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Controlled synthesis of urchin-like Bi_2S_3 via hydrothermal method

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ABSTRACT

The urchin-like Bi_2S_3 nanostructures have been grown by a facile environmentally friendly hydrothermal method. X-ray diffraction (XRD) and Raman spectrum demonstrate that the obtained samples are composed of pure orthorhombic phase Bi_2S_3. Scanning electron microscopy (SEM) images and transmission electron microscopy (TEM) images reveal that it is produced as uniform urchin-like pattern with spherical symmetry. High-resolution (HR) TEM and selected-area electron diffraction (SAED) demonstrate that the nanowires which grow radially from the center of the urchin-like nanostructures toward all directions are single-crystalline and grow along the [001]. It is found that the reaction time, reaction temperature and thiourea (Tu) play key roles for the formation of urchin-like Bi_2S_3 nanostructures. The formation mechanism is ascribed to self-assembly and the intrinsic splitting character of the Bi_2S_3 structure. The urchin-like Bi_2S_3 composed of porous nanorods, solid nanorods and nanowires could be found potential application in optical, catalysts and sensor devices.

1. Introduction

The physical and chemical properties of nanostructured materials are markedly sensitive to size and morphology, and much efforts have been dedicated to achieve rational controlling over the morphology of the nanomaterials [1–7]. Self-assembly is the basis of the structure for all biological organisms, which exhibit massively parallel fabrication processes that generate three-dimensional structures with nanoscale precision. Drawing inspiration from the hierarchy and assembly strategies found in nature, many studies have focused on the fabrication of hierarchically assembled structures from nanoscale building blocks, which could offer opportunities to explore advanced materials with promising properties.

As a direct band gap semiconductor with band gap of 1.3 eV [8], Bi_2S_3 can be used as photovoltaic material, photodiode array and sensor [9–12]. Bi_2S_3 is also a good candidate as a thermoelectric-cooling material. The synthesis and functionalization of the nanostructured Bi_2S_3 with the controlled size, shape, and hierarchy have attracted intensive interest. Various morphologies such as nanowires [13], nanorods [14], nanobelts [15], nanotubes [16], nanowire-arrays [17] and nanoflowers [18] have been synthesized, but there are few reports on the synthesis of urchin-like Bi_2S_3.

In this paper we report the success synthesis of urchin-like Bi_2S_3 in hydrothermal condition, and it is found that the urchin-like Bi_2S_3 consist of either nanorods or nanowires can be realized by simply controlling reaction time.

2. Experimental section

All the reagents were analytically pure and used without further purification. In a typical procedure, 0.25 g of thiourea (Tu) was dissolved in 50 ml distilled water under constant stirring, then 0.61 g of $Bi(NO_3)_3 \cdot 5H_2O$ was added to the above solution. After being stirred at 60 °C for 10 min, the solution was transferred to a Teflon-lined autoclave. The autoclave was transferred into an oven and maintained at 140 °C for different times. After cooling down to room temperature naturally, the precipitates were collected and washed with distilled water and anhydrous ethanol for several times, then dried at 60 °C for 8 h.

The as-prepared products were characterized by powder X-ray diffraction (XRD Philips X'pert PRO), Raman spectra (LABRAM-HR Raman spectrophotometer), Fourier transform infrared spectra (Nexus FT-IR spectrometer), scanning electron microscopy (SEM Sirion 200 FEG), transmission electron microscope (TEM, JEM-2010) and high-resolution transmission electron microscope (HRTEM, JEOL2010).

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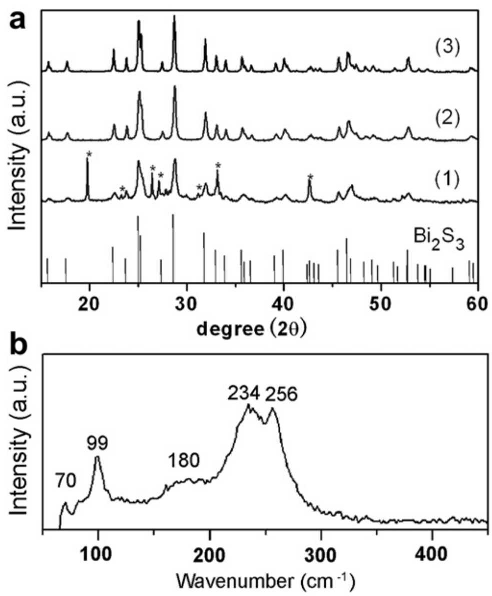

Fig. 1. (a) XRD patterns of the products prepared at 140 °C after reaction for the time of (1) 1 h, (2) 3 h and (3) 20 h (the peaks of the impurity phase are marked with "*"). (b) Raman spectrum of the products prepared at 140 °C for 20 h.

3. Results and discussion

Fig. 1a shows the XRD patterns of the products prepared at 140 °C for different times together with that from the standard JCPDS card (No. 06-0333). One can see that there are some impurity phases (marked with asterisks) besides the Bi_2S_3 phase for the product obtained after reaction only for 1 h, as shown in curve (1) in Fig. 1a. The impurity phase disappear with a prolonged reaction time of about 3 h, see curve (2) in Fig. 1a. From the discussion shown below we will see that the impurity phase is $BiONO_3$. The crystalline quality of Bi_2S_3 increases with increasing reaction time. After reaction for 20 h, all diffraction peaks can be indexed as the orthorhombic Bi_2S_3 with cell constants of $a = 11.15$ Å, $b = 11.30$ Å, and $c = 3.981$ Å (curve (3) in Fig. 1a). Fig. 1b shows the Raman spectrum of the product prepared at 140 °C for 20 h. Five distinct vibration peaks situated at about 70, 99, 180, 234 and 256 cm^{-1} can be seen clearly, and the peak positions are comparable well with the reported values in literature [19]. This result further proves that the product is the orthorhombic Bi_2S_3. The absent peaks at 112.6, 125.2 and 169.4 cm^{-1} might be related to the surface phonon modes [20].

Fig. 2a shows the low-magnification SEM image of the product prepared at 140 °C for 20 h. The morphology of the product is urchin-like sphere with the diameter of 6–8 μm. The high-magnification SEM (Fig. 2b) reveals that each urchin-like sphere is composed of nanowires about 3–4 μm in length and 50 nm in diameter, making the final product present a hierarchical Bi_2S_3 micro/nanostructure. The nanostructure of nanowire was further investigated by TEM, the size of the nanowire is 50 nm in diameter (Fig. 2c), which are in agreement with the SEM observations. Fig. 2d shows a typical HRTEM image taken from the single nanowire, in

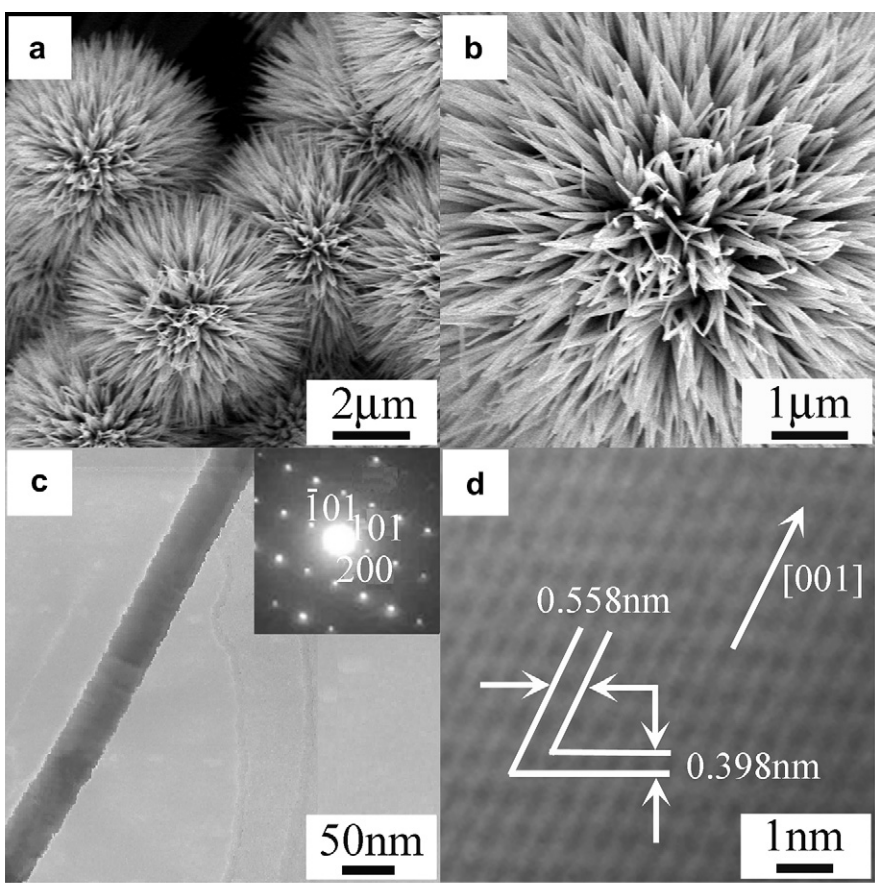

Fig. 2. (a) Low- and (b) high-magnification SEM images of the urchin-like Bi_2S_3 prepared at 140 °C for 20 h; (c) TEM and (d) HRTEM images of individual Bi_2S_3 nanowire in the urchin-like structure (the inset is the corresponding SAED).