LETTER

Preparation of SnO$_2$ hollow nanospheres by a solvothermal method

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During the past decade, considerable efforts have been made to fabricate inorganic materials with hollow nano/micro structures because many interesting optical, electronic, magnetic, catalytic and chemical properties are associated with these structures [1]. Among the methods that have been used for the synthesis of hollow nano/micro structures, hard- and soft-template syntheses are the two mostly used routes [2–6]. The size and morphology of the product can be controlled very well through choosing appropriate template, however, the removal of template is a rather complex process. Recently, a new sacrificial-template route is used to synthesis nanomaterials [7–9], in which the template materials act as one reactant and will be used up after the reaction, hence, the step for the template removal is successfully leaving out.

SnO$_2$ is a wide-band-gap semiconductor (Eg ≈ 3.62 eV, at room temperature) and a well-known material having applications in transparent electrodes [10], gas sensors [11], photocatalyst [12] and dye-sensitized solar cells [13]. One-dimensional nanostructure such as nanoribbons [14] and nanorods [15–16] have been successfully synthesized through solution synthesis. For better understanding the relationship between morphology and property, other morphology SnO$_2$ nanomaterials should also be synthesized. Although there are several reports on the fabrication of SnO$_2$ nanostructures with hollow interiors using different hard template [17–18], the synthesis of SnO$_2$ hollow micro/nano structures through a simple route remains a challenge for material scientists [19–21].

In the present study, we reported a solvothermal route for the preparing SnO$_2$ hollow nanospheres with diameters about ca. 40–120 nm. In this process, a complex compound was used as precursor and reactant. Water was used as another reactant. After the solvothermal process, complex compound precursor was converted to SnO$_2$ product completely.

All the reagents used in this work were chemical purity and used as received. In a typical process, 4 mmol hexamethylene tetramine (HMTA) was dissolved in a mixture of 1 mL distilled water and 30 mL absolute ethanol rring, then precursor precipitation was formed instantly after the addition of 0.5 mmol solid SnCl$_2$ · 2H$_2$O. The suspended material was transferred directly into a Teflon-lined stainless steel autoclave up to 60% of total volume. The sealed autoclave was maintained at 180 °C for 10 h inside an electric oven, and then cooled to room temperature naturally. The product to get a clear solution under continuous sti precipitation was collected by centrifuge and washed several times with water and ethanol before dry under 50 °C for 5 h.

The XRD patterns were recorded using a Japan Rigaku D/max-γA 200 X-ray diffractometer with Cu Kα radiation (λ = 1.54178 Å) in the 2θ range from 5° to 75°. The size and morphology of the as-synthesized product were characterized with JEOL JSM-6700F field emission scanning electron microscopy (FESEM) and JEM-100CXII transmission electron microscopy (TEM) instruments. Infrared spectrophotometer was collected on a Thermo-Nicolet 370 FT-IR instrument. The RT photoluminescence (PL) spectrum was recorded in the range of 380–550 nm on a fluorescence spectrometer (Hitachi M850).

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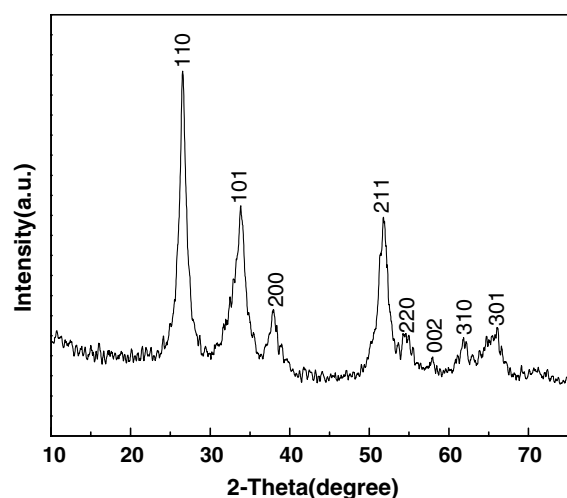Shandong 250100, PRC
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Fig. 1 XRD patterns of SnO$_2$ hollow nanospheres

The XRD pattern of the as-prepared product was illustrated in Fig. 1. All the diffraction peaks could be indexed to the tetragonal phase SnO$_2$ (JCPDS card file.No.88–0287). No characteristic peaks of the precursor and other impurities were detected. However, the diffraction peak of the hollow nanospheres was broadened due to the small crystallite, which could be confirmed later by the TEM observation.

The size and morphology of the obtained product was characterized by TEM and SEM observations as shown in Fig. 2. Both images showed nanospheres with 40–120 nm in diameter. The TEM image showed in Fig. 2a revealed the clear contrast between the outer part and the inner part of these sphere-like structures, which provided good evidence for the hollow structure of the product. High-magnified TEM observation presented that the product was composed of small crystallite. The corresponding selected-

area electron diffraction (SAED) pattern shown in the inset of Fig. 2a confirmed the polycrystalline nature of the SnO$_2$ hollow nanospheres. Obviously, the SEM images showed in Fig. 2b exhibited rough surface. One broken nanosphere could also be seen in the same SEM image, which further proved that the SnO$_2$ product was hollow nanospheres.

In order to make clear the reaction process, characterization of the precursor was conducted. The FTIR spectrum of the precursor showed in Fig. 3a gave a new absorption peak at 497 cm^{-1}, which could be caused by the Sn–N stretching [22–25]. The precursor might be a complex compound between Sn (II) and HMTA. For the easily comparison between precursor and product, the FTIR spectrum of product was showed in Fig. 3b. Seen from the FTIR, the complex compound precursor was transferred into SnO$_2$ product completely through the solvothermal process. Morphology of the precursor was also characterized. SEM and TEM observation of the precursor gave similar images (see ESM) to these showed in Fig 2a and Fig. 2b, which suggested that precursor morphology might predestine the product morphology.

On the basis of above analysis, a possible mechanism under present experimental conditions might be described as following: Complex compound between Sn (II) and HMTA with hollow nanospheres shape was prepared firstly, then the complex compound was hydrolyzed in the solvothermal process. That is, ligand was substituted by hydroxy, the newly formed Sn(OH)$_2$ was oxidized to Sn(OH)$_4$ and subsequently experienced condensation process.

According to the mechanism that we proposed, the ratio of water to ethanol should play great role in the solvothermal process because it would affect the ligand institute. A series experiments was conducted to clarify this by

Fig. 2 Typical images that obtained when different ratio of water to ethanol was used in the solvothermal process: 1 mL distilled water and 30 mL for (**a**) and (**b**); 15 mL distilled water and 15 mL ethanol for (**c**); 30 mL distilled water for (**d**)
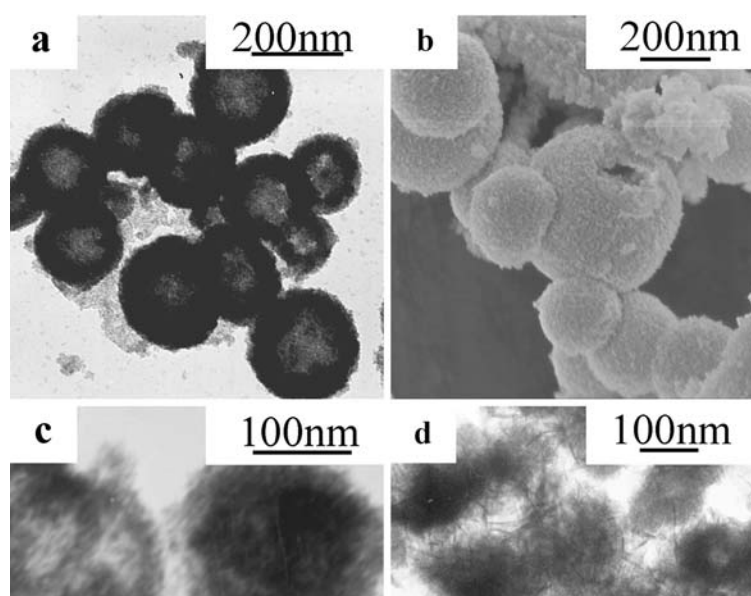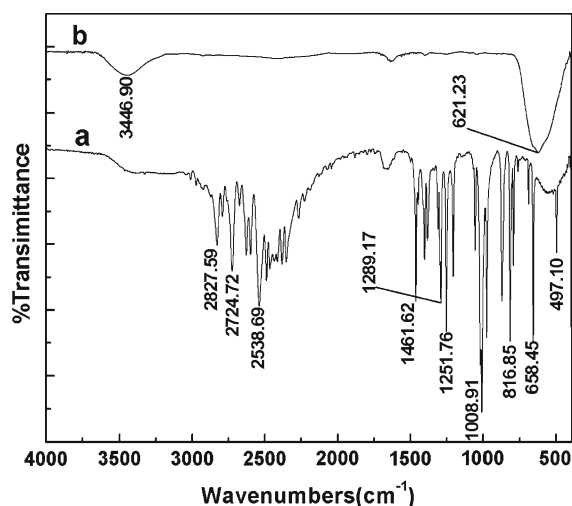
Fig. 3 FT-IR of the precursor (**a**) and the product (**b**)

Fig. 4 A RT PL spectrum from the as-synthesized SnO_2 hollow nanospheres

changing water content from 2% to 100% while other parameters was kept constant, the morphology of SnO_2 changed from hollow nanospheres (Fig. 2a) to conglomeration (Fig. 2c), and then to prickly structure (Fig. 2d). The composition of the product was changed from pure SnO_2 to mixture of SnO_2 and SnO (see ESM)and the color of product changed from white to shiny gray. This could be explained as: The higher water content could provide more hydroxyl ions at the beginning of the solvothermal process, which would increase the ligand release. What's more, the quick reaction destroyed the morphology of the complex compound, and more irregular shape formed. When only water was used in the solvothermal process, the particle growth led to the prickly structure. Another possible reason for the above phenomenon was that the hydrophilic hydroxyl of the ethanol would coordinate with the newly formed Sn^{2+}, thus, the hydrophobic ethylic would protect the product from aggregate upon decreasing water content.

The PL spectrum (Fig. 4) from SnO_2 hollow nanospheres has been measured using an excitation wavelength of 340 nm. The emission spectra revealed one blue emission band centered at 440 nm. The emission might be related with oxygen vacancies. A similar blue emission has been reported in the case of uncapped SnO_2 nanoparticles synthesized by sol–gel method [26]. The present PL result agreed very well with their proposed model. Thus the blue emission could also be attributed to recombination of electrons in the conduction band with deep doubly ionized oxygen vacancies.

A simple solvothermal route was used to synthesize SnO_2 hollow nanospheres, which might be extended to the growth of other metal oxide by proper choosing ligand and the following treatment. Such a rational low-temperature synthetic route might be adapted for the scale up in industry.
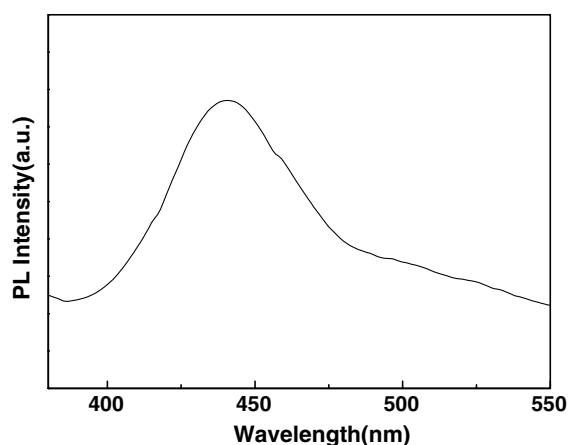
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