Template-free preparation and characterization of hollow indium sulfide nanospheres

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Abstract

In this manuscript we have demonstrated a template-free route to the preparation of hollow In_2S_3 nanospheres by solvothermally treating solid In_2S_3 spheres comprised of small particles at 180 °C for 24 h. This method is simple but highly efficient, which can transform the solid precursors into hollow nanostructures in an extremely high yield. Investigations into the intermediates reveal that the formation of hollow spheres is through the mergence of the smaller particles within the solid spheres by the relatively large ones in the ripening process (i.e., Ostwald ripening). The well crystalline hollow nanospheres have the diameters of 40–70 nm and an average wall thickness of 7 nm. Due to the closeness of the size of hollow nanospheres to the Bohr radius (33.8 nm) of the excition in In_2S_3, an obvious quantum size confinement and morphology-dependent property are observed. Hollow In_2S_3 nanospheres show an intense absorption between 318 and 512 nm, which is blue-shifted to shorter wavelengths relative to that of bulk In_2S_3. Hollow In_2S_3 nanospheres also exhibit a strong photoluminescence. The green band centered 518 nm is due to the band-band transitions and the orange emission centered at 624 nm originates from the indium interstitial defect. These hollow In_2S_3 nanospheres could be used as a distinctive multicolored phosphor and material for producing photoelectrochemical devices.
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1. Introduction

Of various nanostructures, hollow microspheres and nanospheres of inorganic materials have attracted much attention due to their distinct morphologies, excellent properties, and potential applications. The existence of hollow interior imparts them a low effective density and high specific area [1,2], and thus they are expected to apply in the controlling storage and release [2–5], adsorption [3–6], confined-space catalysis [7], microreactors [8], and acoustic insulators [9]. At present, hollow spheres with different diameters and wall thickness were typically synthesized via the layer-by-layer deposition of nanoparticles onto some spherical colloids (e.g., polystyrene beads, silica sol) [10–18]. Then, by calcinations or dissolutions with solvents, col-loidal templates were removed to give hollow structures. A large amount of hollow spheres, including elements, metal sulfides, and metal oxides, have been prepared via this route. In addition to hard colloidal templates, it was found that interfacial reactions around the surface of vesicles or emulsion droplets were also efficient in the production of hollow spheres because of the soft template function of vesicles and droplets [19–26], such as the preparation of hollow structures of CdS, TiO_2, and CdS/TiO_2 composites. Although the template-directed synthesis of hollow spheres is convenient and applicable to many inorganic compounds, it is usually laborious, and in some cases, the shells of hollow spheres built up of nanoparticles were incompact, which would lead to a poor mechanical strength.

Recently, many efforts have been devoted to the template-free fabrication of hollow structures utilizing some interesting physical phenomena [27–29]. For instance, Alivisatos and coworkers have reported on the preparation of hollow CoS spheres through the nanoscale Kirkendall effect [27]. Zeng and coworkers have

pointed out that hollow nanostructures of Cu_2O and TiO_2 could be formed through the ripening of solid spheres comprised of numerous small crystallites [28,29]. During the Ostwald ripening period, owing to the difference of surface energy, crystallites located in the inner space of solid spheres can merge into those on the surface, and meanwhile solid spheres gradually develop into hollow structures. Theoretically speaking, this method should open new opportunities for the template-free preparation of nanoscaled hollow structures. This is because if solid counterparts comprised of small particles are obtained, it is possible to transform them into hollow structures under appropriate ripening conditions.

Of various inorganic semiconducting materials, β-indium sulfide (In_2S_3) has been of great research interest [30–38], which is usually motivated by their good properties and quite interesting structure. β-In_2S_3 is an n-type semiconductor with a medium energy gap between 2.0 and 2.20 eV [39,40], and shows a stable temperature up to 693 K, which seems to be an ideal candidate to substitute toxic CdS as buffer layer in $CuInSe_2$ and $CuInS_2$ based solar cells [41–43]. β-In_2S_3 is also a useful material in the preparation of red and green phosphors and photoelectrochemical cell devices [32,44]. Besides their good physical properties and wide applications, the structure of In_2S_3 is attractive. Owing to tetragonal sites formed by incompletely coordinated sulfur atoms, In_2S_3 can serve as a host for a number of metal ions to form semiconducting and/or magnetic materials [30,45–48], which is in contrast to II–VI compound that tend to expel guest ions [30,49,50]. Furthermore, the optical, electrical, and magnetic properties of doped In_2S_3 can be adjusted not only by its size, but also by the concentration of the guest ion [51,52].

In previous reports about In_2S_3 nanocrystals, it can be found that most of the products present an irregular profile. Owing to the morphology-dependent properties of nanomaterials and good physical properties of In_2S_3 [53], it is deserved to fabricate it into regular nanostructures in order to improve its properties. In this work, we report on the transformation of solid In_2S_3 nanospheres comprised of numerous small particles into hollow structures by a simple Ostwald ripening method. The ripening of solid In_2S_3 nanospheres is preformed on an autoclave because of its ability to provide a high temperature and pressure, which is advantageous to the acceleration of Ostwald ripening rate. Studies on the optical properties of the well-crystallized hollow In_2S_3 nanospheres reveal that they exhibit green and orange emissions.

2. Experimental section

All the reagents were of analytical grade and purchased from Shanghai Chemical Corporation.

In a typical experiment, 0.147 g $InCl_3·4H_2O$ (0.001 mol) and excessive thioacetamide (0.002 mol) were added into a conical flask contained 50 ml distilled water to give a transparent solution. Then, the temperature of the solution was increased to 90 °C and the solution was refluxed at this temperature for 1 h. Yellow colloidal indium sulfides were found to form, which were separated from the solution by centrifugation and washed several times with distilled water and absolute alcohol to remove

unreacted $InCl_3$ and thioacetamide. Afterward, the obtained yellow In_2S_3 colloids were redispersed in 27 ml benzene and the dispersions were transferred into a Teflon-lined stainless steel autoclave with a volume of 30 ml. The sealed autoclave was allowed to heat at 180 °C for 24 h before cooled down to room temperature naturally. The products were found to change their color from the initial yellow to orange after a solvothermal treatment, which were separated from the solution by centrifugation and dried in vacuum at 40 °C for 3 h.

The X-ray powder diffraction (XRD) patterns of the products were recorded on a Rigaku D/max-γ rotation anode X-ray diffractometer (Cu Kα, λ = 1.54178 Å). The transmission electron microscopy (TEM) images and high-resolution transmission electron microscopy (HRTEM) images were taken with a FEI Tecnai G20 microscope with an accelerating voltage of 200 kV. The scanning electron microscopy images were taken with a HITACHI S570 microscope. The ratio between In and S within the products were analyzed using an energy-dispersive X-ray spectrometer (EDS) equipped on a HITACHI S-570 scanning electron microscope. The optical absorption spectra were recorded on a Hewlett-Packard 8453 diode array spectrophotometer using 1 cm quartz cuvettes. The room-temperature photoluminescence spectra were performed on an Edinburgh FLS-920 steady-state/lifetime spectrofluorometer with Xe lamp as the excitation source.

3. Results and discussion

3.1. Characterization of the structure and morphology of In_2S_3 before and after ripening

At the temperature of 90 °C, $InCl_3$ and thioacetamide could react gradually and give yellow colloidal In_2S_3. XRD studies of them (Fig. 1a) reveal that they are composed of β-In_2S_3, as learned from the index of the obtained XRD pattern (Joint Committee on Powder Diffraction Standards, JCPDS Card Files, No 25–390). The weak reflections are related to the poor crystallinity of β-In_2S_3 colloids, and their quite broad feature implies that the size of nanocrystals should be very small. The calculations of the sizes of the crystallites with Scherrer formula indicated their average diameter is 5.2 nm. The atom ratio between In and S within In_2S_3 colloids is determined according to their EDS spectrum (Fig. 1b), where the detected Si arise from the silicon substrate on which the sample was deposited. A comparison of the relative area under the peaks for S and In yields an atomic ratio of 3.14:2; this value is slightly higher than the stoichiometric ratio of 3:2 within In_2S_3. It may be caused by the decomposition of excessive thioacetamide, resulting in free sulfur contained in the precursor.

To learn the morphologies of β-In_2S_3 colloids, they were checked by TEM, and the obtained images are shown in Fig. 2. The low magnification image (Fig. 2a) reveals that colloidal In_2S_3 is composed of large amounts of nanospheres, the average diameter of which is about 50 nm. Furthermore, some details about these In_2S_3 nanospheres are shown in TEM image with a high magnification (Fig. 2b) and HRTEM image (Fig. 2c),