Synthesis and properties of nanoparticles-assembled ZnS-microspheres and CdS-nanoshuttles through a hydrothermal reaction of simultaneous solvent-oxidation-hydrolysis

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Abstract

A new kind of reaction based on a simultaneous solvent-oxidation-hydrolysis process was first developed to synthesize ZnS and CdS. ZnS microspheres and CdS nanoshuttles assembled with nanoparticles were obtained through this method. The products were characterized by XRD, ED, TEM, UV-VIS and PL. The results indicated that ZnS and CdS nanoparticles with 15–20 nm diameters could self-assemble into 1.2 μm-diameter microspheres and about 40 × 100 nm nanoshuttles, respectively. In addition, the formation mechanism of the products was explored.

Key words: solvent-oxidation-hydrolysis, hydrothermal, nanoparticles, nanoshuttles, microspheres, ZnS, CdS

1. Introduction

The perceived need for the further miniaturization of both optical and electronic devices has driven more and more interest in nanoparticles research. Semiconductor nanocrystals are widely studied because of their size-dependent optical and electrical properties. They have been used as optoelectronic applications [1, 2]; nonisotopic biolabels [3, 4]; luminescent, biological or intracellular probes [3, 5]. They also have been used for photodynamic therapy [6]. ZnS and CdS are typically wide-band gap semiconductors. They were widely used as nonlinear optic devices, flat panel displays, photocatalysts, light emitting diodes, and electrochemical cells [7–13]. Over the past years, a variety of chemical methods have been used for the preparation of semiconductor nanoparticles, for example, reactions between the element (or its compounds) and gaseous H_2S, microwave assisted preparation, reverse micelle synthesis, organometallic synthesis, single-source precursor decompose, solvothermal elemental direct reaction, mono-template method and soft-hard dual template method [14–23]. It is believed that properties become sensitive not only to the size but also to the shape and composition of the particles [24]. Low-dimensional assemblies of nanoparticles are becoming of increasing interest if they behave as quantum dots [25]. So preparing low-dimensional assemblies of nanoparticles becomes more important. Here we report the synthesis of a variety of assemblies of ZnS and CdS nanoparticles using a simultaneous solvent-oxidation-hydrolysis reaction. Their novel optical properties are investigated. Our work is not only helpful to the research of inorganic chemistry reactions, but also provides a new idea for preparation low-dimensional assemblies of nanoparticles, which may have potential application in nanoelectronics.

2. Experimental

2.1. Materials

Cd powder used in this work was high purity (99.999 %), all other chemicals in this work, such as

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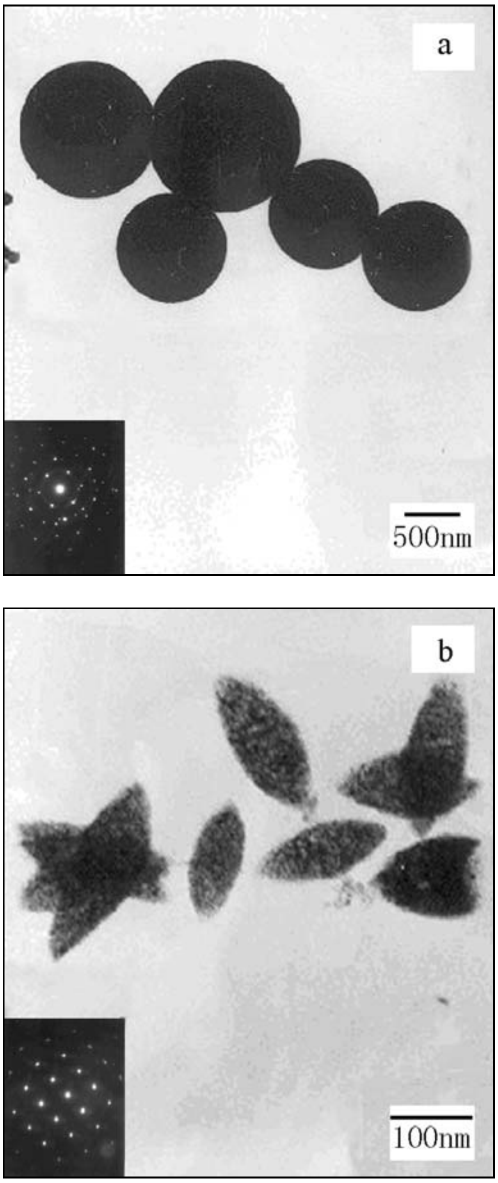

Fig. 1. TEM images of ZnS (a) and CdS (b) as prepared.

Zn powder, NH_2CSNH_2, ethylene diamine (en), and 8-hydroxylquinoline were A. R. reagents. They were purchased from Shanghai Chemical Reagents Company, and used without any pretreatment.

2.2. Synthesis

0.01 mol of M (M = Zn, Cd) powder, 0.02 mol of thiourea (NH_2CSNH_2) and ethylene diamine were put into a Teflon-lined autoclave of 40 ml capacity. Then the autoclave was filled with 25 ml deionized water, N_2 was passed to eliminate oxygen inside the solution. The autoclave was sealed and heated at 180 ℃ for 40 h; then it was let to cool to room temperature naturally. The products were collected by filtration, washed with deionized water and absolute ethanol. The products were obtained and preserved in absolute ethanol for about two weeks for further characterization.

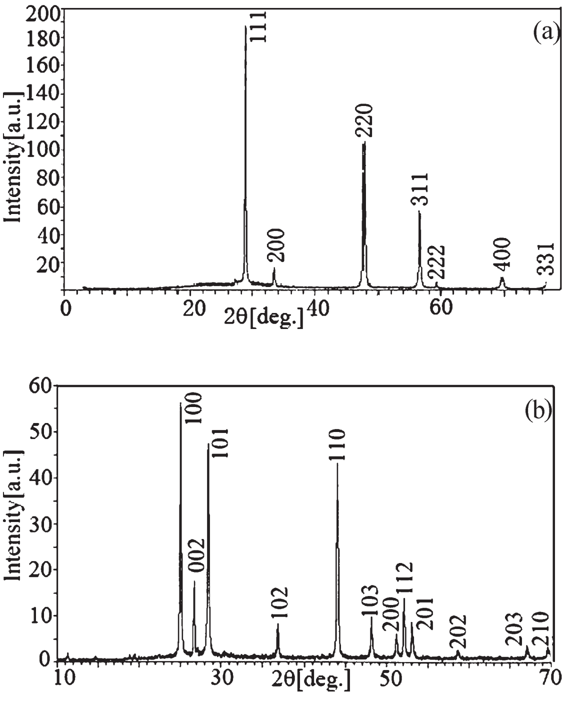

Fig. 2. XRD patterns of ZnS (a) and CdS (b) nanoparticles assemblies.

2.3 Characterization

The crystalline structures were detected by X-ray powder diffraction (XRD, Philips, PW1710, CuKα: λ = 1.5418 Å) and convergent beam electron diffraction (ED, Hitachi, H-800). The size and morphology of the products were observed by transmission electron microscope (TEM, Hitachi, H-800, E = 200 kV). The optoelectronic properties were measured by ultraviolet-visible absorption spectra (UV-VIS, Agilent, 8453) and photoluminescence spectra (PL, Perkin Elmer, LS-55).

3. Results and discussion

3.1. Results

TEM and ED pictures are shown in Fig. 1. Figure 1a is the TEM picture of ZnS. They are tight and saponaceous spheres with diameter of about 1.2 μm. Figure 1b is the TEM picture of CdS product. They are shuttles composed of nanoparticles. The length of these shuttles is from 80 nm to 120 nm, and the width is about 40 nm. The electron diffraction (ED) pattern indicates that both ZnS and CdS nanoparticles are single crystals.

XRD patterns of as-prepared ZnS and CdS are given in Fig. 2. Figure 2a shows that ZnS is well-

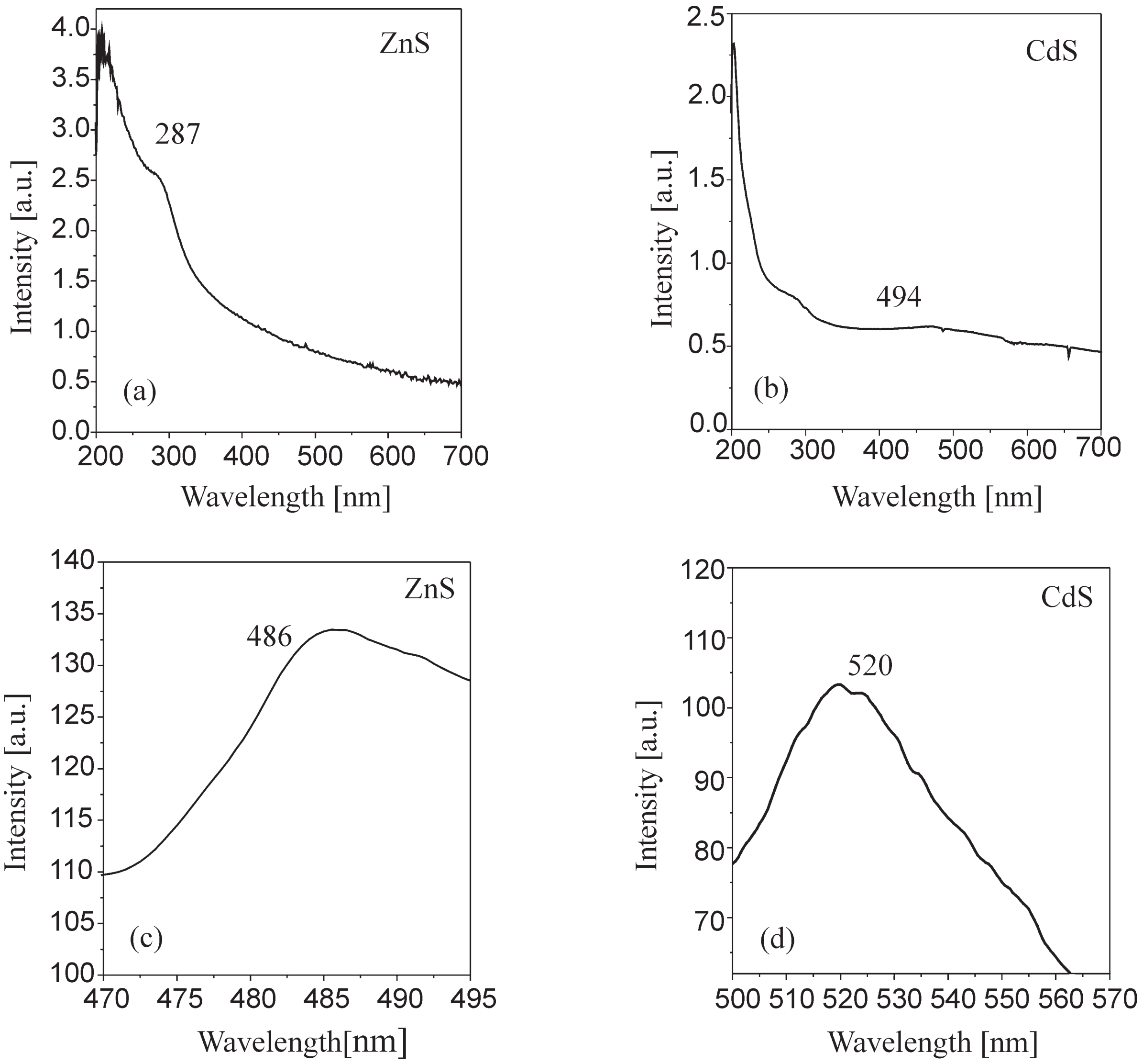

Fig. 3. UV-VIS absorption and PL emission spectra of the products: (a) ZnS – 287, (b) CdS – 494, (c) ZnS – 486, (d) CdS – 520.

-crystallized pure cubic sphalerite phase with a calculated lattice parameter of $a = 5.3926$ Å that is consistent with the reported data (JCPDS 5-0566). The pattern of CdS shows that the products are well-crystallized pure hexagonal greenockite phase with a calculated lattice parameter of $a = 4.138$ Å, $c = 6.725$ Å, very close to the reported data (JCPDS 6-0314). The unusually high peak of [100] shows that the sample has a preferential orientation that is consistent with what is shown in TEM picture.

UV-VIS absorption and PL emission spectra of as-synthesized ZnS and CdS are shown in Fig. 3. Figure 3a is UV-VIS absorption of ZnS. There is a relatively high peak at 287 nm. The absorption peak occurs at 494 nm of CdS UV-VIS (Fig. 3b). There is obvious blue shift between our product and the bulk material (40 nm of ZnS, 30 nm of CdS). The PL spectra were got when excited at 340 nm (ZnS) and 383 nm (CdS), respectively. The PL spectrum of ZnS (Fig. 3c) shows a peak at 486 nm. The emission maximum of CdS occurrs at 520 nm and the intensity is high (Fig. 3d).

3.2. Discussion

The reaction can be suggested as follows:

$$\mathrm{Zn(Cd)} + \mathrm{CS(NH_2)_2} + 2\mathrm{H_2O} \rightarrow$$
$$\rightarrow \mathrm{ZnS(CdS)}\downarrow + 2\mathrm{NH_3} + \mathrm{H_2} + \mathrm{CO_2}.$$

The probable mechanism for the formation of ZnS (or CdS) assemblies of nanoparticles could be suggested as below: first, under hydrothermal condition, Zn (or Cd) powder was oxidized into $\mathrm{Zn^{2+}}$ (or $\mathrm{Cd^{2+}}$) cation by deionized water; then $\mathrm{Zn^{2+}}$ (or $\mathrm{Cd^{2+}}$) coordinated with ethylene diamine forming $[\mathrm{Zn(en)_2^{2+}}]$ (or $[\mathrm{Cd(en)_2^{2+}}]$), respectively; these co-

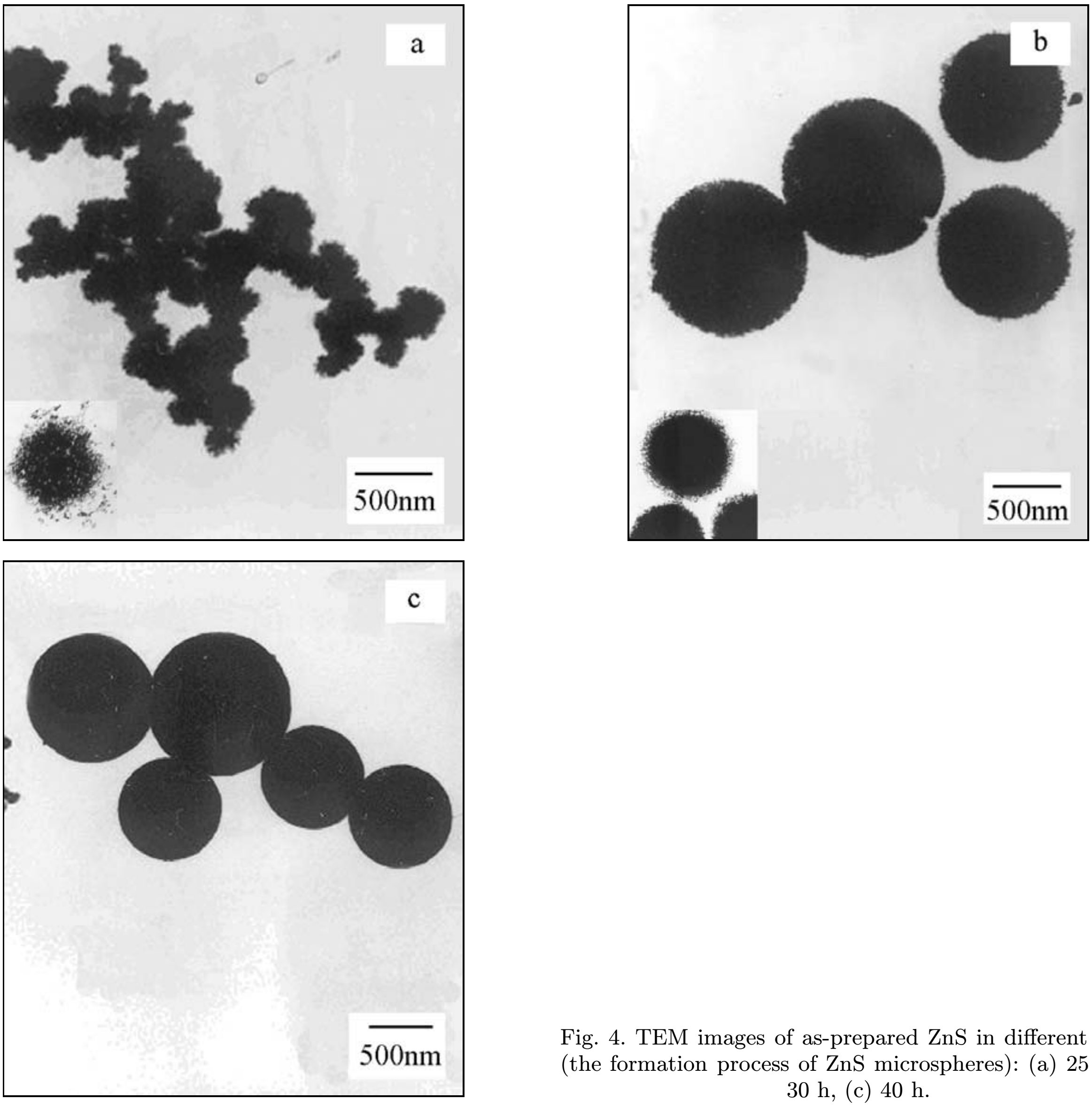

Fig. 4. TEM images of as-prepared ZnS in different stages (the formation process of ZnS microspheres): (a) 25 h, (b) 30 h, (c) 40 h.

ordination cations reacted with $CS(NH_2)_2$, thus ZnS and CdS crystal cores were formed. These reactions happened simultaneously, and no one could realize solely. In order to explain the process, the reaction was separated into 3 steps:

$$\mathrm{Zn(orCd)+H_2O} \xrightarrow{\text{hydrothermal}} \mathrm{Zn^{2+}(orCd^{2+})} \text{(Step 1)}$$

$$\mathrm{Zn^{2+}(orCd^{2+}) + (en)_2} \rightarrow \\ \rightarrow \mathrm{[Zn(en)_2]^{2+}(or[Cd(en)_2]^{2+})} \qquad \text{(Step 2)}$$

$$\mathrm{[Zn(en)_2]^{2+}(or[Cd(en)_2]^{2+}) + CS(NH_2)_2} \rightarrow \\ \mathrm{ZnS(orCdS)}\ \text{(crystal cores)} \qquad \text{(Step 3)}$$

Take ZnS microspheres for example, the formation mechanism of the assembly was discussed. First, nanocrystal cores grow into nanoparticles. These particles with diameter of about 20 nm were formed into catenarian structure in the inducement of ethylene diamine template when the reaction time is 25 h (shown in Fig. 4a). Several ball-like assemblies have come into being in the system (picture inserted in Fig. 4a). With proceeding of the reaction, these ball-like assemblies grow into perfect bigger spheres and separate from each other because of surface tension (Fig. 4b). But these spheres are not tight enough that some particles can be seen at the edge of these spheres (picture inserted in Fig. 4b). Finally, these spheres are assembled better and become bigger and tighter (Fig. 4c). So the reaction time is a very important factor that affects the morphology of synthesized nanocrystals. Ethylene diamine also takes an important role in the assemble process. Figures 5a,b are the TEM images of ZnS and CdS that are prepared without ethylene diamine. They are irregular poly-

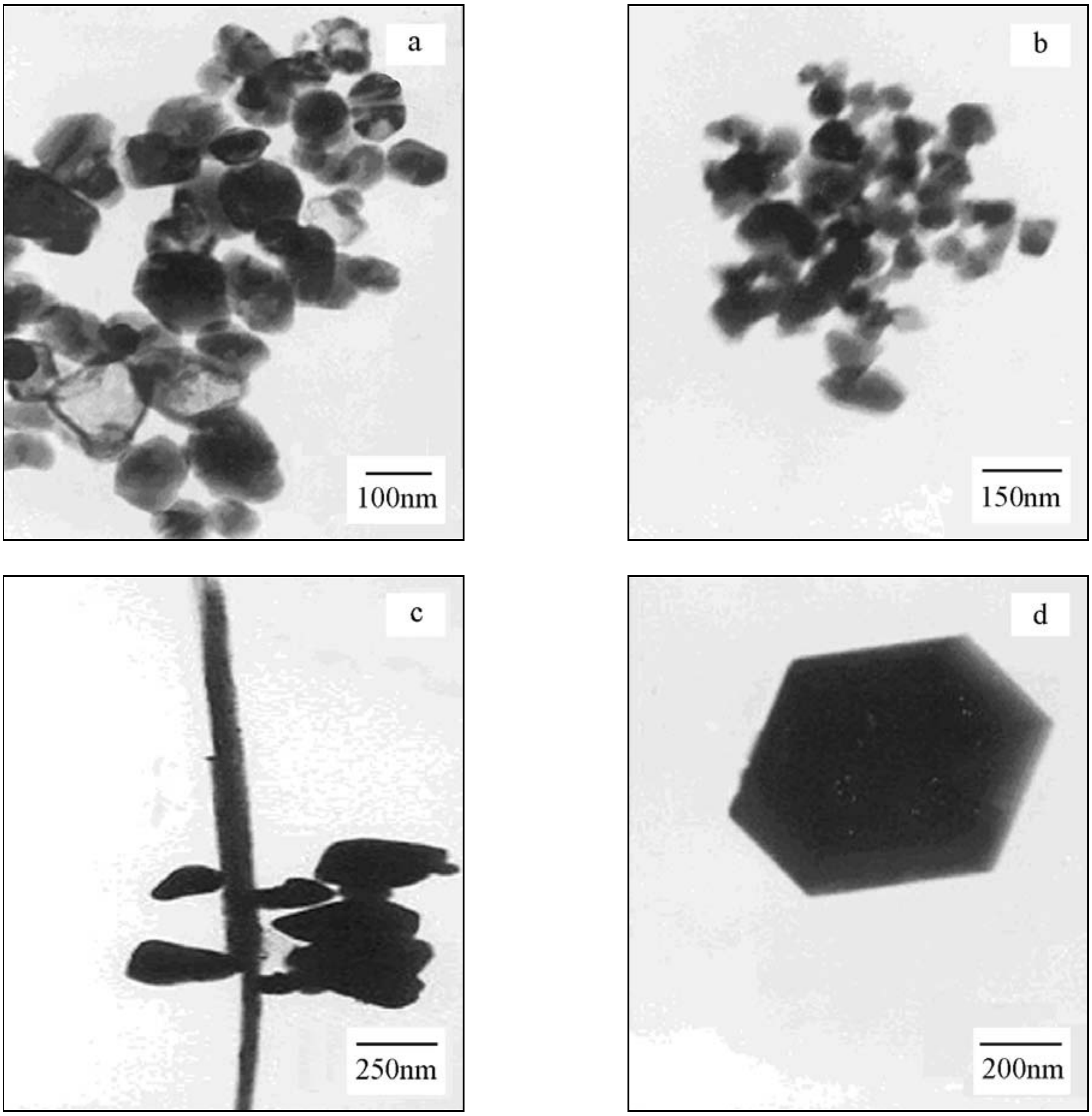

Fig. 5. TEM images of ZnS (a) and CdS (b) prepared without template; ZnS (c) and CdS (d) using 8-hydroxylquinoline as template.

hedrons. Other template reagent has been applied to synthesize novel morphologies of nanoparticles assemblies. Figures 5c,d are ZnS and CdS that were synthesized using 8-hydroxylquinoline as template instead of ethylene diamine. There are particles and nanorods in TEM image of ZnS. There is a tendency to grow into one-dimensional nanomaterial. Figure 5d is a hexahedron. This is a novel morphology of CdS nanomaterial that has never been reported.

4. Conclusion

A new hydrothermal reaction of solvent-oxidation-hydrolysis to fabricate ZnS and CdS was successfully established for the first time. Through this reaction, different morphology assemblies of nanoparticles were obtained. They have differential optical properties. The mechanism of the reaction and the formation process was discussed. This novel method can surely be used to synthesize other metallic sulfides assemblies of nanoparticles, and it may be easily applied to a large-scale manufacture for its merits, such as high yield, simple equipments and low reaction temperature.

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