the substitution of Ti by Sn.

As shown in Figure 4, both anatase and rutile phase coexist at short treatment time, and the ratio of rutile/anatase increases with treatment time prolonging. A similar finding was reported by Zhang and Gao [21] who stated that

FIGURE 2: TEM images of TiO_2 samples prepared with different Sn doping ratios: (a) 0%, (b) 0.25%, (c) 0.50%, (d) 0.75%, (e) 1.00%, and (f) EDX spectrum of 1% Sn doped TiO_2 nanocrystals.

phase transformation occurred simultaneously with particle growth.

It has been shown that the oxygen vacancies of TiO_2 increase if foreign cations replace Ti^{4+} ions [22]. Vemury and Pratsinis [23] found that the formation of rutile phase was enhanced either by introducing dopant oxides with the same crystal structure as rutile or by creating oxygen vacancies by doping cations. It has been reported that the rutile fraction increases at a higher Eu^{3+} addition owing to the creation of oxygen vacancies by replacing the Ti^{4+} sites with subvalent Eu^{3+} ions in the TiO_2 [24]. In our samples, the creation of oxygen vacancies is by replacing the Ti^{4+} sites with Sn^{4+} ions in TiO_2 and therefore the rutile formation can be enhanced. Moreover, it was supposed that there is a relationship between the phase transformation and the

nanocrystal growth process [25] and the preferential growth process aids phase transformation. The minimization of the area of high-energy surface faces promoted by the preferential growth process may be an extra driving force for the phase transformation from anatase to rutile phase.

4. Conclusions

In summary, the promoting roles of Sn^{4+} in both TiO_2 phase transformation and morphology change have been confirmed in our study. The result demonstrated that morphology transition was related to the preferential growth process and the phase transformation was related to the creation of oxygen vacancies caused by Sn. Our observations of preferential growth coupled with phase transformation

FIGURE 3: XPS spectra of the 1% Sn doped TiO_2 nanocrystals.

FIGURE 4: XRD patterns of the 1% Sn doped samples with different times: (a) 3 h, (b) 6 h, (c) 9 h, (d) 12 h, and (e) 15 h.

process led us to understand the preferential growth process aided phase transformation.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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