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Preparation of CdS microtrumpets from a solvent extraction system by a two-phase approach

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ABSTRACT

CdS microtrumpets with the length being of about 4 μm and the bell wall being of 100 nm have been prepared using a cadmium di-(2-ethylhexyl) phosphoric acid chelate as the precursor by a two-phase thermal approach. The products were characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and UV–vis spectroscopy. The effects of temperature, reaction time, and co-surfactant on the morphology were also examined. It was found that the co-surfactant triethanolamine plays a crucial role in the formation of the cubic phase trumpet-like CdS microstructures.

1. Introduction

Owing to their unique electronic and optical properties, CdS nanomaterials have been extensively researched over the past two decades [1,2]. Many CdS nanocrystals such as nanorods [3], nanowires [4], nanotubes [5] and complex nanostructures [6,7] were prepared by various methods. The two-phase thermal approach has also been proved to be a feasible route for the preparation of monodisperse CdS nanocrystals [8–10].

Di-(2-ethylhexyl) phosphoric acid (HDEHP), as a kind of important extractants, has been widely used for the extraction and separation of rare earths and transition metals. Recently, HDEHP has also been used in the preparation of the nanomaterials. Li [11] and Sun [12] successfully synthesized some CeF_3 and Cu nanoparticles using HDEHP as the surfactant and protector for the nanoparticles, respectively. Combining the extraction systems and the two-phase approach would provide a new way for the preparation of nanomaterials, which would shorten the process from the metal separation to the material synthesis. Here we present the preparation of trumpet-like CdS microstructures from an extraction system of HDEHP by a two-phase thermal approach. The effects of the factors on the morphology of the products were examined and a possible formation mechanism was also proposed.

2. Experimental

2.1. Materials

Triethanolamine, diethanolamine, NaOH, HCl, $NH_3{\cdot}H_2O$ were purchased from Beijing Chemical Corporation. Thiourea was obtained from Aladdin. Triethylamine was purchased from Tianjin No. 2 Chemical Reagent Factory. Pentaerythritol was purchased from Tianjin Fuchen Chemical Reagent Factory. Trihydroxymethyl aminomethane was obtained from Tianjin Guangfu Fine Chemical Research Institute. Toluene was purchased from Sinopharm Chemical Reagent Limited Corporation. $CdCl_2{\cdot}2.5H_2O$ was obtained from Beijing Kehua Special Reagent Development Center. All chemicals were of analytical grade and used without further purification. Di-(2-ethylhexyl) phosphoric acid was kindly supplied by Shanghai Rare-earth Chemical Limited Corporation.

2.2. Preparation of cadmium di-(2-ethylhexyl) phosphoric acid ($Cd(DEHP)_2$)

$Cd(DEHP)_2$ was prepared using the acid-base reaction of HDEHP and $Cd(OH)_2$ [13,14]. $Cd(OH)_2$ was freshly prepared by mixing $CdCl_2$ (50 mL, 0.1 mol/L) with excess aqueous ammonium hydroxide (2.5 mL, 5 mol/L). The $Cd(OH)_2$ precipitate was filtered and thoroughly washed with water to remove excess aqueous ammonium hydroxide and then added directly to a biphasic system containing water (50 mL) and a solution of HDEHP in n-heptane (50 mL, 0.2 mol/L) in a separating funnel. The resulting mixture was shaken at 30 °C for 30 min and kept for phase

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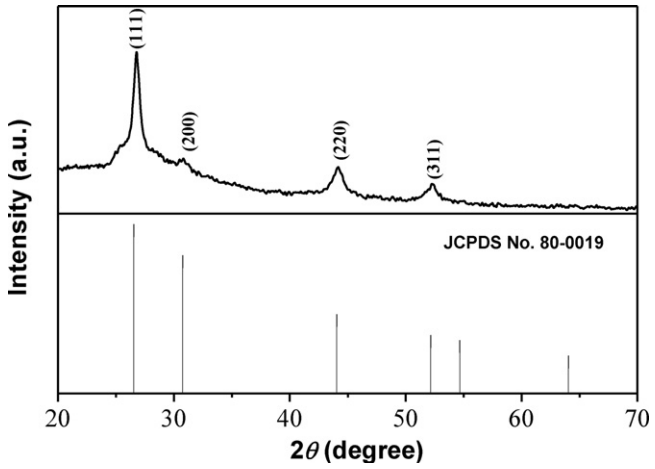

Fig. 1. Powder XRD pattern of the as-prepared CdS microtrumpets.

separation for 2 h. The aqueous phase was then removed, together with any excess $Cd(OH)_2$ at the interface. The organic phase was concentrated using a rotary evaporator to obtain a viscous gel of $Cd(DEHP)_2$ and then dried in vacuum at 80 °C for 48 h. The solution of $Cd(DEHP)_2$ (0.05 mol/L) was obtained by dissolving 1.90 g $Cd(DEHP)_2$ in 50 mL toluene.

2.3. Preparation of CdS

Typically, 0.5 mL thiourea aqueous solution (0.2 mol/L), 3.0 mL triethanolamine aqueous solution (0.1 mol/L), and 2.3 mL H_2O were loaded into a 20 mL Teflon-lined stainless-steel autoclave. And then 0.7 mL $Cd(DEHP)_2$ solution (0.05 mol/L in toluene) and 1.5 mL toluene were transferred into the autoclave without any stirring. The autoclave was sealed and heated at 150 °C for 6 h. After reaction, the autoclave was cooled down to room temperature with tap water.

2.4. Characterization

The yellow products were precipitated and washed with absolute ethanol for several times. The SEM samples were prepared by dropping a drop of the product in ethanol on a silicon substrate. The TEM samples were prepared by dropping the diluted ethanol solution onto 400-mesh carbon-coated copper grids. The copper grids were dried in air naturally.

The powder X-ray diffraction (XRD) was determined using a D8 Focus diffractometer (Bruker) with Cu *K*α radiation (λ = 1.5405 Å) and a scanning rate of 10°/min. UV–vis spectra were recorded on a UV–vis-NIR spectrophotometer (HITACHI U-4100). Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) pattern were recorded using a JEM-2011 microscope with an accelerating voltage of 100 kV. The morphology of the samples was inspected using a field emission scanning electron microscopy (HITACHI S-4800).

3. Results and discussion

The crystalline phase of the as-prepared product was identified by powder X-ray diffraction (XRD). As shown in Fig. 1, the peaks of the XRD pattern can be indexed to the cubic phase (space group: *F*-43*m* (2 1 6)) of CdS with lattice constant *a* = 5.773 Å (JCPDS 80-0019).

The morphology of the as-prepared CdS samples were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As shown in Figs. 2 and 3, the products were some trumpet-like CdS structures with the length being of 3–5 μm and the ring wall being of 100–120 nm. The cavities of the trumpets can be easily observed. It is found that the surface is not smooth and the trumpet is composed by some small particles. Selected area electron diffraction (SAED) pattern on a single trumpet (Fig. 3b) also indicates a polycrystalline sample.

To investigate the effect of temperature on the morphology of CdS, the preparations were also repeated at 130 °C and 180 °C. As shown in Fig. 4, compared to those obtained at 150 °C, only a few trumpet-like products can be obtained along with some nano/micro-particles at 130 °C. When the reaction temperature is increased to 180 °C, no trumpets can be obtained but some uneven hollow microspheres and nanoparticles. Some broken hollow spheres can also be found. All the hollow spheres are made up by some nanoparticles.

To study the growth of trumpet-like products, time-dependent experiments were carried out with other parameters kept unchanged. When the feeds reacted for 3 h, the products are mainly some nanoparticles (Fig. 5a). However, if the reaction time was extended to 10 h, the trumpet-like products crossed with each other and some aggregates of the small particles also appeared (Fig. 5b). So a certain amount of time like 6 h is helpful to obtain the trumpet-like CdS in good shape.

Fig. 6 shows the SEM images of the products obtained with different amounts of triethanolamine. It is obvious that some irregular microspheres formed if there is no triethanolamine in the system (Fig. 6d). When triethanolamine was added, the morphology was changed to trumpet-like (Fig. 6a–c). With the increasing concentration of triethanolamine, the half-baked trumpet became full-grown (Fig. 6c). So triethanolamine plays a crucial role in the formation of the trumpet-like architectures.

To further evaluate the effect of triethanolamine on the formation of the trumpet architectures, some other ligands such as triethylamine, diethanolamine, trihydroxymethyl aminomethane and pentaerythritol were chosen for comparison. All the control experiments were carried out at a similar condition. The pH values of the solutions were adjusted by 1.0 mol/L NaOH

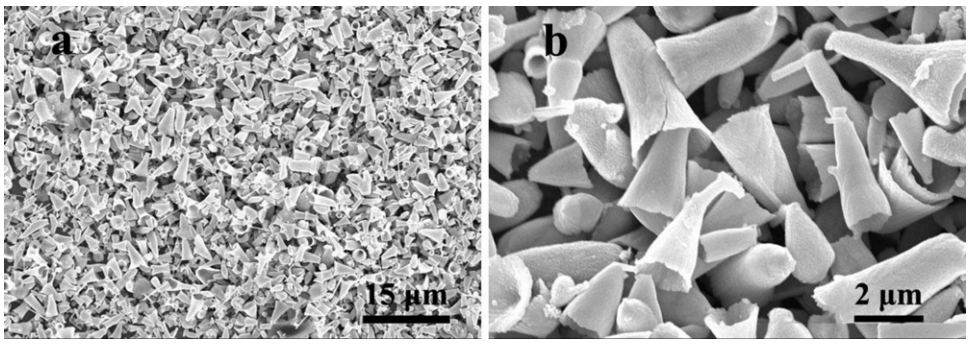

Fig. 2. SEM images of the trumpet-like CdS products obtained at 150 °C.

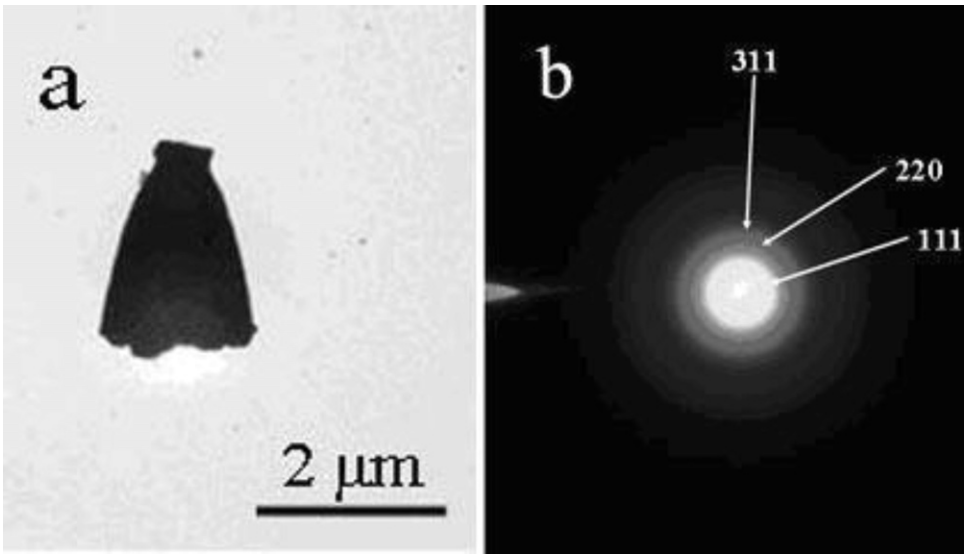

Fig. 3. TEM image of the trumpet-like structure and the SAED pattern.

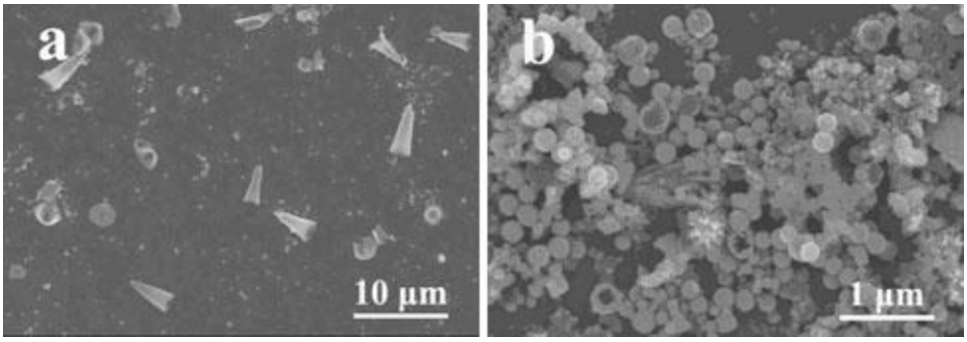

Fig. 4. SEM images of the products obtained at 130 °C (a) and 180 °C (b).

and 1.0 mol/L HCl to 9.7 as that with triethanolamine. As shown in Fig. 7, the products obtained with triethylamine or pentaerythritol are some irregular aggregates while some half-baked trumpet obtained with diethanolamine and some lotus seedpod-like structures obtained with trihydroxymethyl aminomethane. It is obvious that the simultaneous existence of hydroxyl group and bared nitrogen atoms (the hydrogen atoms ignored) is crucial for the formation of the trumpets and lotus seedpods. If the reaction is well controlled, the full-grown trumpets would be also obtained with diethanolamine. The formation of the lotus seedpod-like products should be due to the different structure of trihydroxymethyl aminomethane compared to triethanolamine.

Based on the above observations, a possible mechanism can be proposed. As reported by Wu et al. [15], 2-octanol acts as a co-surfactant in the formation of microemulsion of the HDEHP system. In these systems we discussed, triethanolamine, triethylamine, diethanolamine and trihydroxymethyl aminomethane can play a similar role as 2-octanol but pentaerythritol cannot act as the co-surfactant due to its tetrahedral arrangement of four hydroxy groups. All the microemulsions provide some microreactors for the formation of CdS nuclei. When the reaction processes under hydrothermal conditions, the emulsions broke and CdS nuclei aggregated into some irregular blocks for the common emulsions such as those with triethylamine and

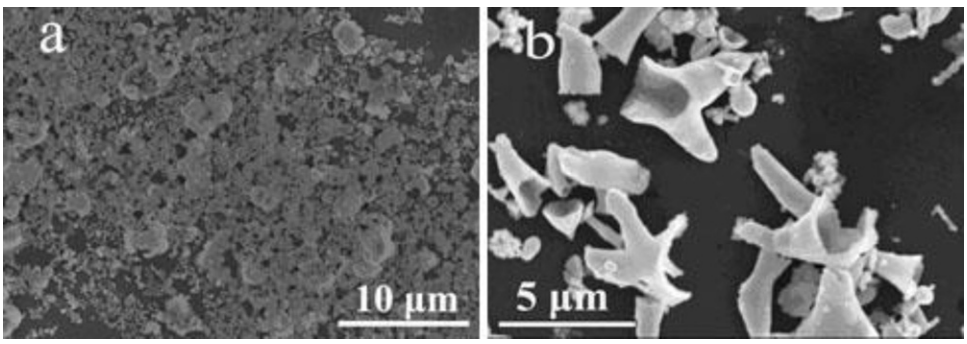

Fig. 5. SEM images of the products obtained for different reaction time (a, 3 h; b, 10 h).

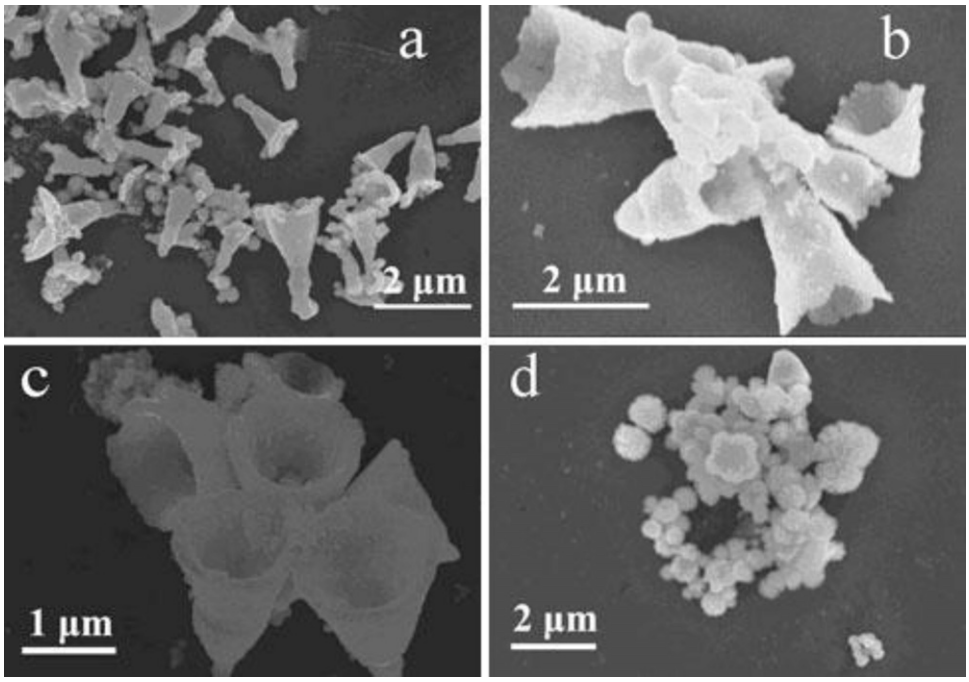

Fig. 6. SEM images of the products obtained with different amount of triethanolamine (a, 0.15 mmol; b, 0.4 mmol; c, 0.53 mmol; d, blank) at 150 °C.

pentaerythritol. However, due to different coordination ability of oxygen and nitrogen atoms toward the cadmium cations, CdS nuclei will assemble in a certain way with the help of triethanolamine, diethanolamine and trihydroxymethyl aminomethane, that is, the co-surfactants act as a soft template for the assembly of the trumpets and lotus seedpods. Additionally, because of the different coordination abilities of ≡N, ═NH and $-NH_2$ toward the cadmium cations, the products exhibits trumpet-like shape with triethanolamine or diethanolamine while lotus seedpod-like shape with trihydroxymethyl aminomethane.

Group II–VI semiconductor nanocrystals are generally intended for photonic or optoelectronic applications. The optical characterization of the trumpet-like CdS products is shown in Fig. 8. The absorption spectrum displays a peak at ca. 480 nm. The blue-shift from the bulk band gap of CdS (517 nm, [16]) might be attributed to the quantum confinement effect of the nanoparticles of the

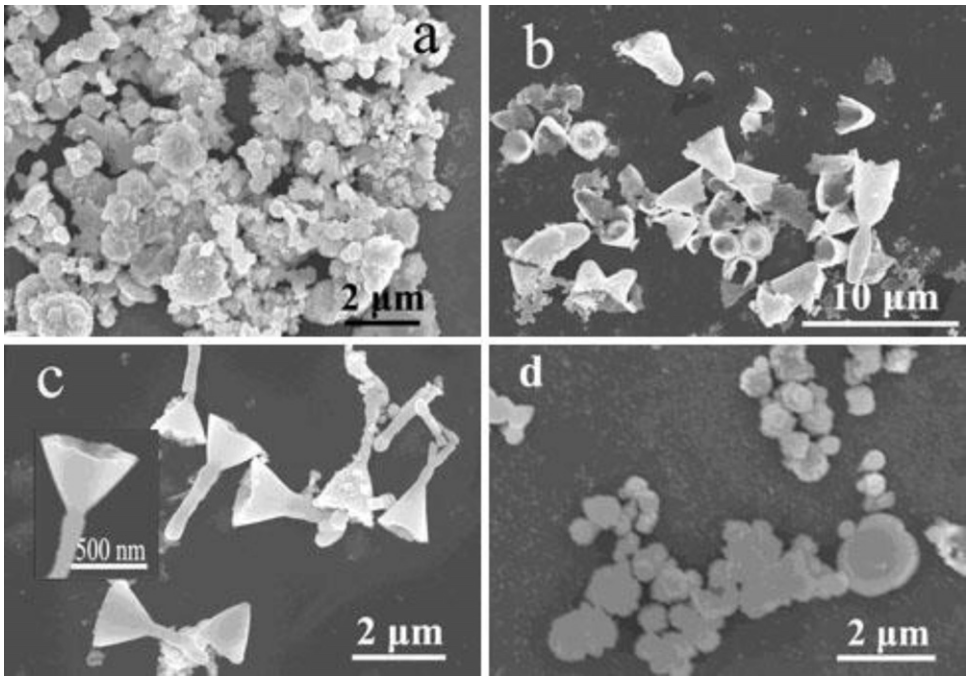

Fig. 7. SEM images of the products obtained at a same pH with (a) triethylamine, (b) diethanolamine, (c) trihydroxymethyl aminomethane (inset: enlarged view) and (d) pentaerythritol.

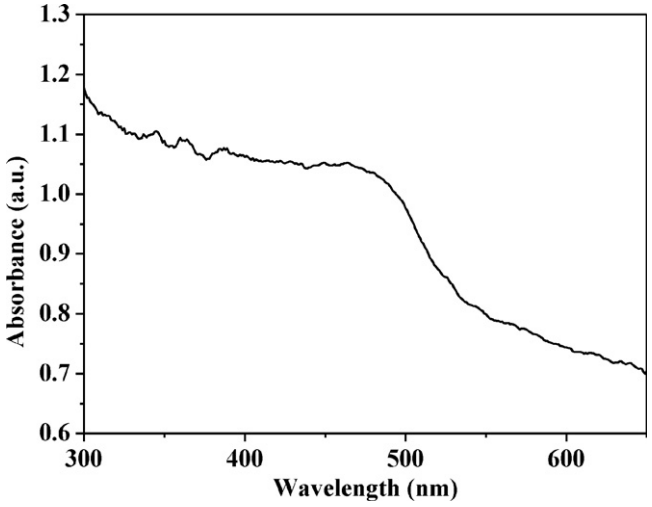

Fig. 8. Absorption spectra for the trumpet-like CdS products at room temperature.

trumpet-like CdS. However, the relatively large size of the CdS trumpets leads to optical scattering which leads to the extension of the absorption spectrum [16].

4. Conclusions

In summary, we developed a two-phase thermal method with the extraction system to prepare the trumpet-like CdS microstructures which are reported for the first time. The products are in the cubic phase of CdS and triethanolamine plays a crucial role in the formation of the trumpets. The effects of other factors like temperature, reaction time and the concentration of triethanolamine were also examined. The UV–vis absorption spectra of the products indicate the quantum confinement effect for the trumpet-like CdS. In addition, some lotus seedpod-like CdS products can be obtained with trihydroxymethyl aminomethane. It is expected that some other sulfide trumpets or lotus seedpods in nano/microscale can be fabricated by this method.

Acknowledgments

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