Shape-controlled synthesis of polyhedral CdS flowerlike architectures and their optical properties

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Abstract: Fabrication of polyhedral CdS flower-like architectures have been achieved on a large scale through a mixed solvothermal method. The obtained CdS are characterized by X-ray diffraction, field-emission scanning electron microscopy and transmission electron microscopy, and the results indicate that the CdS flower-like architectures with diameters of 1.5-2.0 μm are hexagonal wurtzite phase and are assembled by some pyramids with the bottom side length of about 440 nm, which have some crystallographic faces. A series of relevant experiments through altering experimental parameters, indicate that the temperature, starting materials and solvent play key roles for the shape evolution of CdS flower-like architectures. The studies of optical properties for polyhedral CdS flower-like architectures indicate that the UV–vis spectroscopy shows a blue-shift absorption peak at 500 nm compared to that of bulk CdS, the photoluminescence spectroscopy shows an emission peak at 640 nm and another strong emission peak at 695 nm, which are believed to be attributed to excitonic emission and deep levels.

Keywords: CdS • Flower-like architectures • Solvothermal synthesis • Field-emission scanning electron microscopy • Optical properties

1. Introduction

A variety of micro/nanostructured semiconductors have been synthesized by solution-based self-assembly due to their unique photoelectric properties and potential applications [1-4], which are size and shape dependent [5,6]. In order to obtain the micro/nanomaterials with specific properties, great efforts have been made to the controlled synthesis of the self-assembled hierarchical structures with different size, morphology and growth pattern [7]. Meanwhile, various applications of hierarchical structures, such as field-effect transistors [8], gas sensors [9], photovoltaic devices [10], electromechanical devices [11] and scanning probe microscopy [12], were studied widely.

As one of the most important II–VI semiconductors, CdS has a Bohr radius of 2.4 nm and direct band gap of 2.42 eV, and has been extensively investigated due to its excellent physical and chemical properties. Recently, CdS displays good performance in in photoelectric conversion [13], light-emitting diodes for flat panel displays [14], photoconductors [15], thin film transistors [16], biological labeling [17], and other fields. Therefore, various fabrication techniques have been used to prepare CdS crystals such as thermal evaporation processes [18], hydrothermal method [19],
chemical vapor deposition [20], sol-gel method [21], thermal decomposition method [22], and solvothermal process [23]. In the solution phase method, organic solvents are often used. For example, Yan et al. used ethylenediamine as the solvent and structure-directing agents to prepare CdS nanowires materials through a solvothermal approach [24]. Xiong et al. used tetraethylenepentamine and distilled water as mixed solvent, and CdS with various novel hierarchical nanostructures were synthesized by adjusting the Cd(Ac)₂/dithizone molar ratio and the volume ratio of H₂O and tetraethylenepentamine [25]. In the gas-phase approach, high temperature or metal-organic precursor is usually required for the synthesis of CdS multipods. For example, high quality, uniform one-dimensional CdS micro/nanostructures with different morphologies are fabricated through a thermal evaporation process at 800 and 850°C [26]. By pyrolyzing Cd(S₂CNEt₂)₂, well-aligned CdS nanotubes were synthesized within the nanochannels of porous anodic alumina membranes [27]. However, most organic solvents are environmentally unfriendly and metal-organic precursors are difficult to access. Most of the synthetic schemes described above required the use of rather complicated procedures or the pre-synthesis of cluster precursors. Therefore, it is necessary to develop a very simple procedure for large scale synthesis, which remains a challenge for chemists and material scientists. In addition, it was suggested that the size, morphology, and micro/nanostructure are very important factors for determining the optical and electronic properties of CdS nanocrystals.

Among these methods, solvothermal method is one of the least expensive and most effective methods for fabricating hierarchical structures. It is well known that solvothermal reaction is the development of hydrothermal reaction. In the liquid or supercritical conditions, reactants dispersing in the solution become more reactive, and products can be prepared slowly. The process is relatively simple and easy to control, and can effectively prevent the volatilization of toxic substances. In the present work, we propose a simple mixed solvothermal approach to synthesize polyhedral CdS flower-like architectures without using any special additives such as cysteamine or polyvinylpyrrolidone (PVP) at 160°C for 12 hours. Advantages of the approach are that there is also no need for post-treatment to get rid of the template materials, the raw materials are economical, and no toxic byproducts are produced. To acquire products with better purity and quality, some reaction conditions have also been investigated. To our best knowledge, there are few reports on polyhedral CdS microstructures. Therefore, the proposed simple and novel method is especially meaningful for the morphological synthesis of CdS and other similar sulfides micro/nanostructures.

2. Experimental procedure

All chemicals used in this work are A. R. regents from the Shanghai Chemical Factory (China). In a typical procedure, 1 mmol of CdCl₂ and 1 mmol of S powder were dissolved in 20 mL ethylene glycol and 20 mL oleic acid to form a mixture solution, and the solution was transferred into a Teflon-lined autoclave with 50 mL capacity. The autoclave was sealed and maintained at 160°C for 12 hours. The system was cooled to room temperature naturally. The final products were yellow precipitates on the bottom of the autoclave, which were repeatedly washed with deionized water and ethanol several times to remove organic and inorganic impurities. Then the samples were dried in a vacuum box at 60°C for 6 hours, and kept for further characterization.

The products were characterized by XRD recorded on a Rigaku (Japan) D/max-γA X-ray diffractometer using Cu Ka graphite-monochromatized radiation (λ=1.54178 Å). FESEM (JEOL JSM-6700F) was employed to observe the morphologies of products. TEM images were taken on a HITACHI-H7650 transmission electron microscope at an acceleration voltage of 200 kV. At room temperature, UV–vis and photoluminescence measurements were carried out on a JGNA Specord 200 PC UV–vis spectrophotometer and a Perkin-Elmer LS-55 luminescence spectrometer using a pulsed Xe lamp, respectively.

3. Results and discussion

The XRD pattern of the products synthesized by a mixed solvothermal method at 160°C is shown in Fig. 1. All diffraction peaks can be well indexed by a hexagonal wurtzite phase CdS with space group P63mc with lattice constants a=4.14 and c=6.72 Å (JCPDS 41-4019). No diffraction peaks from other phases can be detected, which implies a high purity of the obtain products.

The morphology and structure of the products were measured by FESEM and TEM. Fig. 2 shows the images of the CdS products prepared in a mixing solvent of 20 mL ethylene glycol and 20 mL oleic acid at 160°C. The low magnification FESEM image in Fig. 2a indicates that the products are large-scale uniform polyhedral CdS flower-like architectures with
diameters of 1.5-2.0 μm. The detailed morphology was further characterized by high-magnification FESEM. Fig. 2b shows that the flower-like CdS architectures were assembled by some pyramids, and the side length of the hexagonal crystallographic faces is about 440 nm. The TEM images in Fig. 2c also displays that the products are flower-like CdS architectures, and Fig. 2d exhibits individual flower-like CdS architecture with the size of about 2 μm, being consistent from FESEM results.

In order to study the growth process of the flower-like CdS architectures, a series of experiments were designed with different reaction conditions, including the reaction temperature, starting materials and composition of solvent. Reaction temperatures were considered to play a crucial role for the solvothermal growth of crystals. In this process, it should be pointed out that no CdS products were synthesized below 140°C, which implied that the lower reaction temperature is not beneficial to the formation of CdS. Fig. 3 displays the corresponding FESEM images obtained at 140 and 200°C. The results of FESEM reveal that the morphologies of the products are different at different temperatures. When the reaction temperature is 140°C, there are a small amount of yellow products, and the FESEM images are shown in Figs. 3a and 3b. Fig. 3a shows that the products are composed...
of many hexahedral pyramids, which stack together, and the size is difficult to observe. From Fig. 3b, it is found that there are two types of flower-like structures. One has quite large crystallographic faces that are the base of the pyramids, with the side length of about 750 nm; the other has much small crystallographic faces, which is possibly the apex of a pyramid. When the temperature is 160 or 180°C, high yield flower-like CdS architectures will be obtained. Fig. 3c shows a low magnification FESEM image of the products at 200°C. The products are composed of many ball-flowers, but the size is not even, the diameter of ball-flowers is from 0.8 to 4 µm. This is in comparison with the flower architectures at 160°C, where the crystal face of ball-flower at 200°C becomes smaller and the diameter becomes bigger, shown in Fig. 3d. Secondly, the starting materials in the reaction system are also very important factors in determining the shapes of the products. With other conditions kept as constant, the products are composed of nanoplates when CdSO₄ is used as cadmium source. From Fig. 4a, these nanoplates were stacked together and have different morphologies. Fig. 4b shows that the size of the nanoplates is not uniform. When lauryl mercaptan is used as the sulphur source, the products are composed of many ball-flowers, but the size is different, shown in Figs. 4c and 4d. Apart from reaction temperature and starting materials, solvent also plays an important role in the formation of the high yield and uniform flower-like CdS architectures. With other conditions kept as constant, Fig. 5 shows that in the control experiment, different morphologies of the products could be achieved by adjusting solvent. It can be clearly observed that the size and shape of CdS depend on the type of solvent used. Fig. 5a shows the products synthesized in 40 mL ethylene glycol are nanoparticles with diameter of about 30 nm. The products synthesized in 30 mL ethylene glycol and 10 mL oleic acid as solvent (Fig. 5b), are composed of large amounts of flower-like architectures with the size ranging from 0.5 to 2 µm, which is similar to the result in Fig. 2. A FESEM image of the products obtained using 10 mL ethylene glycol and 30 mL oleic acid as solvent (Fig. 5c), displays polyhedral structures,
but the size is not uniform ranging from 0.1 to 1.5 µm. However, those synthesized in 40 mL oleic acid as the solvent (Fig. 5d), have different morphology, which is block structure with macropores. Under solvothermal conditions, the density, viscosity and dispersion of solvents affect the growth of crystals. Additionally, the solvent often acts as a ligand and forms metal complexes with metal ions to reduce the reaction rate. Meanwhile, solvents may be used as adsorbents, and adsorb on a lattice plane to restrain or hinder its growth. Therefore, it is believed that an appropriate solvent is better for the control of morphology and size of the synthesized CdS products.

A lot of research revealed that the morphology and structure of semiconducting materials have great effects on their optical performance. UV-Vis absorption spectroscopy is an important technique to investigate the optical performance of semiconducting materials. Fig. 6 displays UV-vis absorption spectra of the polyhedral CdS architectures dispersed in absolute ethanol. The sample shows an absorption peak at 500 nm that is blue shifted from bulk CdS (512 nm). The reason for the blue shift of band gap energy can be ascribed to the well-known quantum confinement effect [28,29]. The room temperature PL spectra of the polyhedral CdS architectures were measured with the excitation wavelength of 400 nm using a Perkin-Elmer LS-55 luminescence spectrometer. The PL spectrum of the polyhedral CdS flower-like architectures shows two emission bands around 640 and 695 nm in Fig. 7. The peak at 640 nm is excitonic emission, and the peak at 695 nm can be attributed to deep levels associated with the sulfur vacancies, extrinsic defects, or impurities, in agreement with the previous report [30]. The previous reports also revealed that CdS micro/nanostructures usually have two emission peaks corresponding to excitonic and trapped luminescence. Shen studied the PL properties of the deposited CdS multipod-based structures with two emission bands. The intense peak at 505 nm is due to the near-band-edge emission of CdS and the low intense broad emission at 670 nm can be connected with the structure defects, ionized vacancies, or impurities [31]. Zhao et al. displayed the PL spectrum of netted spherelike CdS nanostructures, which holds a
broad emission peak at 570 nm from excitonic emission, and a weak shoulder peak at 610 nm connected with deep levels [32]. However, the positions of emission peaks are often different because of the different shapes, sizes and phases of the semiconductor micro/nanostructures.

4. Conclusions

In summary, polyhedral CdS flower-like architectures has been successfully fabricated through a facile solvothermal route using ethylene glycol and oleic
acid as mixed solvents. The polyhedral CdS flowerlike architectures with diameters of 1.5-2.0 µm were self-assembled by some hexagonal pyramids. The influencing factors of shape evolution were investigated and discussed, including reaction temperature, composition of solvent and starting materials. UV-vis absorption spectra of polyhedral CdS architectures reveal that the absorption peak at 500 nm with blue-shift from bulk CdS can be ascribed to quantum confinement effect. The PL spectrum of the polyhedral CdS flowerlike architectures displays a weak emission band at 640 nm, and a strong emission band at 695 nm from deep levels.

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