Cent. Eur. J. Chem. • 8(5) • 2010 • 1027–1033
DOI: 10.2478/s11532-010-0075-2

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Central European Journal of **Chemistry**

Synthesis and optical properties of self-assembled flower-like CdS architectures by mixed solvothermal process

Research Article

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Received 18 January 2010; Accepted 4 May 2010

Abstract: Self-assembled CdS architectures with flower-like structures have been synthesized by a mixed solvothermal method using ethylene glycol and oleic acid as the mixed solvent at 160°C for 12 h. The results of X-ray diffraction (XRD) patterns, field-emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) images indicate that the product exists as the hexagonal wurtzite phase and conatins of larger numbers of flower-like CdS architectures with diameters of 1.8-3 μm. The selected-area electron diffraction (SAED) pattern and the high resolution transmission electron microscope (HRTEM) image reveal that the grain has better crystallinity. The optical properties of flower-like CdS architectures were also investigated by ultraviolet–visable (UV–vis) and photoluminescence spectroscopy at room temperature. A strong peak at 490 nm is shown in the UV-vis absorption, while an emission at 486 nm and another strong emission at 712 nm are shown in the PL spectrum.

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

1. Introduction

It is generally believed that the properties of nanomaterials depend not only on their chemical composition, but also on their structures, including phases, sizes, size distributions, shape, and dimensionality [1-5]. To date, a wide variety of inorganic materials, including metal, metal oxide, sulfide, hydrate, and other minerals, have been successfully prepared with nanostructures [6-11]. During the past few decades, much attention has been focused on nanocrystals and one-dimensional (1D) nanostructures, owing to their fundamental significance in investigating the dependence of various physical properties on dimensionality and size reduction as well as their potential applications in the fabrication of electronic, optoelectronic, electrochemical, and electromechanical devices with nanoscale dimensions. Recently, morphology–controlled synthesis and self-assembly of nanoscale building blocks into three-dimensional (3D) complex architectures have been a research hot spot. Some groups have fabricated diverse architectures with nanoparticles, nanorods, or nanosheets as building blocks [12-14]. It is expected that if the morphology and assembly mode of original building units can be controlled, their secondary architecture would be adjustable to meet different needs. Therefore, the work on morphology-controlled and organization-designed syntheses needs to be developed for more novel properties and applications of nanomaterials.

Semiconductor nanostructures play important roles in many areas of modern science and technology, especially in nanoscale photonic and electronic devices, such as direct-current nanogenerators, light-emitting diodes, polarization sensitive photodetectors, and optically and electrically driven lasers [15-19]. Various morphologies of semiconductor nanostructures

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have been reported, including nanowires, nanobelts, nanocombs, nanosprings, nanorings, nanotubes, and nanodots [20]. Among semiconductors, cadmium sulfide (CdS) is a well-studied semiconductor with a direct band gap of 2.42 eV at room temperature, and is a vital photoelectric material and an efficient absorbing material for solar cells. Therefore, various CdS nanostructures, including nanowires, nanotubes, and nanobelts, have been synthesized by many methods [21-27]. Du and coworkers reported the syntheses of CdS nanorods with Na_2S and ethylenediamine (EDA) by solvothermal method [28]. Yao *et al.* reported the controlled synthesis of CdS and CdSe nanoflowers, branched nanowires, and nanotrees with wurtzite structure by a solvothermal approach in a mixed solution [29]. Xie *et al.* have reported kinds of branch-like CdS mircopatterns in a methanol/water system [30]. It has been demonstrated that the hydrothermal and solvothermal techniques are effective methods to prepare low-dimensional nanomaterials of sulfides. However, it remains a significant challenge to develop controlled and effective methods for the large-scale syntheses of novel hierarchical structures assembled from independent and discrete nanobuilding blocks.

In the present work, the mixed solvothermal synthesis of flower-like CdS architectures was reported at 160°C for 12 h. The flower-like architectures are assembled by some smaller grains with an average diameter of about 50 nm. To our best knowledge, there are few reports on the CdS microstructures with complex morphology, such as the self-assembly of flower-like CdS architectures. Therefore, the described simple and novel method is especially significant for further morphological syntheses of CdS and similar sulfide based nano- and microstructures.

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 $CdCl_2$ and 1 mmol of NH_2CSNH_2 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 different temperatures (140°C-220°C) for 12 h to obtain different products. The system was allowed to cool to room temperature without any cooling equipment. The final products were yellow, and had precipitated out of solution and collected on the bottom of the autoclave. These samples were repeatedly washed with deionized water and ethanol several times to remove organic and inorganic impurities. Then the samples were dried in a vacuum at 60°C for 4 h and kept for further characterization.

The products were characterized by XRD, recorded on a Rigaku (Japan) D/max-γA X-ray diffractometer, equipped with graphite-monochromatized Cu Kα radiation (λ=1.54178 Å). FESEM (JEOL JSM-6700F) was employed to observe the morphologies of products. TEM, HRTEM images and SAED pattern were taken on a Hitachi H-800 transmission electron microscopy and a JEOL 2010 high resolution transmission electron microscope performed at 200 kV. Energy dispersive X-ray spectroscopy (EDS) analysis was carried out on an X-ray energy spectrum instrument equipped with INCA300 (Oxford). 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

Fig. 1 shows the XRD pattern of the product synthesized at 160°C for 12 h. It can be seen that all diffraction peaks can be indexed as the hexagonal wurtzite phase (space group $P6_3mc$) of CdS with lattice constants α=4.14, c= 6.72 Å, which is very consistent with the values in the standard card (JCPDS 41-4019). No peaks related to Cd, CdO and other cadmium compound are observed, indicating the high purity of the final product. Relatively broaden peaks signify that the CdS grains are small in size. The diameters of the grains are about 50 nm, as estimated by the Scherrer formula.

FESEM was employed to characterize the morphology of the CdS product prepared at 160°C for 12 h, as shown in Fig. 2. Panoramic FESEM images

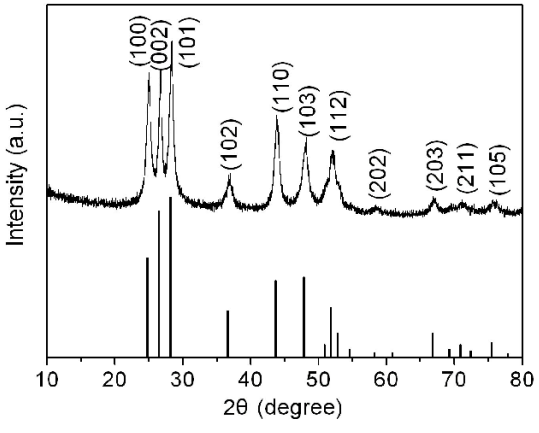

Figure 1. XRD pattern of the flower-like CdS architectures obtained at 160°C for 12 h.

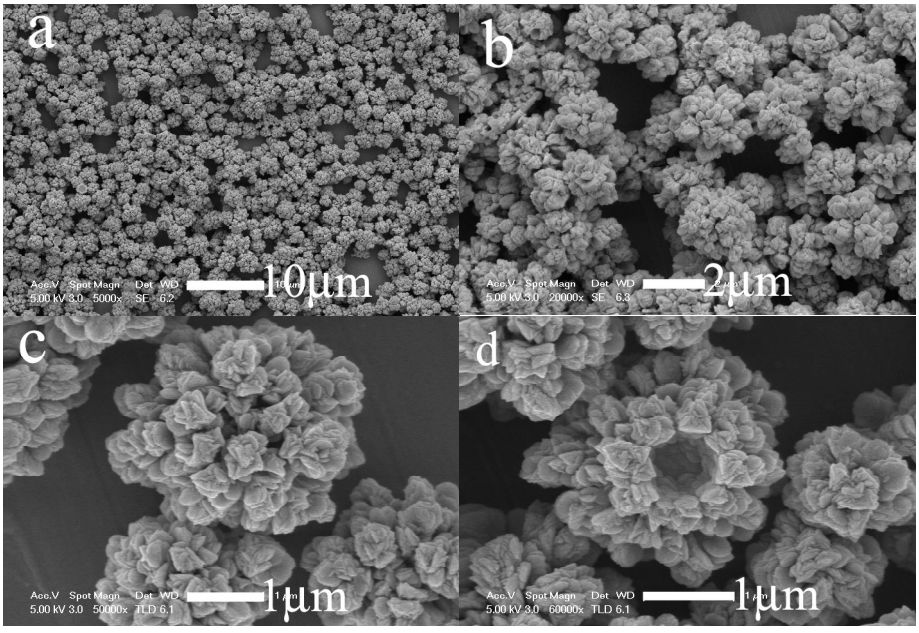

Figure 2. FESEM images of the flower-like CdS architectures obtained at 160°C for 12 h: (a) and (b) low magnification FESEM images; (c) and (d) high magnification FESEM images.

(Figs. 2a and 2b) confirm the large-scale production of uniform 3D flower-like architectures with diameters of 1.8-3 μm, and the yield is almost 100%. In order to calfiry the CdS structures, high-resolution FESEM images, as shown in Fig. 2c clearly reveal that the flower-like CdS architectures are assembled by some smaller grains. In addition, it can be seen that the CdS architectures are hollow structures from Fig. 2d.

More details of the flower-like CdS structures were investigated by TEM, SAED and HRTEM. From the TEM images, a lot of flower-like CdS architectures can be seen in Fig. 3a, which is in agreement with the FESEM result (Fig. 2). Fig. 3b shows a TEM image of an individual structure. The TEM analysis of the selected area of Fig. 3b in Fig. 3c and the SAED pattern (inset in Fig. 3b), indicates that there are some grains together. Fig. 3d is the HRTEM image of the edge of the gains in Fig. 3c, which indicates that the measured space of the lattice fringes is 0.33 nm, corresponding to the (002) plane of wurtzite phase CdS. The results of HRTEM images and SAED pattern indicate that the grain has better crystallinity. In Fig. 3e, the results of EDS confirm that Cd and S elements are presented in the sample, and the signals of elemental Cu come from the supporting TEM grid during measurements.

A series of relevant experiments have been carried out by altering experimental temperature to investigate the shape evolution of the flower-like CdS structures, the results indicate that the temperature plays a key role. The temperature course of reaction is studied by means of FESEM images. CdS could not be obtained under 140°C, with other reaction conditions remaining constant, which indicates that the growth process of CdS needs a more energy. Figs. 4a-4e show a series of FESEM images in the morphologies at different reaction temperatures corresponding to 140, 160, 180, 200, and 220°C, respectively. From the results of FESEM shown in Figs. 4a-4j, it is found that the products have different morphologies at different temperature. Flower-like structures can be assembled from 140°C to 180°C, and the diameters of the architectures are 1-3 μm, which are shown in Figs. 4a-4f, but the size and morphology of the flower-like CdS architectures obtained at 160°C are more uniform than those of the products obtained at 140 and 180°C. Figs. 4g-4j shows that the products are flower-like structures when reaction temperatures are increased to 200 and 220°C. The flowers are not assembled to architectures, because the size is also bigger than those of the products at low temperatures. In addition, the XRD results (shown in Figs. 5a-5d) indicate that the crystallinity of the product is improved and the size of the product is bigger at higher temperature. As we know that the nucleation rate of CdS and spatial hindrance effect the self-assembly of architectures. At lower temperature, the reactants have bad dispersion and centralize the underside of the system due to the higher viscosity of solvent, which also confines the crystal nucleus to grow bigger. In addition, the nucleation rate is lower at lower temperature. So there is enough product and time to assemble to flower-like CdS architectures

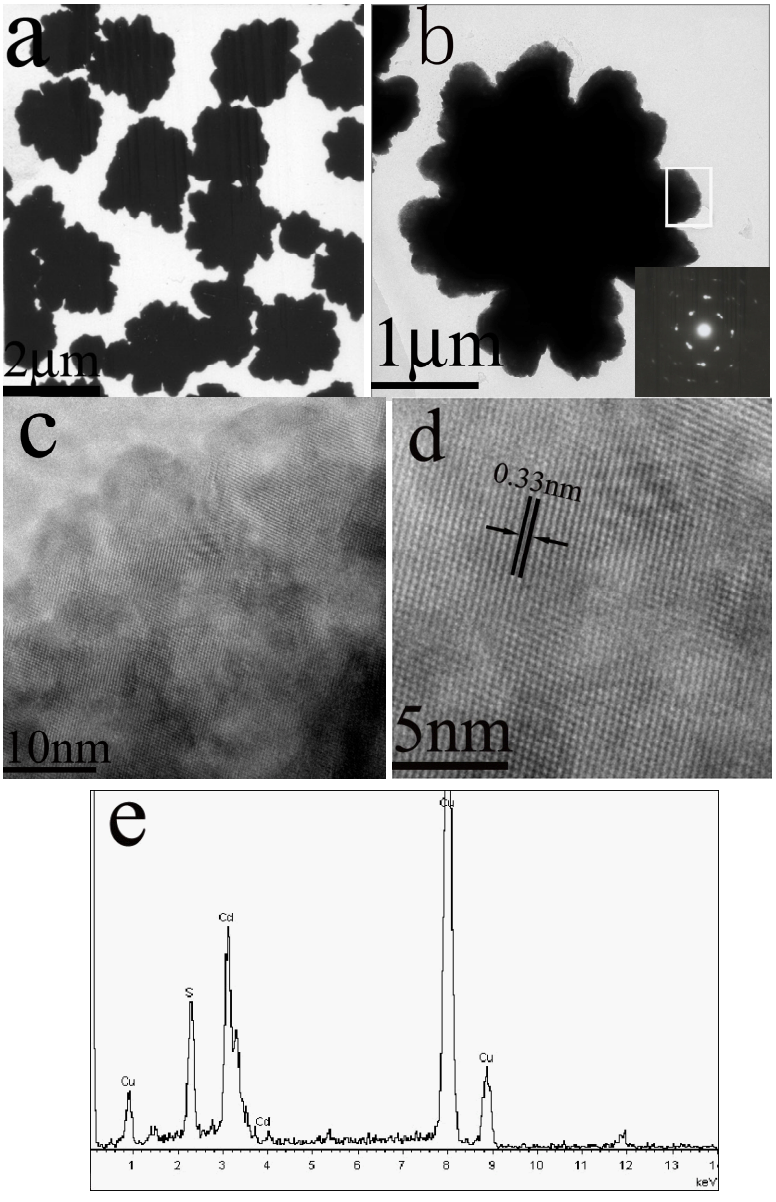

Figure 3. (a) TEM image of flower-like CdS architectures; (b) TEM image of a flower-like CdS architecture, and its SAED pattern (inset); (c) high resolution TEM image of the selected area in Fig. 2b; (d) HRTEM image of the edge of a petal in Fig. 3c; (e) EDS spectrum of the flower-like CdS architecture.

because of the higher viscosity and lower nucleation rate. According to the experimental results, flower-like CdS architectures could be formed when the reaction temperature ranged from 140°C to 180°C, and 160°C was the optimal temperature for the growth of flower-like CdS architectures with well defined morphology and uniform size. At higher temperature, for example 200°C and 220°C, the crystals can grow freely because of the higher growth rate and the lower viscosity of solvent, which results in larger crystal growth in a short time. Due to greater spatial hindrance, flower-like CdS architectures were not assembled at these higher temperatures.

The difference in optical properties for different morphologies of CdS structures has attracted significant attention recently. The room temperature UV-vis absorption of the flower-like CdS architectures is recorded and shown in Fig. 6b. The sample was dispersed in absolute ethanol by an ultrasonic disperser. The absorption peak of the flower-like CdS architectures is at 490 nm, which shows a blue-shift compared with that of bulk CdS (512 nm) in Fig. 6a. This indicates the presence of the quantum confinement effect, which is similar to those in previous reports [31,32]. The PL spectrum of bulk CdS and the flower-like CdS

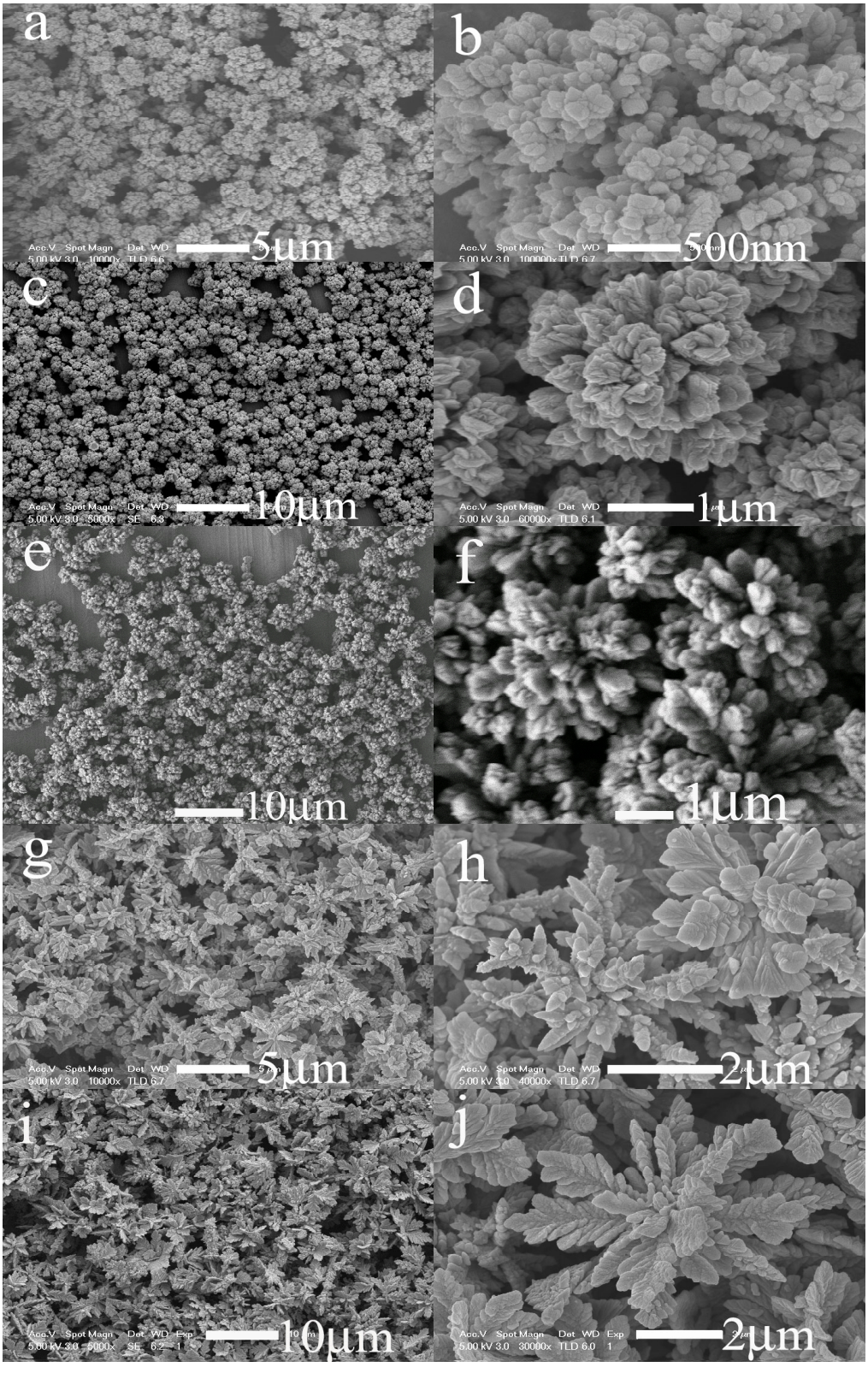

Figure 4. Different magnification FESEM images of the products with the temperatures: (a) and (b) 140°C; (c) and (d) 160°C; (e) and (f) 180°C; (g) and (h) 200°C, (i) and (j) 220°C respectively.

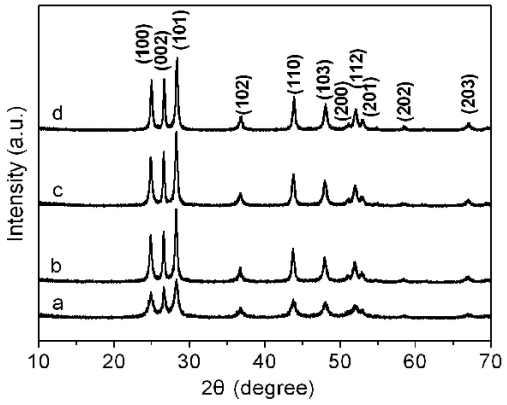

Figure 5. XRD patterns of the products with the temperatures: (a) 140°C; (b) 180°C, (c) 200°C, and (d) 220°C, respectively.

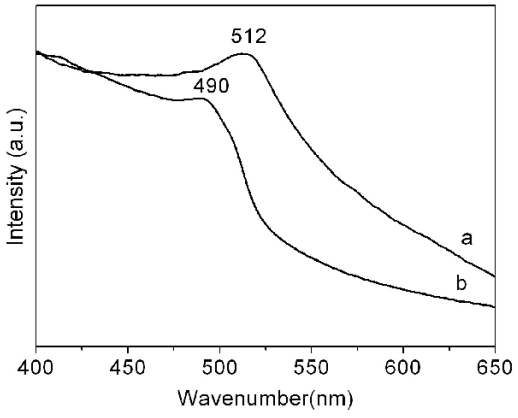

Figure 6. UV–vis absorption spectrum at room temperature: (a) bulk CdS; (b) the flower-like CdS architectures.

architectures exited at 400 nm, as shown in Fig. 7. The PL spectrum of the flower-like CdS architectures shows two emission bands around 486 and 712 nm in Fig. 7b, respectively. The emission peak around 486 nm might be assigned to electron-hole recombination of CdS [33]. The discrepancy of 486/490 nm peak position in PL/absorption spectra is probably due to the insufficient accuracy of peaks that are broad and have different line shape. The emission peak at 712 nm might be attributed to the self-activated emission of CdS, in agreement with previousl reports [34,35]. In the past several years, the luminescence mechanisms of CdS nanostructures have been extensively studied. Usually, two emissions are observed from CdS semiconductor nanostructures, excitonic and trapped luminescence. Shen reported that two emission bands were observed in the PL spectrum of CdS multipod-based structures [36]. In the results, the intense peak is at 505 nm because of the near-band-edge emission of CdS, whereas a very low

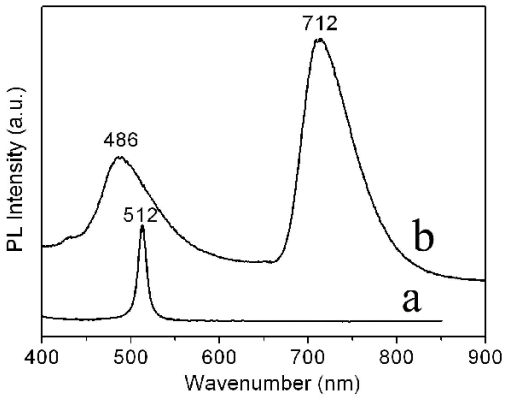

Figure 7. PL spectrum at room temperature: (a) bulk CdS; (b) the flower-like CdS architectures.

intensity broad peak centered at 670 nm is attributed to the structure defects, ionized vacancies, or impurities. Zhao *et al*. reported the photoluminescence properties of netted sphere-like CdS nanostructures with a broad emission peak at 570 nm and a weak shoulder at 610 nm associated with the sulfur vacancies, extrinsic defects, or impurities [37]. Differences in optical properties have been researched widely, and the results indicate that they mainly come from different shapes, sizes and phase structures of the semiconductor nanocrystals.

4. Conclusions

In summary, 3D flower-like CdS architectures with diameters of 1.8-3 μm were synthesized via a simple mixed solvothermal procedure. It was found that the reaction temperature played an important role in the shape evolution of the flower-like CdS architectures. The UV-vis absorption shows an strong peak at 490 nm with a blue-shift compared to that of bulk CdS (512 nm). The PL spectrum of the 3D flowerlike CdS architectures shows one weak emission at 486 nm and another strong emission at 712 nm, which comes from the electron-hole recombination and the self-activated emission of CdS, respectively.

Acknowledgements

This work was supported by National Natural Science Foundation of China (No. 20901072), natural science fund of university in Jiangsu (09KJD430006) and start fund for advanced professionals of Jiangsu University of Science and Technology (No.35060810).

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