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Full Length Article

Dealloying synthesis of SnO_2—TiO_2 solid solution and composite nanoparticles with excellent photocatalytic activity

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ABSTRACT

A novel rutile $TiO_2/Sn_{0.42}Ti_{0.58}O_2$ composite photocatalyst was first synthesized by dealloying method using $Cu_{60}Ti_{30}Sn_{10}$ amorphous ribbons as precursors. The prepared sample was characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), UV–vis diffuse reflectance spectroscopy (DRS) and photoluminescence techniques (PL). The results of XRD, SEM and TEM and XPS show that the rutile $TiO_2/Sn_{0.42}Ti_{0.58}O_2$ has been successfully synthesized and the sample is composed of large quantities of fine nanoparticles with sizes of 15–60 nm, which have been assembled into a much larger structure with novel football-like surface. While PL and DRS results show that rutile $TiO_2/Sn_{0.42}Ti_{0.58}O_2$ has a lower PL intensity compared with pure rutile TiO_2 and $Sn_{0.42}Ti_{0.58}O_2$ and an intermediate value of band gap energy (3.01 eV) between those of the rutile TiO_2 (2.97 eV) and $Sn_{0.42}Ti_{0.58}O_2$ (3.04 eV). Moreover, the photocatalytic activities of the samples were evaluated by decomposing rhodamine B (RhB) dye (10 mg/L) under the ultraviolet (UV) light irradiation. The results show that the photocatalytic performance of rutile $TiO_2/Sn_{0.42}Ti_{0.58}O_2$ is much higher than those of pure rutile TiO_2 and $Sn_{0.42}Ti_{0.58}O_2$.

1. Introduction

Semiconductor photocatalytic technique has been considered as a high-efficient, green and promising solution to decontaminate environmental pollution [1–3]. As an important multifunctional n-type wide band gap semiconductor, Tin dioxide (SnO_2) has attracted great attention in basic research and practical applications, such as gas sensors [4–6], lithium-ion batteries [7,8], solar cells [9,10] and electrode materials [11,12]. For the application of photocatalysis, SnO_2 has been a research focus owing to its low cost, non-toxicity, high catalytic activity and excellent chemical stability [2,13]. Nevertheless, the fast recombination rates of the photogenerated electron-hole pairs and the wide band gap energy (E_g = 3.6 eV) hinder the development of the application of SnO_2. According to recent research, semiconductor composite technique could be an effective method to solve out these drawbacks [14–17], and titanium dioxide (TiO_2) could be the perfect candidate for coupling with SnO_2, the reasons can be summarized as follows: (1) TiO_2 is the most widely used photocatalyst, which is very efficient and environment-friendly [18–20]; (2) Rutile TiO_2 has a relative low band gap of 3.0 eV, which can be acted as an ideal sensitizer for SnO_2; (3) The electronic energy levels of TiO_2 match well with those of SnO_2, thus promoting the separation and transfer of photoinduced carriers at their interfaces [21–23]; (4) SnO_2 and TiO_2 have several similarities in crystal structure (rutile phase, tetragonal system), ionic radius (0.690 Å for Sn^{4+} and 0.605 Å for Ti^{4+}) and electronic properties [18,22,24]. Hence, they can also form solid solution in SnO_2—TiO_2 coupling system, which can improve photocatalytic activity by changing the electronic structure and surface areas.

For the sake of fabrication of the composite structures with high catalytic activity, all sorts of preparation methods have been developed. For example, Yu et al. [25] prepared three-dimensional (3D) hetero-hierarchical CuO—ZnO nanocomposite via hydrothermal reaction after in situ crystallization on Cu foil, the hetero-structured CuO—ZnO displayed higher photocatalytic reduction capacity than pure CuO and ZnO. Issarapanacheewin et al. [26] used doctor blading technique to fabricate CeO_2/Bi_2WO_6 composite film, the three-layered films of CeO_2/Bi_2WO_6 showed superior photocatalytic performance compared to pure CeO_2 and Bi_2WO_6. Yuan et al. [23] reported TiO_2/SnO_2 double-shelled hollow spheres synthesized by two-step liquid-phase deposition (LPD) method using carbon sphere templates, the TiO_2/SnO_2 hollow spheres exhibited enhanced photocatalytic activity, with respect to the cases of pure SnO_2 and TiO_2. Unfortunately, these methods usually suffer from many disadvantages such as complicated synthesis procedures, rigorous reaction conditions and sophisticated experimental apparatus. As a better alternative, the dealloying method is proposed. It can easily be realized by directly leaching the amorphous ribbons in

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acid solution, which is a very simple preparation process. In the dealloying method, amorphous alloys are expected to be an ideal precursor material. This is because that the solidification process of amorphous alloys is conducted by rapid cooling, thus avoiding composition segregation, ensuring homogeneous composition and structure, laying a foundation for dealloying synthesis of uniformly distributed composite nanostructures [27]. Ma et al. [28] prepared homogeneous anatase TiO_2 hierarchical nanospheres by chemical dealloying $Cu_{70}Ti_{30}$ amorphous alloys, the 3D nanospheres are compose of 2D nanosurface platelets with a rough surface, having a thickness of 10–15 nm and length of 100–200 nm. Zhu et al. [29] fabricated monolithic nanosized anatase TiO_2 hexagonal prism by chemical dealloying $Cu_{60}Ti_{40}$ metallic glasses, the nanosized hexagonal prisms has a side length of 400–500 nm and edge length of 1 μm. Wang et al. [27] synthesized uniform rutile TiO_2 nanoflowers by chemical dealloying $Cu_{60}Ti_{30}Y_{10}$ amorphous ribbons, the 3D nanoflowers are composed of large quantities of 2D rice-like nanorods, having a diameter of 40–150 nm and length of 100–250 nm. However, there is little report about metal oxide solid solution or composite photocatalyst prepared by dealloying the amorphous alloys, which could have better photocatalytic performance compared with the single metal oxide.

In this paper, we report rutile-type $Sn_{0.42}Ti_{0.58}O_2$ solid solution and rutile $TiO_2/Sn_{0.42}Ti_{0.58}O_2$ composite nanoparticles, which were synthesized via dealloying method for the first time. This method combines the advantages of simple process and easy operation. Considering the superiority of the monolithic phase with a homogeneous composition and structure down to subnanoscale, $Cu_{60}Ti_{30}Sn_{10}$ amorphous ribbons were chosen as precursors. The fabricated rutile $TiO_2/Sn_{0.42}Ti_{0.58}O_2$ photocatalyst exhibited higher efficiency for photocatalytic decomposition of Rhodamine B (RhB) compared to pure rutile TiO_2 and $Sn_{0.42}Ti_{0.58}O_2$.

2. Experimental

2.1. Preparation

The ingots of $Cu_{70}Ti_{30}$ and $Cu_{60}Ti_{30}Sn_{10}$ were prepared by arc melting a mixture of pure metal elements with purities 99.99 wt% in a Ti-gettered argon (Ar) atmosphere. Then, the ingots were remelted in a quartz tube by high frequency induction and rapidly quenched into a copper wheel to form corresponding glassy ribbons with a thickness of 20–30 μm and a width of 2 mm. The obtained amorphous ribbons were cut into 3–4 cm in length and then immersed in 14.4 M HNO_3 solution for different hours (72 h for $Cu_{70}Ti_{30}$, 168 and 336 h for $Cu_{60}Ti_{30}Sn_{10}$). The solution was kept at 70 °C by a water bath. After dealloying, the products were filtered and washed with deionized water for eight times and then dried in a vacuum drying oven at 50 °C for 12 h. In order to increase the crystallinity, the samples were also calcined at 700 °C for 2 h. Finally, the as-fabricated products were ground in an agate mortar for 6 min to obtain the powder. For convenience, $Cu_{70}Ti_{30}$ amorphous ribbons subjected to immersion in 14.4 M HNO_3 solution at 70 °C for 72 h is denoted as the CT-72H sample, while the samples synthesized by dealloying $Cu_{60}Ti_{30}Sn_{10}$ amorphous ribbons in 14.4M HNO_3 solution at 70 °C for 168 and 336 h are labeled as CTS-168H and CTS-336H, respectively.

2.2. Characterization

The crystal structure and phase composition of the samples were characterized by X-ray diffraction (XRD) using a D8-Discover diffractometer with Cu-K_α radiation (λ = 1.5406 Å), the accelerating voltage and the applied current were 30 kV and 20 mA, respectively. The morphology characteristics of the samples were investigated by FEI-3D scanning electron microscopy (SEM) operating with an accelerating voltage of 10 kV, and transmission electron microscopy (TEM) using a G2-20 instrument operating at 300 kV. X-ray photoelectron spectroscopy (XPS) analysis was performed on PHI-5000 Versa Probe spectrometer equipped with Al-K_α radiation ($h\gamma$ = 1486.6 eV) at the source for excitation, the spectrum was calibrated with binding energy 284.6 eV for C 1s electron. In addition, the optical properties were estimated by UV–vis diffuse reflectance spectroscopy (DRS) using a TU-2450 spectrophotometer equipped with an integrating sphere assembly, $BaSO_4$ was used as the reference sample and the spectra were recorded within the wavelength range of 250–800 nm. The photoluminescence emission spectra (PL) were recorded using a Fluoromax-4 fluorescence spectrophotometer with excitation wavelength of 350 nm at room temperature, and the emission was scanned between 400 and 700 nm.

2.3. Photocatalytic measurements

The photocatalytic activities of the samples were evaluated by the decomposition of RhB under simulated ultraviolet (UV) irradiation by using a 300 W mercury lamp (λ = 365 nm). The initial RhB concentration was 10 mg/L. A total of 25 mg photocatalyst were added into 50 mL RhB solution. Prior to light irradiation, the whole suspension was stirred in the dark for 30 min to ensure the establishment of the adsorption-desorption equilibrium. Then, 3 mL of the suspension was extracted every 30 min during the photocatalytic process to test the residual concentrations of RhB. The concentration of RhB solution was evaluated by measuring the change in maximum absorbance through TU-1810 UV–vis spectrophotometer.

3. Results and discussion

3.1. Characterizations of samples

Fig. 1a shows the XRD patterns of the $Cu_{70}Ti_{30}$ and $Cu_{60}Ti_{30}Sn_{10}$ ribbons, the ribbons exhibit only one broad peak in the patterns,

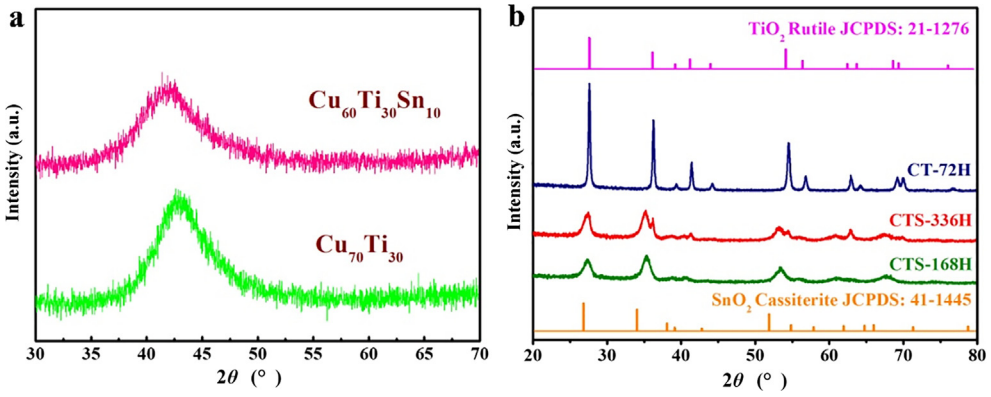

Fig. 1. XRD patterns of (a) amorphous ribbons and (b) its dealloying products.