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Luminescent and photocatalytic properties of hollow SnO_2 nanospheres

Yanhua Zhu, Lingling Wang*, Guifang Huang, Yifeng Chai, Xiang Zhai, Weiqing Huang

School of Physics and Microelectronics and Key Lab for Micro-Nano Physics and Technology of Hunan Province, Hunan University, Changsha 410082, China

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ABSTRACT

Size tunable solid SnO_2 (STO) and hollow SnO_2 (HTO) nanospheres were prepared by a sacrificing template method. The peaks around 390 nm were observed in photoluminescence (PL) spectra. Based on the results, the PL intensity exhibits morphology-dependence and size-dependence, and HTO structure displays better optical properties than STO structure. The degradation of Methyl Orange (MO) in aqueous solution is selected as a probe reaction to evaluate the catalytic activity of nano-SnO_2. The result shows that HTO structure presents stronger photocatalytic (PC) activity. According to the result of specific surface area testing, the improved PL and PC properties of HTO structure can be mainly explained by the surface effect induced by large specific surface area. This work is meaningful for developing nanomaterials with enhanced optical and photochemical properties.

1. Introduction

Recently, great interest has been attracted on nanostructures owing to their unique properties and novel applications [1] due to the so-called quantum size effect. As a potential luminescent material, semiconductor nanoparticle shows fascinating optical properties with many technological applications in optics and optoelectronics [2]. In addition, semiconductor nanomaterial is also considered as potential candidate for chemical and environmental applications due to its high catalytic efficiency [3–5].

As an n-type semiconductor oxide with wide band gap (Eg 3.6 eV at 300 K), SnO_2 is well-known for its potential applications in many fields. Plenty of papers have reported the optical properties of SnO_2 nanostructures synthesized by these methods. The PL peaks at 355, 390, 460 and 580 nm have been observed [6,7]. In solar applications, SnO_2/Cu_2O solar cell has been reported in recent report [8]. Additionally, a number of reports are also linked to the chemical and environmental applications of nano-SnO_2 [9]. The hetero-structural materials such as SnO_2/TiO_2 [10], SnO_2/α-Fe_2O_3 [11] and SnO_2/CuO [12] have been investigated extensively for their excellent performance in photocatalytic degradation of various organic substances.

Nonetheless, there is still room for improvement. As is known, surface defects are the most common defects on crystal surfaces. Such defects can directly or indirectly contribute to PL [13]. Therefore, enlarging the surface area of an optical material is an efficient way to enhance PL intensity. For normal solid nanostructures, the frequently-used method to increase specific surface area is to decrease the size of particles. However, due to some effects such as scattering and resonance, to fabricate ultra-small nanoparticles does not help enhance PL intensity. Thus, to find another method to get materials with large specific surface area is significant for improving the optical properties of nanomaterial [32–37].

Furthermore, for chemical or environmental application, such as organic degradation and water purification, most studies are mainly focused on nanofilms and nanosheets. However, because of the limitation of substrate, these substrate-based nanostructures are not design-friendly and efficient for some special use. On the other hand, normal non-substrated solid nanoparticles are imperfect as well. Owing to the dispersed granular morphology, it is hard to develop such a material with high adsorption of reactant molecules and high utilization of excitation light. Therefore, it is meaningful to develop a granulated nanomaterial with high PL intensity and strong PC activity.

Based on these issues, the nanomaterials with hollow structure are considered as a potential solution and have received wide attention. The hollow Cu_2O nanocubes with unique optical properties have been fabricated [14]. The hollow spheres of Eu^{3+}-doped lanthanides compounds have been studied [15]. The enhanced PC properties of $Co_3O_4/BiVO_4$ [16], $TiO_2/PtCl_4$ [17], $(BiO)_2CO_3$ [18–21] hollow microspheres have been reported. Herein, we report the luminescence and catalysis properties of HTO nanospheres, which

Abbreviations: STO, solid tin oxide; HTO, hollow tin oxide; PL, photoluminescence; MO, methyl orange; PC, photo-catalysis; XRD, X-ray diffraction; FE-SEM, field emission scanning electron microscope; TEM, transmission electron microscope; UV, ultra-violet.

* Corresponding author. Tel.: +86 13508484833.
E-mail address: llwang@hnu.edu.cn (L. Wang).

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have large specific surface area and proper particle size. We believe that, compared with normal solid structure, the higher PL intensity and the stronger PC activity of HTO nanostructure will be much more potential and useful for optical and chemical applications.

2. Experimental

2.1. Synthesis

The synthesis of STO nanospheres was followed by a low temperature combustion synthesis approach. $SnCl_4{\cdot}5H_2O$ and concentrated nitric acid were mixed into a beaker at a molar ratio of 1:1 to transform into tin nitrate. Urea, boric acid and water were added in a proper ratio as well. The solution was handled by ultrasonic dispersion for 10 min, and then transferred into a preheated muffle furnace heating at 600 °C for about 5 min. The product was cooled and grinded, and then the STO nanospheres were obtained. In these processes, we changed the ratio between urea and boric acid in order to prepare samples with different sizes.

The HTO nanospheres were synthesized by a sacrificing template method. The general synthesis method mainly includes the adsorption of metal ions from solution to the surface layer of carbonaceous spheres and subsequent removal of the carbonaceous cores via calcinations [22]. The experiment procedures are as follow: Glucose solution (1 mol L^{-1}, 20 mL) was poured into a 25 mL autoclave, then the autoclave was transferred into an oven maintaining at a heating temperature between 180 and 250 °C for 12 h. The product was centrifugal separated, washed three times with distilled water and anhydrous alcohol, and finally dried at 450 °C for 6 h. The obtained colloidal carbonaceous spheres were used as templates. $SnCl_4$ was mixed with ethanol at a molar ratio of 1:20, and the solution pH value was tuned by hydrochloric acid to different pH values, then tetraethyl orthosilicate (TEOS) was added into the solution. After a 30 min magnetic stirring, 200 mg colloidal carbonaceous spheres were put into the solution, and kept stirring for 24 h. In this process, Sn^{4+} ions combined with the unsaturated bonds on the surfaces of carbonaceous spheres and composed the shell of tin hydroxide outside carbonaceous core. Then the product was centrifugal separated and washed with distilled water and anhydrous alcohol, dried in an oven at 40 °C for 12 h, and annealed at 450 °C for 4 h. During the annealing, carbonaceous core were removed from the core-shell structure, and the reserved shell were oxidized and formed the hollow structure. It is worth mentioning that the sizes and structures of different metal oxide hollow spheres are predominantly determined by the templates [22]. Therefore, we can control the size of carbonaceous spheres by changing heating temperature in order to prepare size-tunable HTO nanospheres.

2.2. Characterization

The morphology and crystal structure of as-synthesized nano-SnO_2 were characterized by X-ray diffraction (XRD) using a Rigaku D/MAX-2400 utilizing Cu Kα radiation, field emission scanning electron microscope (FE-SEM) employing a JEOL JSM-6700F electronic microscope, transmission electron microscope (TEM) images were collected with a JEOL JEM-2010 high-resolution transmission electron microscopy. The room temperature PL spectra of samples were recorded on a Hitachi F-4500 FL spectrophotometer with a Xe lamp as the excitation light source. The specific surface areas of HTO and STO were measured by BET (Brunauer, Emmett and Teller) method.

2.3. PC activity test

The PC activity of HTO was evaluated by studying the photocatalytic degradation of aqueous MO solution. 50 mg nano-SnO_2 (HTO or STO) was suspended in 50 mL of 10 mg L^{-1} MO aqueous solution. The solution was continuously stirred for about 30 min at room temperature to establish an adsorption-desorption equilibrium between the MO and photocatalyst. The PC reaction proceeded in an ultraviolet photochemical reactor (BL-GHX-V, Beijing Bilon Lab Equipment Co. Ltd). MO degradation rate was analyzed by UV–vis spectroscopy at its maximum absorption wavelength of 464 nm.

3. Results and discussion

3.1. Crystal structure

The images of as-synthesized SnO_2 are shown in Fig. 1, where Fig. 1(a) and (b) are the SEM images of unannealed nano-SnO_2, and Fig. 1(c) is the TEM image of HTO nanospheres, respectively. According to the observation, the size of particles is in the range of 100 to 200 nm, and we can find from Fig. 1(a) and (b) that the SnO_2 nanoparticles are with similar size and spherical shape. However, the particles are still solid and undistributed. It is because of the products are not annealed and the carbonaceous cores which were used as templates were still inside of particles. Therefore, we removed carbonaceous cores by annealing and obtained the image of HTO nanospheres showed as Fig. 1(c). Generally, the nanoparticles present a porous spherical structure, and there is a brightness difference between center and border area, which indicates these structures are hollow. That is because the carbonaceous cores have transformed into carbon oxide (CO, CO_2) and escaped through these micropores during annealing, and only porous SnO_2 shells are reserved. Furthermore, the unbroken hollow spheres indicate carbon oxide gas escaped without any destruction to SnO_2 shells.

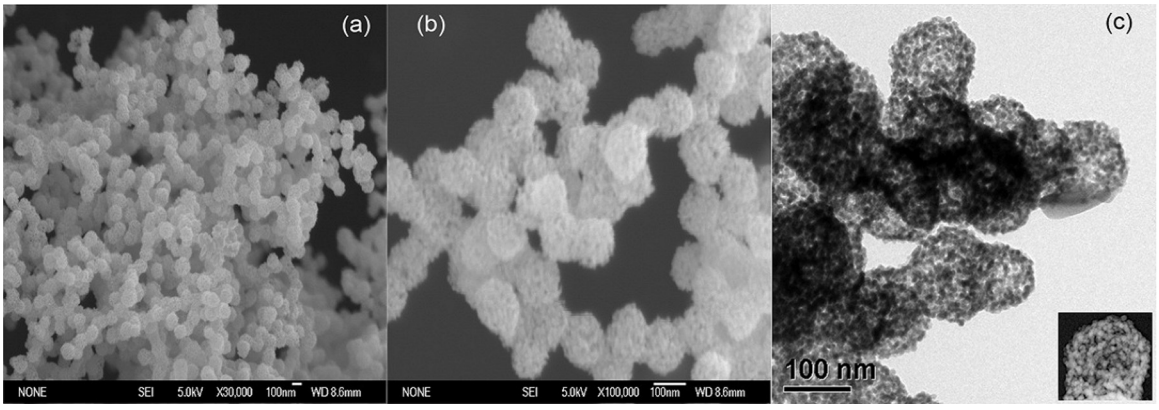

Fig. 1. Images of HTO nanoparticles. (a and b) The SEM images of unannealed HTO structure, (a) 30,000×, (b) 100,000×, respectively. (c) The TEM image of HTO nanospheres.