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Inorganic Chemistry Communications 7 (2004) 344–346

INORGANIC CHEMISTRY COMMUNICATIONS

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Synthesis of indium hollow spheres and nanotubes by a simple template-free solvothermal process

Yunxia Zhang *, Guanghai Li, Lide Zhang

Institute of Solid State Physics, Chinese Academy of Sciences, P.O. Box 1129, Hefei 230031, People's Republic of China

Received 28 November 2003; accepted 8 December 2003
Published online: 8 January 2004

Abstract

Indium hollow spheres and nanotubes were successfully synthesized via a simple template-free solvothermal route at different temperatures. The products were characterized by X-ray powder diffraction and transmission electron microscopy.

Keywords: Indium; Hollow spheres; Nanotubes; Solvothermal

In recent years, metal nanoparticles have attracted extensive attention for their potential applications in optics, electronics, photoelectronics, catalysis, sensing, clinical diagnostics, surface-enhanced Raman scattering (SERS), information storage, and energy conversion/storage [1,2]. While metal nanoparticles with hollow structures are particularly interesting due to their low density, large specific area, mechanical and thermal stability, and surface permeability [3,4]. A variety of hollow spheres have been successfully fabricated by various methods, such as template-assisted process (by coating the template with a thin shell of the desired materials and subsequently removing the template by calcination or solvent etching), including polystyrene latex spheres [5], resin spheres [6], microemulsions [7], polymer micelles [8], polymer-surfactant complex micelles [9], ultrasonication [10], and etc. However, very few approaches have achieved practical significance owing to very high cost of the methods. It is very important to explore a simple and cheap access to preparing inorganic hollow spheres.

Indium is widely used in the field of electronics for semiconductor devices, thermistors and optical devices, electronics soldering (alloys), for control rods in reactors, and also used to improve some dental alloys [11]. It is easily alloyed and converted. Indium semiconductor compounds such as InP [12] and InAs [13], are used in infrared detectors, high-efficiency photovoltaic devices and high-speed transistors. In addition, Indium is easily oxidized to In_2O_3, which has been widely employed as a microelectronic device material in solar cells, flat-panel displays, sensors, and architectural glasses [14]. Indium nanoparticles is expected to have better catalytic and recording properties than coarse-grained indium particles. Nevertheless, the studies on the fabrication of indium nanoparticles are very few. Kimoto and Nishida [15] produced nanocrystalline indium powder by vacuum deposition techniques. Zhao et al. [16] prepared indium nanoparticles via a novel solution route. Liu et al. [17] reported the preparation of nanocrystalline indium powders by γ-irradiation. Katerina [18] adopted the organometallic route to synthesize indium nanoparticles. In this study, we report the preparation of indium hollow spheres adopting a simple solvothermal route without using any template for the first time.

All the reagents were of analytical grade and were used without further purification. In a typical process, 0.221 g anhydrous $InCl_3$ and 0.098 g Zn powder (the mol ratio of $InCl_3$ to Zn is 1/1.5) were added to a 50 ml Teflon-lined stainless steel autoclave. Then the autoclave was filled with 90% absolute ethanol and the solution

* Corresponding author. Tel.: +865515591437; fax: +865515591434.
E-mail address: zyxqm@263.net (Y. Zhang).

1387-7003/$ - see front matter
doi:10.1016/j.inoche.2003.12.010

was constantly stirred for 30 min. The autoclave was sealed and maintained at 120 °C for 20 h, then cooled to room temperature naturally. The dark grey products were filtered, washed several times with distilled water and absolute ethanol to remove the impurities, and then dried at 70 °C for 4 h.

The purity and composition of the products were characterized by powder X-ray diffraction (XRD) using a Rigaku D/Max γA X-ray diffractometer with Cu Kα radiation ($\lambda = 1.54178$ Å). The morphologies of the samples were observed with a transmission electron microscope (TEM, Hitachi H-800) performed at 200 kV. And the microstructures of the samples were analyzed with a high-resolution transmission electron microscope (HRTEM, JEOL-2010).

The X-ray diffraction (XRD) pattern of the samples prepared at 120 °C is shown in Fig. 1. All the peaks can be indexed to the body-centered tetragonal Indium (JCPDS 72-1184), and no characteristic peaks of impurities, such as unreacted Zn and In_2O_3, were observed which substantiates that our as-prepared products are very pure. It can be easily seen that the peaks are fairly broad, indicating the small particle size. According to the Scherrer's equation, the size of these particle composing indium hollow spheres was about 8 nm.

Fig. 2 is several typical transmission electron microscopy (TEM) images of the samples prepared at 120 °C. The strong contrast between the dark edge and the brighter center of indium nanospheres revealed their hollow features. The outer diameter of these nanospheres is about 100–150 nm, as shown in Fig. 2(a). TEM images at higher magnification (shown in Fig. 2(b) and (c)) clearly indicate that these nanospheres are composed of very small indium nanoparticles, which is in agreement with the results of XRD. The corresponding selected area electron diffraction (shown in the inset in Fig. 2(c)) exhibits diffuse ring pattern indicated that these indium hollow spheres are polycrystalline.

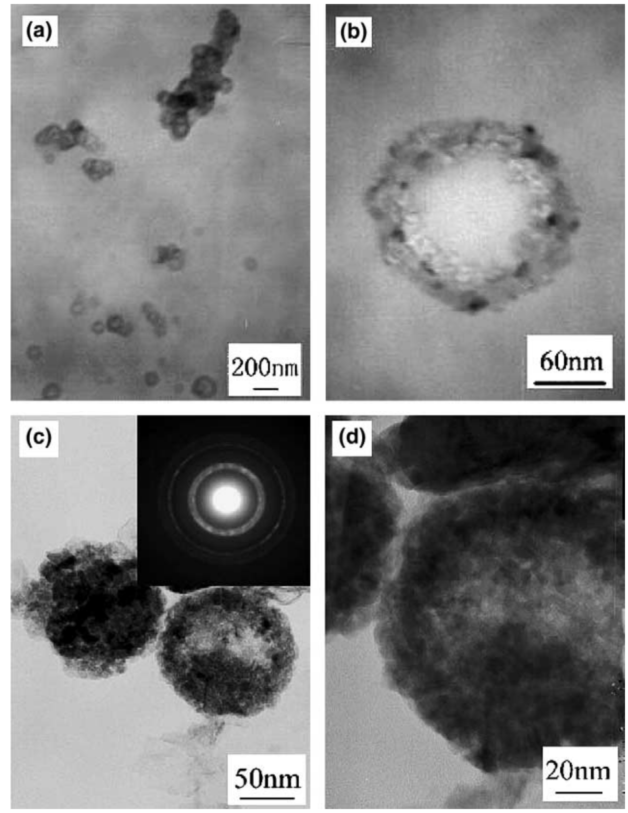

Fig. 2. Several typical TEM images of samples prepared at 120 °C.

The HRTEM image in the Fig. 2(d) further confirmed the hollow nature of these indium nanospheres.

Fig. 3 is a typical TEM image of the samples prepared at 150 °C. Unfortunately, it is difficult to obtain clearer TEM image of indium nanotubes due to their high sensitive to the electron beam. From Fig. 3 (a), it can be seen that the diameter of indium nanotubes is about in the range of 80–120 nm. Fig. 3(b) is a typical TEM image of a single nanotube in which the opening and

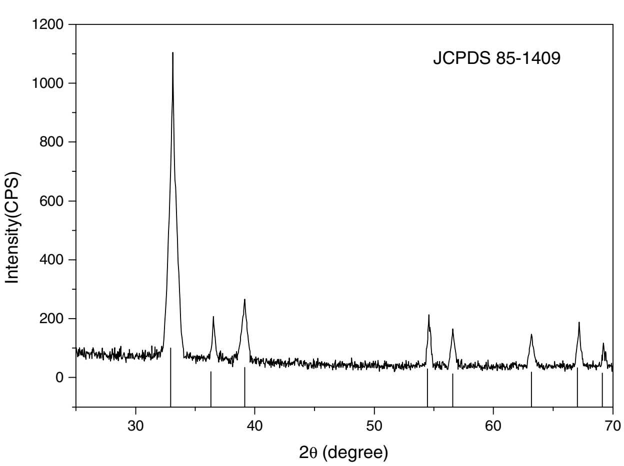

Fig. 1. XRD pattern of as-prepared indium nanospheres.

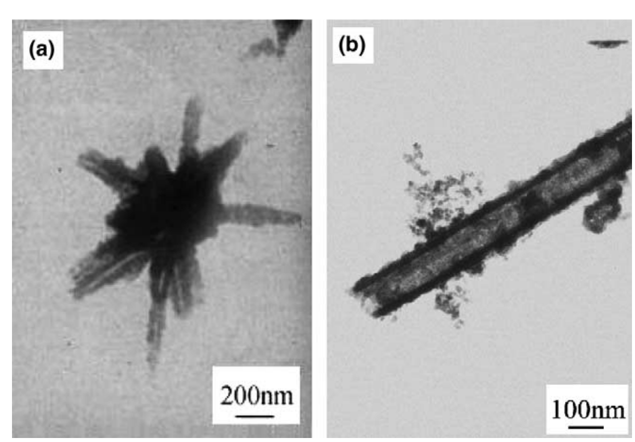

Fig. 3. Two typical TEM images of samples prepared at 150 °C.

obvious contrast in the terminal fully display the character of the nanotubes.

In the solvothermal process, the solvent played an important role in the formation of indium. In our experiment, absolute ethanol was chosen as a solvent. As a control experiment, when water was used as the solvent, the products contained In_2O_3 besides indium. Of course, the reaction temperature also affects the morphology of the as-prepared samples. The yield of indium hollow spheres was lower at lower temperature, such as 90 °C. On the other hand, indium nanotubes were the main product besides the hollow spheres at 150 °C. These indicate that the growth kinetics affects the morphology of the final product.

The mechanism of the formation of the indium hollow spheres and nanotubes is still under investigation. The template mechanism was firstly excluded because no template was used in our experiments. We think it is possible that the formation of indium hollow spheres is connected with the hole nucleation theory [19]. As for the formation indium nanotubes, it is perhaps related to the self-catalysis of indium particles. Indium nanoparticles will melt at 150 °C (the melting point of the indium nanoparticles is lower than that of indium bulk (156 °C)). Then indium nanotubes grew via a liquid–solid mechanism.

In conclusion, indium hollow spheres and nanotubes were successfully synthesized adopting $InCl_3$ and Zn powder as raw materials by a simple solvothermal process without using any template. Our method is very simple compared with other methods for synthesizing metal hollow spheres preparing method. Indium hollow spheres and nanotubes will be expected to offer many novel catalytic and optical properties over their solid counterparts.

Acknowledgements

This work was supported by National Major Project of Fundamental Research: Nanomaterials and Nanostructures (Grant No. G19990645).

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