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D-penicillamine assisted hydrothermal synthesis of Bi_2S_3 nanoflowers and their electrochemical application

Ming Zhang [a], De-Jun Chen [a], Rui-Zhi Wang [a], Jiu-Ju Feng [a,b], Zhengyu Bai [a], Ai-Jun Wang [a,b,*]

[a] School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, 453007, China
[b] College of Chemistry and Life Science, College of Geography and Environmental Science, Zhejiang Normal University, Jinhua, 321004, China

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ABSTRACT

Single crystalline flower-like Bi_2S_3 nanostructures were successfully synthesized via a simple, facile and green hydrothermal method, with the assistance of *D*-penicillamine. The products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM), and found their morphologies mainly depend on the ratios of Bi^{3+} to *D*-penicillamine, as well as the reaction temperature and time. And the possible growth mechanism has been discussed in some detail. In addition, the as-prepared Bi_2S_3 nanoflowers show good hydrogen storage ability. This strategy can be potentially expanded to prepare other metal chalcogenides materials.

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1. Introduction

In the past two decades, control synthesis of advanced inorganic materials with different shape and size have attracted great attention, owing to their fundamental significance in elucidating the relationship of various physical and chemical properties with shape and size, as well as their promising applications in electrochemical, electronic, optoelectronic and electromechanical nanodevices [1–7].

Among these nanomaterials, synthesis of metal sulfides [8] have received great success for promising applications in hydrogen storage, sensors and electronic based devices [9–12]. The preparation, properties and applications of metal dichalcogenide such as MoS_2, TiS_2 and WS_2 have been extensively studied [13]. Many methods have been developed for the construction of one dimensional (1D) metal sulfides including template-guided procedures [14], single-source precursor method [15–17], hydrothermal or solvothermal methods [18–20], thermolysis [21], chemical vapor deposition [22], sonochemical methods [23], microwave irradiation [24] and electrodeposition [25,26]. However, expensive and toxic organic agents are usually used and a series of complicated procedures are often employed, along with the inevitable releasing of pungent H_2S from the sulfur sources (e.g. Na_2S, H_2S, thiourea, thioactamide and sodium thiosulfate). Therefore, it is necessity to search a simple, facile, green and inexpensive method for large-scale synthesis of 1D metal sulfides.

Recently, biomolecule-assisted synthesis is a popular method in the preparation and assembly of a variety of semiconductors where biomolecules have been served as structure-directing agents and the sulfur sources. Xie et al. prepared Bi_2S_3 flowerlike patterns with well-aligned nanorods in the *L*-cysteine solution [9]. Qian's group synthesized a variety of morphologies of PbS using a facile *L*-cysteine-assisted solvothermal method [27] and various dendritic hierarchical structures in the *L*-methionine solution [28], respectively. This thought-provoking work inspires us to search a facile and more economical strategy to prepare metal sulfides with the help of small biomolecules. Thus, very recently, we have prepared hierarchical PbS microstars with octa-symmetric-dendritic arms in the presence of *D*-penicillamine under solvothermal conditions [29]. It would be interesting to develop a simple *D*-penicillamine-assisted biological method to prepare other sulfide nanomaterials with control morphology and novel properties.

It is known that *D*-penicillamine contains —SH, $-NH_2$ and —COOH groups, which can interact with inorganic cations to form the precursor complexes. Furthermore, the sulfur atom in the —SH group can be used as a sulfur source to prepare metal sulfide nanomaterials. Herein, a simple, facile and green method was developed in the control synthesis of single crystalline Bi_2S_3 nanoflowers with high hydrogen storage ability. In addition, the growth mechanism of the flower-like Bi_2S_3 nanostructures was also discussed in some detail.

2. Experimental section

2.1. Chemicals

D-Penicillamine ($C_5H_{11}NO_2S$) and Nafion solution (5 wt.%) were purchased from Sigma-Aldrich. Bismuth nitrate, potassium hydroxide

* Corresponding author at: College of Chemistry and Life Science, College of Geography and Environmental Science, Zhejiang Normal University, Jinhua, 321004, China. Tel./fax: +86 579 82282269.
E-mail address: ajwang@zjnu.cn (A.-J. Wang).

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and ethanol were obtained from Aladdin Chemistry Co. Ltd (Shanghai, China). N_2 and H_2 were purchased from Yuxin gas manufacture Co. Ltd (Xinxiang, China). All other chemicals were analytical grade and used as received without further purification. All the aqueous solutions were prepared with twice-distilled water in the whole experiments.

2.2. Synthesis

In a typical synthesis, 0.485 g of $Bi(NO_3)_3 \cdot 5H_2O$ and 0.224 g of *D*-penicillamine were put into 35 mL of water under stirring to form a homogeneous solution. The mixture was transferred to a 50 mL Teflon-lined stainless steel autoclave, sealed, maintained at 160 °C for 10 h, and then naturally cooled to room temperature. The precipitates were collected, and completely washed with water and ethanol, respectively, and dried in vacuum at 60 °C.

Controlled experiments were performed only by varying the amount of *D*-penicillamine, the reaction time or temperature, while the other conditions were kept constant.

2.3. Characterization

The scanning electron microscopy (SEM) images were taken with a JEOL -JSM-6390LV field emission scanning electron microscope. The X-ray diffraction (XRD) analysis was recorded by using a Bruker-D8-AXS diffractometer using a Cu Ka source. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were recorded with a JEOL JEM-2100 system at 200 kV accelerating voltage. All TEM and HRTEM samples were prepared by depositing a drop of diluted samples on copper grid coated with carbon film and allowed to dry in air. Fourier Transform Infrared (FT-IR) spectra were obtained from a Spectrum GX spectrometer (PerkinElmer Company, USA).

2.4. Electrochemical experiments

2.4.1. Apparatus

Electrochemical experiments were performed on a CHI 660D electrochemical workstation (CH Instruments, Chenhua Co., Shanghai, China), using a conventional three-electrode cell, where a platinum wire as counter electrode, a saturated calomel electrode (SCE) as reference electrode, and the Bi_2S_3 modified electrodes as working electrode.

2.4.2. Electrode preparation

The working electrode was prepared by dropping 10 μL of a 10 mg/mL suspension on the surface of the GCE and dried in air. Afterwards, 2 μL of a Nafion solution (0.1 wt.%) was spread on the electrode surface. All of the experiments were performed at room temperature in a 5 M KOH solution, and bubbled with nitrogen and hydrogen, respectively.

3. Results and discussion.

3.1. Characterization of the Bi_2S_3 nanoflowers

Fig. 1 shows the typical products prepared in a 35 mL aqueous solution containing 0.485 g of $Bi(NO_3)_3 \cdot 5H_2O$ and 0.224 g of *D*-penicillamine under hydrothermal temperature of 160 °C and reaction time of 10 h. As shown by the representative SEM images, the products are mainly composed of numerous uniform and well-defined flower-like nanostructures (Fig. 1A). The high-magnification SEM image (Fig. 1B) shows that every petal from the flowers contains many nanorods with 3.0-6.0 μm in length and 100-500 nm in diameter.

As displayed by the representative TEM (Fig. 1C) and HRTEM (Fig. 1D) images of the typical products, the lattice fringes are clear and uniform with a value of 0.344 nm (Fig. 1D), which is in good agreement with the (101) lattice spacing of Bi_2S_3 [30]. It reveals that the Bi_2S_3 nanorods in the flowerlike patterns are highly crystalline. This conclusion is also supported by the corresponding selected area electron diffraction (SAED) pattern (Inset in Fig. 1D). The index of the spots in the SAED pattern is also revealed single crystallinity of the resulting nanorods.

As shown in the XRD analysis, all of the diffraction peaks can be perfectly indexed to Bi_2S_3 (Fig. 2, curve c), which are consistent with the standard values (JCPDS card No. 17-0320), suggesting high purity of the product. Furthermore, the strong and sharp diffraction peaks verify good crystallization of the products.

3.2. Effects of the experimental parameters

Different morphologies of the Bi_2S_3 nanostructures were obtained with different molar ratios of Bi^{3+} to *D*-penicillamine by varying the amount of *D*-penicillamine from 0.149 to 0.605 g, while other conditions are kept constant. Nearly no product was obtained when the molar ratio is 2:1. Nevertheless, using the molar ratio of 2:2, many cracker-barrel flowers are appeared, which are composed of many immature sharp needle-like structures (Fig. 3A). Increasing the molar ratio to 2:3, the products contain many Bi_2S_3 flowers with high aspect ratios that are several micrometers in length and less than 500 nm in diameter (Fig. 3B). When the molar ratio is 2:5, there are soccer-like balls with the diameter of 1.0–2.5 μm (Fig. 3C), which are composed of many smaller rods fused together. Meanwhile, there are several smaller flower-like structures left. However, when the molar ratio is 2:8, the products are mainly soccer-like balls (Fig. 3D).

Besides, the morphologies of the products are very sensitive to the hydrothermal temperature, while the other conditions remain unchanged. When the hydrothermal temperature is below 100 °C, nearly no product is obtained. As the temperature is 120 °C, there are many immature flower-like nanostructures with wide size distributions, which contain many tiny petals as building blocks (Fig. 4A). In this case, the quality of the products is very poor, as supported by the XRD analysis (Fig. 2, curve a). With the increase of the temperature to 140 °C, the shape and size of the petals are further growing (Fig. 4B). When the temperature is elevated to 180 °C, only network-like nanoflakes are appeared (Fig. 4C). Some of them were broken into pieces when the temperature is up to 200 °C (Fig. 4D). Moreover, when the temperature is above 140 °C, the products have high purity and good crystalline of Bi_2S_3 (Fig. 2, curve b-e).

To elucidate the growth mechanism of the flower-like Bi_2S_3 nanostructures, we have investigated their temporal morphological evolution by taking SEM images at different reaction time intervals. Fig. 5A illustrates some immature flowers and many petal-like structures as the reaction proceeds to 2 h. And the products mainly have impurity, as verified by the XRD experiments (Fig. S1, curve a, Supporting Information). When the reaction proceeds from 6 to 12 h, individual Bi_2S_3 flower-like patterns mainly grow in the elongated directions, while the density of the petals drops down (Fig. 5B-C). After 16 h, some Bi_2S_3 microspheres are emerged, which are assembled by numerous thin and interconnected nanoflakes (Fig. 5D). Besides, when the reaction time is over 6 h, the products contain Bi_2S_3 nanostructures with high purity (Fig. S1, curve b-e, Supporting Information).

3.3. Possible growth mechanism of the Bi_2S_3 flowers

D-Penicillamine molecules possess many functional groups (e.g. $-NH_2$, $-COOH$ and $-SH$), which have a strong tendency to coordinate with inorganic cations such as Pb^{2+} [29]. Bi^{3+} might coordinate with *D*-penicillamine to form the corresponding complexes like *L*-cysteine [9]. As shown in the FT-IR spectra (Fig. 6, curve a-d), the characteristic peaks of the Bi_2S_3 are gradually intensified and the corresponding peaks of the $-NH_2$, $-COOH$, and $-SH$ become weak by extending the hydrothermal reaction time. The disappearance

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