

Poly (vinyl alcohol)-assisted solvothermal growth of CdS dumbbells and necklaces

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Abstract Novel dumbbell-like and necklace-like CdS was synthesized via a facile solvothermal route using poly (vinyl alcohol) as assistant agent. The as-prepared samples were characterized by X-ray diffraction, scanning electron microscopy, and photoluminescence spectrophotometer. Based on time-resolved experiments and comparative experiments, a possible nonequilibrium–equilibrium growth mechanism was initially proposed.

Keywords Semiconductor · Nanostructures · Chemical synthesis · Crystal growth

Introduction

As one of the most important II–VI group semiconductors, CdS is now widely used in photoelectric conversion for solar cell [1], in light-emitting diodes for flat panel display [2], and in photocatalyst for chemical reaction [3] based on its special properties. During the past decades, much effort has been focused on the synthesis of CdS with specific size and morphology [4–6]. Compared with the size control, the morphology control is more difficult to realize by classical chemical routes. In the past few years, shape-controlled growth of CdS is successful in some reports,

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such as multi-armed CdS [7], branch-like CdS micropatterns [8], and CdS nanoflowers and nanotrees [9]. However, it is still necessary to design and develop new route to fabricate other novel CdS structures for their wide applications.

In this article, a convenient solvothermal route using poly (vinyl alcohol) (PVA) as assistant agent was explored to synthesize CdS dumbbells and necklaces. Time-resolved experiments and comparative experiments were carried out to show the growth history of CdS, and a possible growth mechanism was preliminarily proposed and discussed.

Experimental section

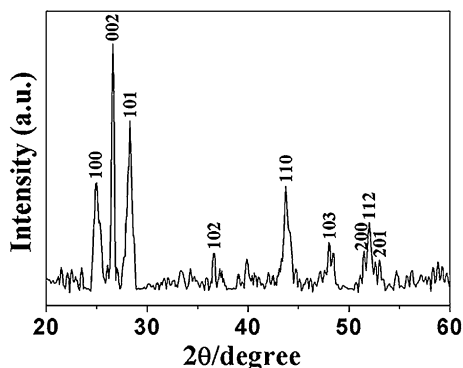
All chemicals are analytical grade and used without further purification. In a typical procedure, 1 mmol $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$, 2 mmol thioglycolic acid (TGA), and 0.1 g PVA were put into a 50 mL Teflon-lined autoclave, and then 40 mL distilled water was added into the autoclave as solvent. The autoclave was sealed and maintained at 150 °C for 72 h and then cooled to room temperature naturally. Yellow precipitates were rinsed several times with deionized water and absolute alcohol. And, the product was dried at 50 °C for 10 h.

X-ray diffraction (XRD) analysis was performed on a Rigaku D/max-rb with Ni-filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). A JEOL JSM-6380LA scanning electron microscope (SEM) was used to examine the morphology of the samples. IR spectrum was taken on a Bruker Vector-22 FTIR spectrometer. Photoluminescence (PL) spectrum was recorded on an Edinburgh FLS920 luminescence spectrophotometer.

Results and discussion

Figure 1 shows the XRD pattern of the as-prepared product. All the strong diffraction peaks in Fig. 1 can be indexed to hexagonal wurtzite CdS phase with lattice constants $a = 4.132 \text{ \AA}$ and $c = 6.733 \text{ \AA}$, which are in good agreement with those in JCPDS Card 653414. No other impurities can be detected, indicating the high purity of the product.

Fig. 1 XRD pattern of the resultant product



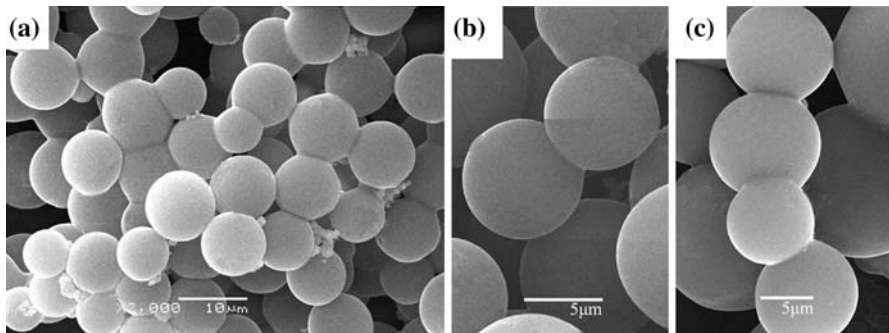


Fig. 2 SEM images of the product: **(a)** general view **(b)** typical dumbbell-like CdS microparticles, **(c)** typical necklace-like CdS microparticles

Figure 2 shows the typical SEM images of CdS sample obtained using PVA as an assistant agent. Microparticles with smooth surface can be clearly observed. In Fig. 2a, the sample consists dominantly of well-defined dumbbell- and necklace-like CdS microparticles, which is particularly true in Fig. 2b and c. The diameter of the particles ranges from 7.5 to 10 μm . The difference in the number of CdS microparticles results in the morphology of dumbbells and necklaces. In addition, some spherical nanoparticles can also be observed in the sample.

The room-temperature PL spectrum of CdS microparticles is shown in Fig. 3. Under the excitation of 400 nm, the microparticles emit green light at 546 nm, which can be ascribed to the near-band-edge emission resulted from the combination of electron and hole [10]. The result is similar to Xu's report [11], while there is considerable red shift compared to those of bulk CdS material and CdS nanowires [12]. The broadened PL peak in Fig. 3 is caused by the wide size distribution of CdS product.

In order to investigate the morphology evolution of dumbbell- and necklace-like CdS microparticles, time-resolved experiments were carried out. The SEM images of the as-prepared samples are illustrated in Fig. 4, depicting clearly the formation process of CdS microparticles. When the solvothermal reaction was conducted at 150 $^{\circ}\text{C}$ for 10 h, the sample was mainly composed of near-spherical CdS particles of 1–3 μm in diameter, as shown in Fig. 4a. The inset in Fig. 4a clearly shows the rough surface of the particles. As the reaction time reached 24 h, the CdS dumbbells and necklaces began to occur, but many defects can be observed on the surface of microparticles, as can be seen in Fig. 4b. The inset in Fig. 4b shows the initial formation of a CdS dumbbell. Extending the reaction time to 48 h, the defects on the surface of the particles reduced greatly (Fig. 4c). After 72 h reaction, most of the particles coalesce into dumbbells and necklaces with smooth surface, as shown Fig. 4d.

In order to explore the influence of PVA and TGA during the formation process of CdS dumbbells and necklaces, five comparative experiments were carried out. The results of the comparative experiments are listed in Figs. 5, 6, and 7.

Fig. 3 PL emission ($\lambda_{\text{ex}} = 400 \text{ nm}$) spectrum of the as-synthesized CdS

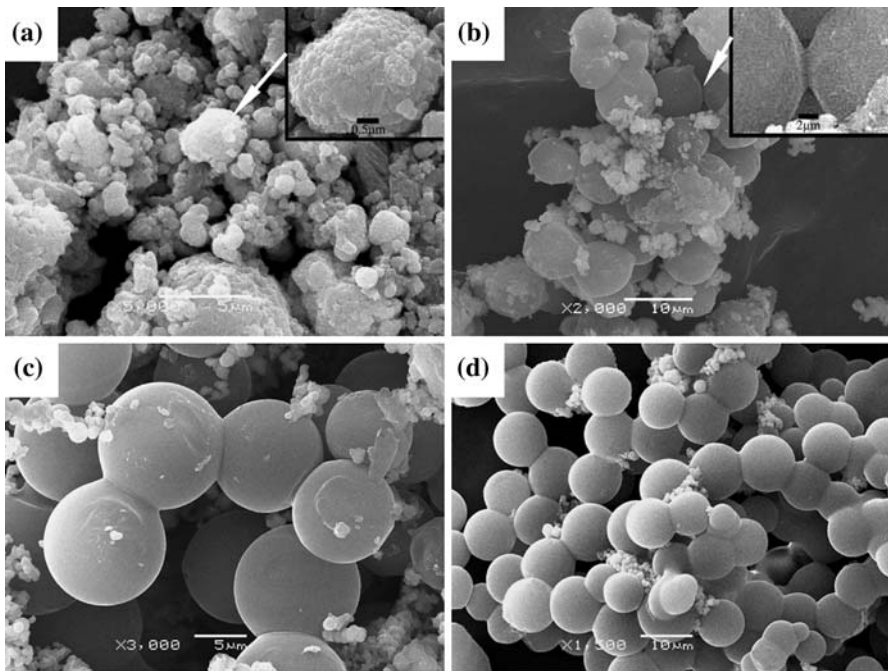
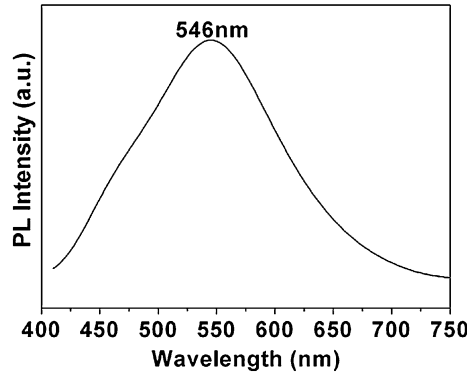


Fig. 4 SEM images of the samples obtained from a series of parallel reactions for different durations: (a) 10 h, (b) 24 h, (c) 48 h, and (d) 72 h. *Insets* in (a) and (b) are the high magnification images of the sites pointed by *white arrow*

When PVA was absent while other experimental conditions were kept unchanged, the product was composed of CdS microspheres with rough surface and diameter ranging from 1 to 3 μm , as can be seen in Fig. 5a. When PVA was increased to 0.5 g, only irregular microparticles composed of several over-merged microspheres were obtained, as shown in Fig. 5b. Thus, the appropriate addition of PVA is important for the formation of CdS dumbbells and necklaces.

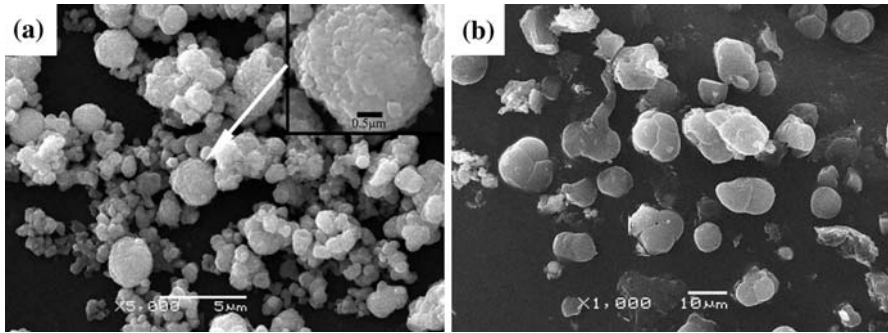


Fig. 5 SEM images of CdS products synthesized by using different amount of PVA: (a) 0 g, (b) 0.5 g. The *inset* in (a) is the high magnification image of the sites pointed by *white arrow*

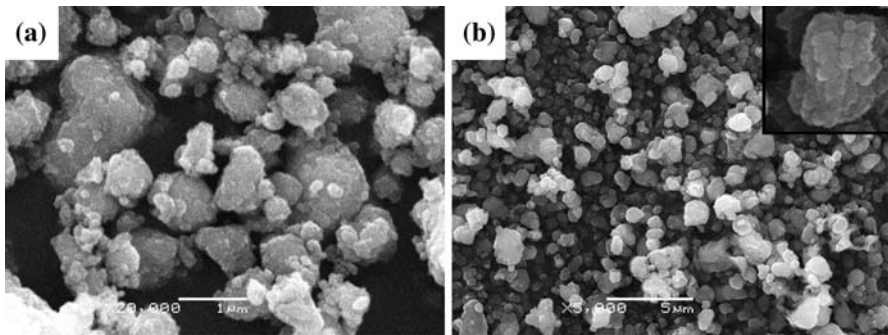


Fig. 6 SEM images of CdS products obtained with different polymers assistant: (a) poly (ethylene glycol), (b) polyvinylpyrrolidone. The *inset* in (b) is the high magnification image

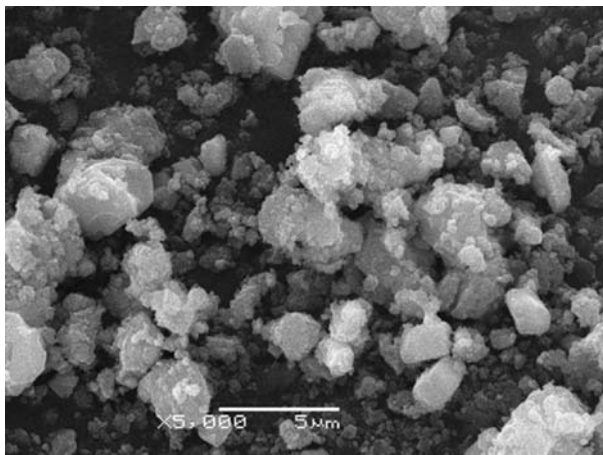
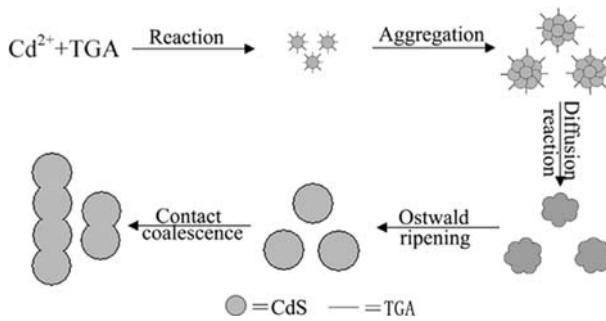


Fig. 7 SEM images of CdS product synthesized by using sodium sulfide instead of TGA



Scheme 1 Proposed growth process of CdS dumbbells and necklaces

When using poly (ethylene glycol) and polyvinylpyrrolidone instead of PVA, while other experimental were kept unchanged, the SEM images in Fig. 6 show that both products are composed of CdS irregular particles with rough surface and diameter ranging from 300 nm to 2 μm , which is similar to that synthesized without PVA (Fig. 5a). Thus, the PVA with hydroxyl groups has very important role.

When TGA was replaced by sodium sulfide, while other experimental conditions were kept unchanged, the product was also composed of CdS microspheres, as shown in Fig. 7. Therefore, both PVA and TGA are necessary for the formation of CdS dumbbells and necklaces with smooth surface.

According to the above experimental results, a possible nonequilibrium–equilibrium growth mechanism of CdS dumbbells and necklaces could be proposed. As shown in Scheme 1, at the early stage of reaction, C–S bonds in TGA are gradually broken, and the S^{2-} released combines with Cd^{2+} to form the initial CdS particles. Due to the strong interaction between CdS surface and S atoms in TGA, the residual TGA can effectively caps on the surface of CdS particles, leading to the non-equilibrium growth of CdS. Afterwards, these capped CdS particles aggregate owing to the H-bond interaction among TGA. With the prolongation of reaction time, the number of TGA on the surface of CdS particles is exhausted gradually, but there are some PVA with hydroxyl group surrounding CdS particles. At this time, the growth of CdS particles changes from the non-equilibrium growth to an equilibrium one. During the equilibrium growth, diffusion-control reaction first occurs in CdS aggregation [13], giving rise to the formation of spherical CdS microparticles with rough surface. At the same time, Ostwald ripening effect also promotes the decrease of small particles and the growth of big particles [14]. Meanwhile, the H-bonds among PVA capped on CdS microparticles cause the adjacent microparticles contact mutually and begin to coalesce. Moreover, the rough surface becomes smooth. And, finally, the CdS dumbbells and necklaces are formed.

Conclusion

In summary, CdS dumbbells and necklaces have been synthesized successfully via a solvothermal route using PVA as an assistant agent. A nonequilibrium–equilibrium

growth mechanism was proposed for elucidating the formation of dumbbells and necklaces. The reaction of PVA with TGA provides an appropriate condition for the growth of CdS dumbbells and necklaces. This facile approach is expected to be extended to fabricate other novel semiconductor microparticles by selecting appropriate assistant agents.

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