

Controllable synthesis and catalytic activity of SnO₂ nanostructures at room temperature

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Abstract: SnO₂ hollow spheres and rod bundles were prepared using SnSO₄ as raw material and sodium dodecyl benzenesulfonate and poly(vinyl pyrrolidone) as templates at room temperature through oxidation-crystallization of colloidal spheres in different systems. The products were characterized with X-ray diffractometer, X-ray photoelectron spectrometer, transmission electron microscope and scanning electron microscope. Meanwhile, the catalytic performance of the SnO₂ hollow spheres and rod bundles toward CO oxidation was studied. The result indicates that SnO₂ hollow spheres with the uniform size exhibit a better catalytic activity toward CO oxidation, suggesting that the morphology of the materials has exerted a noticeable influence on the catalytic performance.

Key words: SnO₂; hollow spheres; rod bundles; CO oxidation

1 Introduction

Tin oxide, SnO₂, is an n-type semiconductor with a wide band gap ($E_g=3.6$ eV, at 300 K) and is well known for potential applications as excellent gas sensors[1], electrode materials in Li/SnO₂ batteries[2], catalysts[3] and so on. The performance of these devices is influenced by the nanosized structure of SnO₂ crystals, including their size, morphology and so on. Thus, much attention has been focused on the synthesis of well-defined SnO₂ nanocrystals, and various SnO₂ nanostructures such as nanorods[4], nanoflakes[5], and hollow spheres[6] have been successfully synthesized. For example, ZHONG et al[6] used polystyrene particles as templates to fabricate mesoscale hollow spheres of SnO₂ with an average diameter of 400 nm.

Since 1989, low temperature CO oxidation has received much attention due to the important applications in indoor air cleaning and automotive exhaust treatment [7]. To our knowledge, most of the studies on noble metal based catalysts have been reported. However, high cost of noble metals and their sensitivity to sulfur poisoning have stimulated the search for substitute catalysts. Because of the price and the limited availability of previous metals, considerable attention has been paid to various metal oxides. Previously, Au-SnO₂

catalysts have exhibited extraordinarily high activity for CO oxidation at 80 °C, in which SnO₂ can enhance the catalytic activity[8]. Tin oxide materials have been widely used as catalysts in chemical reactions, including synthesis of vinyl ketone[9], oxidation of methanol[10] and so on. Therefore, it is believed that SnO₂ nanomaterials display potential catalytic activity for CO oxidation. In this work, the catalytic properties of the prepared SnO₂ hollow nanospheres and rod bundles were examined.

Among many preparative methods for well-defined structures, template-assisted synthesis is an effective approach in which hard templates[11–12], and soft templates[13–14] have been utilized. Surfactant tends to self-assemble to form micelles with desired structures and have been widely used as soft templates[15]. In this work, SnO₂ hollow spheres and rod bundles on a large scale in the air at room temperature were fabricated using surfactants as soft templates. And the products were characterized.

2 Experimental

2.1 Chemicals

Stannous sulfate (SnSO₄), sodium dodecyl benzene-sulfonate(SDBS), sodium dodecyl sulfate(SDS), cetyltrimethyl ammonium bromide(CTAB) and poly-(vinyl

pyrrolidone) (PVP, polymerization degree 360) were of analytical grade and were used as received.

2.2 Synthesis of SnO₂ hollow spheres

SnSO₄ (1 mmol) and SDBS (1.5 mmol) were dissolved in 10 mL distilled water and stirred at room temperature for 8–10 h. After the reaction was completed, the white products were collected from solution, rinsed several times with distilled water and absolute ethanol, and then dried under vacuum at 40 °C for 4 h.

2.3 Synthesis of SnO₂ rods

SnSO₄ (1 mmol), SDBS (1 mmol), PVP (0.05 g) and 10 mL distilled water were mixed, and stirred at room temperature for 8–10 h. After the reaction was completed, the white products were collected from solution, rinsed with distilled water and absolute ethanol, and then dried under vacuum at 40 °C for 4 h.

2.4 Characterization

The samples were characterized by X-ray powder diffraction (XRD) with a Japan Rigaku D/max rA X-ray diffractometer equipped with graphite monochromatized high-intensity Cu K_α radiation ($\lambda=1.541\ 78\ \text{\AA}$), recorded with 2θ ranging from 20° to 70°. The transmission electron microscopy (TEM) images and electron diffraction (ED) patterns were performed with a Hitachi Model H-800 instrument with a tungsten filament, using an accelerating voltage of 200 kV. The field emission scanning electron microscopy (FE-SEM) images were taken on FEI Sirion-200 SEM. XPS was performed on ESCALAB MKII with Mg K_α ($h\nu=1\ 253.6\ \text{eV}$) as the excitation source. The binding energies obtained in the XPS spectral analysis were corrected for specimen charging by referencing C 1s to 284.6 eV.

2.5 Catalytic activity measurements

The catalytic activity of SnO₂ catalysts towards CO oxidation was carried out in a continuous flow reactor. The reaction gas, a mixture composition of about 1% CO and 0.5% O₂ in nitrogen, was fed to a 0.3 g catalyst at a rate of 70 mL/min. Steady-state catalytic activity was measured at each temperature with the reaction temperature rising from room temperature to 630 °C in step of 20 °C. The effluent gas was analyzed on-line by an on-stream gas chromatograph (SP-6800A) equipped with a Porapak Q column (5 Å molecular sieve columns). The activity test was reproducible within the error of 5%.

3 Results and discussion

The typical X-ray powder diffraction (XRD) patterns of the as-prepared samples are shown in Fig.1. All the

sharp and strong diffraction peaks in Figs.1(a) and (b) could be readily indexed to the tetragonal phase of SnO₂ (JCPDS card No. 41-1445), with lattice constants of $a=4.738\ \text{\AA}$, and $c=3.187\ \text{\AA}$, which was found to match well with the standard XRD pattern. No characteristic peaks are observed for the impurities.

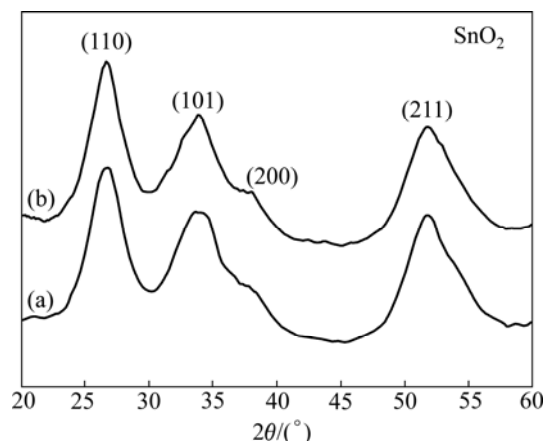


Fig.1 XRD patterns of as-prepared products: (a) SnO₂ hollow spheres; (b) SnO₂ rod bundles

To further characterize the product, XPS was carried out to investigate the surface compositions and chemical states of the as-prepared product obtained in different systems. Fig.2 shows typical spectra of SnO₂ hollow spheres, which resemble that of SnO₂ rod bundles. The binding energies obtained in the XPS analysis were corrected for specimen charging by referencing C 1s to 284.6 eV. The sample appears as a spin-orbit doublet at about 486.8 eV (3d_{5/2}) and about 495.2 eV (3d_{3/2}) (Fig.2(a)), which is in agreement with the reported values in Ref.[2]. The O 1s binding energy of 531.5 eV (Fig.2(b)) indicates that the oxygen atoms exist as O²⁻ species in the compounds. Consequently, based on the results of XRD and XPS measurements, the as-synthesized products could be determined as SnO₂.

The structure and morphology of the products were investigated by SEM and TEM. Morphologies of SnO₂ hollow spheres are displayed in Fig.3. From the panoramic morphology shown in Fig.3(a), a bright contrast (dark/bright) between the boundary and the center of the spheres is seen, confirming their hollow structure. The external diameter of the hollow spheres is 200–250 nm and the thickness of the shell is 20–30 nm. The inset in Fig.3(a) corresponds to the SAED pattern performed on the shell, and the circular characteristic indicates the polycrystalline SnO₂ shell. FESEM observations (Fig.3(b)) also reveal that the SnO₂ nanospheres are hollow. Interestingly, the morphology of the product is changed from hollow spheres to rod-like bundles as the used surfactant is changed from SDBS to the polymer(PVP)-surfactant(SDBS) complexes. It could

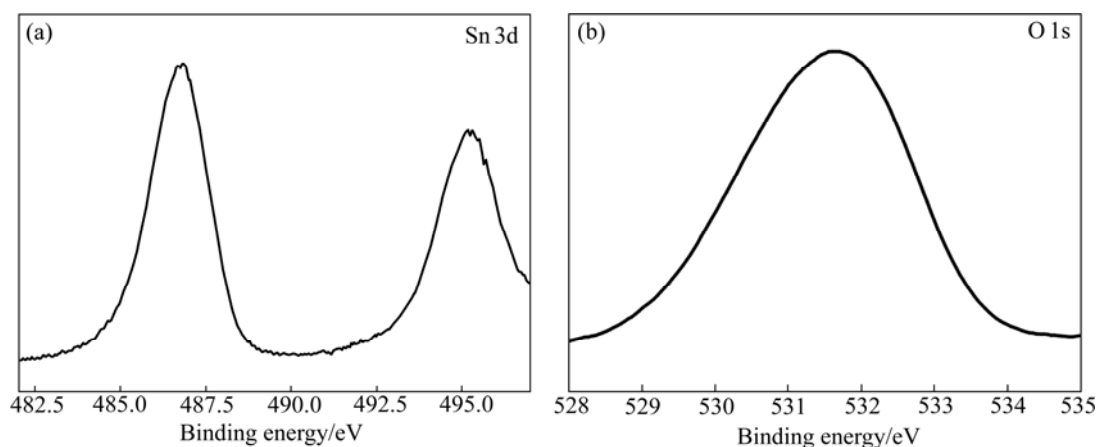


Fig.2 XPS spectra of SnO₂ hollow spheres: (a) Sn region; (b) O region

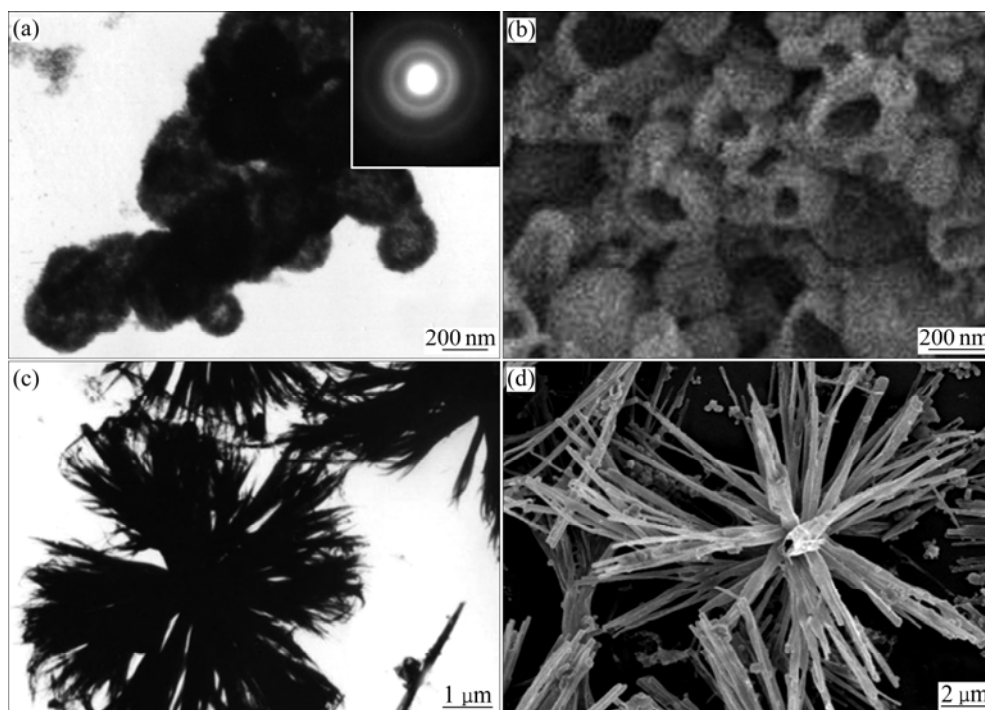
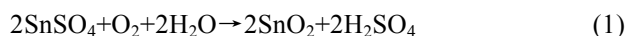


Fig.3 Electron microscopy images of SnO₂ nanostructures: (a) TEM image of SnO₂ hollow spheres (inset showing corresponding ED patterns); (b) SEM image of SnO₂ hollow spheres; (c) TEM image of SnO₂ rod bundles; (d) SEM image of SnO₂ rod bundles

be observed from Fig.3(c) that many rods stick together in the middle forming rod bundles. A typical SEM image (Fig.3(d)) displays that the rods grown from the middle have almost uniform widths of about 200 nm and lengths up to several micrometers.

In the experiment, the reaction system was maintained in the air. The reaction process in the system can be expressed by the following equations:



On the basis of the above observation, the formation of SnO₂ hollow spheres can be explained by surfactant-assisted oxidation-crystallization mechanism. SDBS has the tendency to form vesicles, which could act

as the soft templates[16]. TEM image shown in Fig.4(a) for the diluted solutions of SDBS system indicates the well-defined micelles. As SDBS is an anionic surfactant, Sn²⁺ can strongly adsorb on the surface of the vesicles, which provides domains for the subsequent oxidation and crystallization in the solutions. In another case, the surfactant SDBS associating with the polymer PVP chains forms micellar aggregates, which can act as templates for the precipitation and crystallization of SnO₂. There exists an interaction between PVP and SDBS micelle due to the electric attraction between the anionic SDBS micelle and the positive charged PVP, resulting in the adherence of SDBS micelles to PVP. Therefore, the surfactant SDBS associating with the

polymer PVP chains form micellar aggregates as shown in Fig.4(b), which can act as template for the precipitation and crystallization of SnO_2 . SDBS can act as stabilizer for the crystals, preventing particles from precipitation and aggregation. PVP has been proved to be face-inhibited function surfactant favoring the 1D growth[17]. Thus, the SDBS-stabilized particles adsorbed on the polymer PVP chains are connected into rods[18–19].

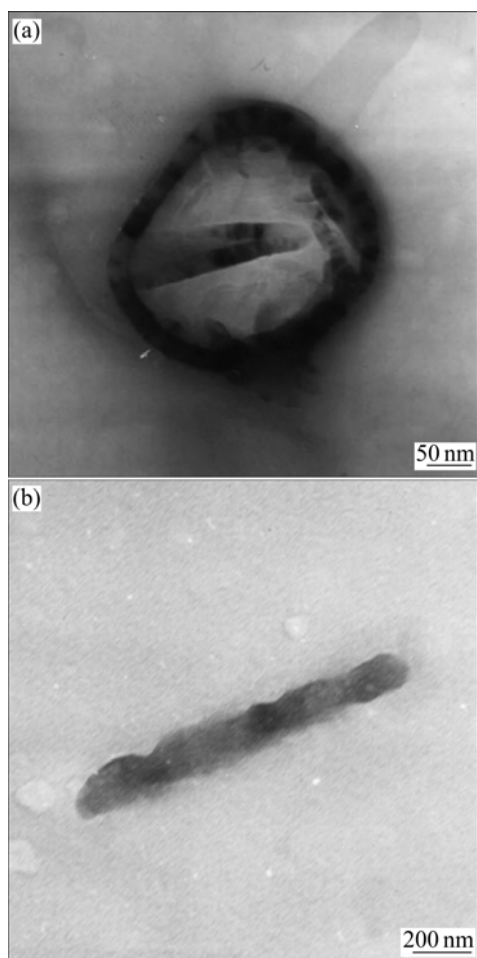


Fig.4 TEM images of micelles formed in reaction system: (a) SDBS micelle; (b) SDBS–PVP micelle

Recently, the development of carbon monoxide oxidation catalysts has been an active research area due to the many important environments and technological applications including CO gas detection sensors and air purification[20]. Commercial catalysts for CO oxidation were usually noble-metal-based materials such as platinum-tin oxide. Therefore, more economical and effective alternative catalysts are being sought[21]. Among various materials, metal oxides have been widely used due to their low cost and availability[22]. In the current work, the catalytic activities of different SnO_2 samples for CO oxidation were investigated. Table 1 and Fig.5 show the relationship between CO conversion and

temperature with the obtained SnO_2 materials as catalysts. The CO oxidation could be described in the following equation:



The CO conversion over each sample generally increases with the increase of reaction temperature. SnO_2 hollow spheres exhibit excellent catalytic activity above 350 °C and reach 100% conversion at 400 °C. When SnO_2 rod bundles function as catalyst, the catalytic activity decreases considerably. 100% CO conversion is achieved at 430 °C. The activity of SnO_2 chains is similar to that of SnO_2 rod bundles. The curve of SnO_2 particles with the diameter of 200 nm indicates that it is much more inactive than either the SnO_2 hollow spheres or rod bundles. Without SnO_2 samples as catalysts, CO oxidation starts at 430 °C and reaches 100% conversion at 630 °C. From the current measurements, it is clear that the catalytic activity of SnO_2 hollow spheres is better than that of other samples, which reduces the oxidation temperature of CO greatly. Most probably, the catalytic performance may be ascribed to the hollow spheres, in that, more chemicals (gases) could access reactive centers

Table 1 CO conversion at different temperatures

Catalyst	Reaction temperature/°C	CO conversion/%
Without catalyst	410	0
	450	4.5
	510	29.8
	550	51.4
	590	75.8
	630	100
SnO_2 hollow spheres	350	0.6
	370	2.4
	390	98.6
	410	100
SnO_2 rod bundles	350	0.2
	370	2.19
	390	39.5
	410	98.9
	430	100
SnO_2 particles	370	0
	390	1.3
	410	2.6
	430	5.8
	470	97
	491	100

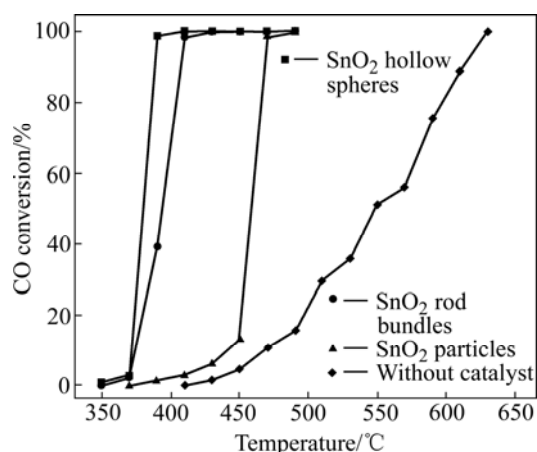


Fig.5 Effect of reaction temperature on CO conversion

of the porous frameworks and have more chances to participate in reactions[23], greatly improving the catalytic efficiency of the obtained materials. Thus, SnO₂ hollow spheres reveal possibilities to be applied as suitable catalyst for CO oxidation.

4 Conclusions

1) The present study describes a micelle system generated by SDBS for the preparation of SnO₂ hollow spheres on a large scale. Such a system may represent a promising microreactor for the synthesis of other inorganic materials with unique properties.

2) SnO₂ rod bundles are successfully fabricated by using the complex surfactant of SDBS and PVP micelles as templates. Their cooperative functions contribute to the final morphology of SnO₂ rod bundles.

3) The obtained SnO₂ hollow spheres and rod bundles exhibit potential catalytic activity toward CO oxidation, which may be useful in industrial applications.

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