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Fabrication and characterization of honeycomb-like superstructures consisting of ZnS nanosheets

LI Jun-ping(李军平), XU Yao(徐 耀), ZHAO Ning(赵 宁), WEI Wei(魏 伟), WU Dong(吴 东), SUN Yu-han(孙予罕)

State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China

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Abstract: Honeycomb-like superstructures consisting of ZnS nanosheets with uniform thickness of about 20nm and lateral dimension of several micrometers were built up from in-situ generated ZnS nanoparticles in the presence of ethylene diamine tetraacetic acid and butylamine. The result of HRTEM reveals that the size of the primary ZnS nanoparticles constituting the superstructures is about 2-4 nm. Upon their organization into complex superstructures, the quantum-confined effect of the ZnS nanosheets keeps well. The possible growth mechanism for ZnS superstructures was also proposed.

Key words: ZnS nanosheets; colloidal assemblies; quantum-confined effect; UV-absorption spectroscopy

1 Introduction

In the past decade, the synthesis of nanoparticles with controlled size, structure and morphology has stimulated intensive interest, which is the first step towards realization of functional nanosystems. Recently, much effort has been exerted in exploring the strategies to organize these nanoscale building blocks into ordered assemblies or superstructures and investigating their collective properties [1-8]. To date, some ordered superstructures or complex functional architectures have been constructed through covalent or non-covalent interconnect strategies. YU et al [9] reported the assembly of $BaCrO_4$ and $BaSO_4$ nanofibers toward hierarchical superstructures using sodium polyacrylate as structure directing agent in mineralization process. SHI et al [10] reported the fabrication of $BaCrO_4$ superstructures from inorganic nanobelts in catanionic reverse micelles. Recently, KIMURA et al [11] have also demonstrated the organization of Au nanoparticles into a 3D network structure by a site-exchange reaction. However, there are few reports concerning the assembly of ZnS building blocks into hierarchical nanostructures or superstructures.

As typical semiconductor materials of the II-VI group, ZnS nanocrystals have been widely investigated. Various forms of ZnS nanostructures have been synthesized, including nanoparticles [12, 13], nanowires [14,15], and nanotubes [16]. Recently, YU et al[17] reported the synthesis of $ZnS(NH_2CH_2CH_2NH_2)_{0.5}$ hybrid nanosheets using the solvothermal routes. Hollow ZnS nanospheres have also been synthesized in aqueous solution of a triblock copolymer [18]. Here, we report the synthesis of honeycomb-like superstructures under mild conditions using EDTA as stabilizer and BA as the structure directing agents.

2 Experimental

In a typical synthesis, 1.095 g $Zn(CH_3COO)_2{\cdot}2H_2O$ and 1.60 g EDTA were mixed in 50 mL distilled water, together with 5 mL of BA to form a clear liquid. Following, 50 mL of 0.1 mol·L^{-1} Na_2S aqueous solution was added. The color of the system changed gradually form clear to blue, and finally a white precipitate was obtained. After aged for 24 h at room temperature, the precipitate was filtered and washed thoroughly with hot water and ethanol. To further remove organic residues, the resulting products were dispersed in 100 mL ethanol, followed by solvothermal treatment at 140 ℃ for 24 h. The final products were again filtered, washed with

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Corresponding author: XU Yao; Tel: +86-351-4049859; Fax: +86-351-4041153; E-mail: xuyao@sxicc.ac.cn

ethanol and hexane, and dried in air at 110 ℃. The obtained products were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD). The XRD patterns were recorded using Rigaku Dmax-2000 diffractometer with Cu K_α radiation. SEM was performed on Philips XL30S-FEG apparatus. TEM was recorded on a Hitachi Model H-9000NAR instrument with accelerating voltage of 200 kV. UV-vis diffusion reflection spectrum was collected at room temperature on Shimadzu UV-2501PC using $BaSO_4$ powder as a standard.

3 Results and discussion

Fig.1 shows the typical SEM images of as-synthesized products. It reveals that the product exhibits sheet-like morphology and a large number of sheets are arranged in bundles of honeycomb-like superstructures. A higher magnification SEM image indicates that the superstructures exclusively consist of sheets with a thickness of about 20nm and lateral dimensions of about 1.0 μm (Fig.1(b)). Furthermore, each sheet is built of thin layers in stacks.

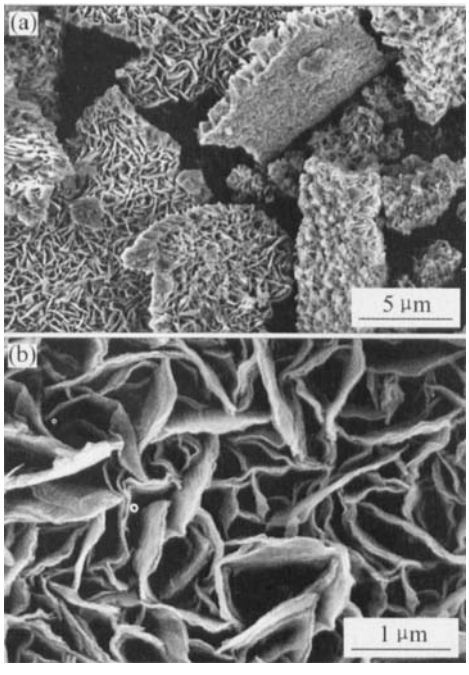

Fig. 1 SEM images of sample: (a) Low magnification; (b) High magnification

The structure and morphology of the products were further characterized by TEM. The TEM studies suggest that the products are composed of sheets with irregular shape, and no other morphology is observed. A top-view of a sheet is shown in Fig.2(a), the sheets are not perfect planes with lateral dimensions of about 1.0 μm. A high magnification image of the sheets (Fig.2(b)) reveals that the sheets are stacked by a few of very thin layers. HRTEM observation (Fig.2(c)) shows that each layer consists of nanosized ZnS grains with diameter of about 2–4 nm, indicating the layer is built up from ZnS nanoparticles. Energy-dispersive X-ray spectroscopy (EDX) of the samples shows that atomic composition ratio of Zn/S is always about 1 ∶ 1, which is in good agreement with that of the stoichiometric composition of ZnS.

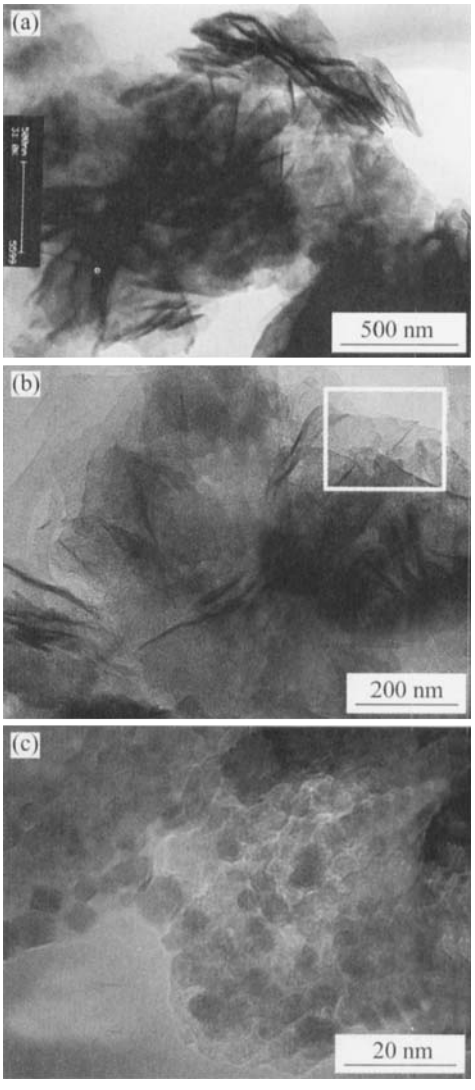

Fig.2 TEM images of sheet: (a) Low magnification; (b) High magnification; (c) High resolution

A typical XRD pattern of the samples is shown in Fig.3. All the peaks can be indexed to the hexagonal ZnS (JCPDS: 36-1450), corresponding to the (100), (002), (101), (102), (110), (103) and (112) crystal planes of wurtzite ZnS, respectively. No extra peaks or any impurities are detected, indicating the high purity of the products.

To examine the optical properties of ZnS superstructures, the room temperature UV-vis diffusion reflection spectrum of the solid powders are shown in