

## Silica gel-assisted solvothermal production of CdS, Cu<sub>x</sub>S (x=1, 2) and ZnS with different morphologies

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**Abstract:** CdS, Cu<sub>x</sub>S (x=1, 2) and ZnS with different morphologies were produced by the solvothermal reactions of M(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O (M=Cd, Cu and Zn) and NH<sub>2</sub>CSNH<sub>2</sub> in hexane with and without silica gel as a hard template at 200 °C for 24 h. The product phases were detected using X-ray diffraction (XRD). Different morphologies were characterized using a scanning electron microscope (SEM). The existence of silica gel in modeling morphologies of the sulfides was characterized using Fourier transform infrared (FTIR) spectrometer. Raman spectra of different products show the vibrations at the same wavenumbers, although they are composed of different morphologies. Photoluminescence (PL) emissions of the corresponding phases with different morphologies are at the same values, but their intensities are increased by template adding.

**Key words:** solvothermal reaction; silica gel; CdS; Cu<sub>x</sub>S; ZnS

### 1 Introduction

Presently, inorganic sulfides such as CdS, CuS, Cu<sub>2</sub>S and ZnS have high scientific and technological interest as photonic crystals. CdS is a semiconducting material having a direct-band gap of 2.42 eV, and is able to apply for light-emitting diodes and nonlinear optics[1]. Cu<sub>x</sub>S (x=1, 2) are able to apply for solar cells, solar absorbers, selective radiation filters for architectural windows and electroconductive films on polymers[2]. Their mixed phases are supposed to be the stoichiometric compounds. In the case of ZnS, it has a wide band gap of 3.66 eV at 300 K and shows different luminescent properties, such as photoluminescence, electroluminescence, mechanoluminescence and thermal luminescence[3]. There are different processes used to produce the sulfides, such as CdS nanoparticles by chemical process[4], CdS by free surfactant solvothermal synthesis[5], Cu<sub>x</sub>S (x=1, 2) by asynchronous-pulse ultrasonic spray pyrolysis[2], nano- and micro-sized CuS crystals by cyclic microwave radiation[6], CuS with different morphologies by solvothermal-microwave

process[7], CuS nanoparticles by sonochemistry[8], ZnS nanoballs, nanoparticles and based materials by microwave-assisted synthesis[9–11], ZnS microspheres and hollow nanospheres by hydrothermal synthesis[12], and ZnS nanoparticles by mechanochemical synthesis[13].

Recently, there are a wide variety of porous materials that have been used as the templates to model the product morphologies[14]. Among them are soft templates (surfactants) and hard templates (active carbon and mesostructured silica gel)[14–15]. There is the limitation of using active carbon, which may be oxidized by the infiltrated or metallic salts[14]. Therefore, a more inert hard template such as porous silica gel is appropriate for assisting the formation of high-surface area (nanostructured) inorganic materials[14–15]. Silica gel is also readily available, inexpensive and easy to be washed out by water. In the present research, CdS, CuS-Cu<sub>2</sub>S mixture and ZnS with different morphologies were solvothermally produced with and without adding silica gel. The effects of the template on the products were also studied using different techniques.

## 2 Experimental

Each 0.005 mol of metal acetates [ $\text{Cd}(\text{CH}_3\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Cu}(\text{CH}_3\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Zn}(\text{CH}_3\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ ] and  $\text{NH}_2\text{CSNH}_2$  was separately dissolved in 35 mL hexane and mixed in Teflon containers with and without 0.25 g silica gel as a hard template. The reactions solvothermally proceeded at 200 °C for 24 h. The precipitates were washed with distilled water and 95% ethanol, and dried at 70 °C for 24 h. The products (Table 1) were intensively characterized using a X-ray diffractometer (XRD) operated at 20 kV, 15 mA and using  $K_\alpha$  line from a Cu target, a scanning electron microscope (SEM) operated at 15 kV, a Fourier transform

**Table 1** Different codes of products

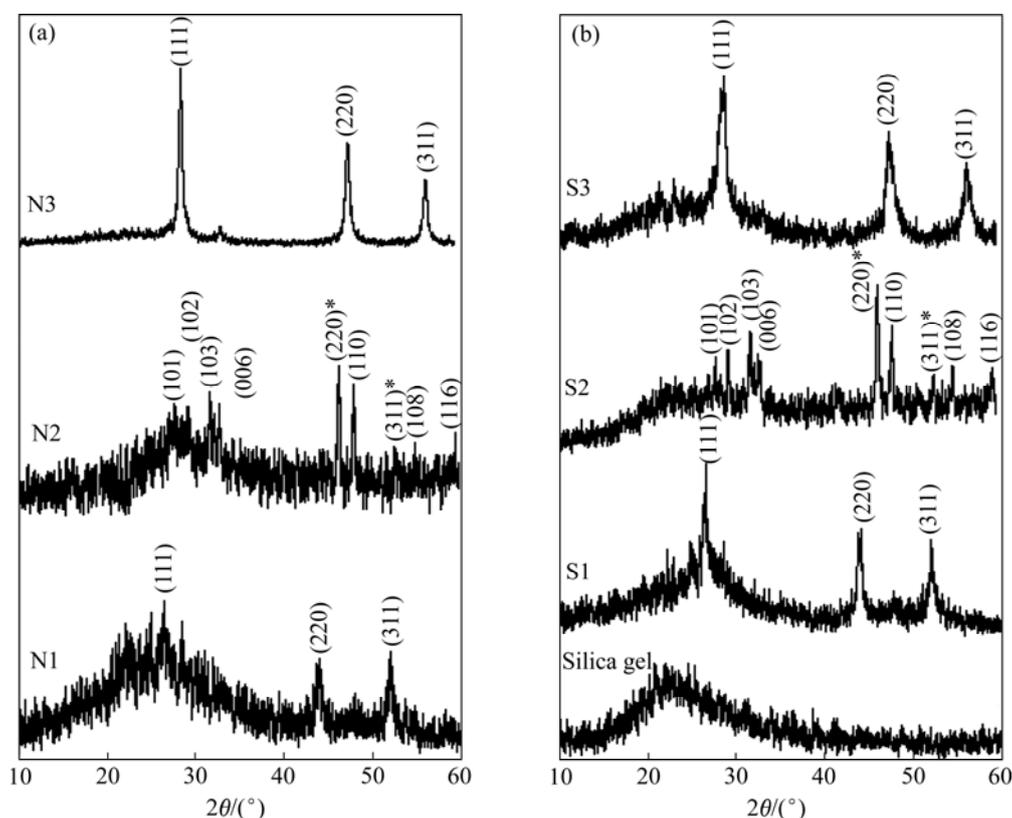
| Product code | Reactants  | Template   |
|--------------|--|------------|
| N1           | $\text{Cd}(\text{CH}_3\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ , $\text{NH}_2\text{CSNH}_2$ | –          |
| N2           | $\text{Cu}(\text{CH}_3\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ , $\text{NH}_2\text{CSNH}_2$ | –          |
| N3           | $\text{Zn}(\text{CH}_3\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ , $\text{NH}_2\text{CSNH}_2$ | –          |
| S1           | $\text{Cd}(\text{CH}_3\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ , $\text{NH}_2\text{CSNH}_2$ | Silica gel |
| S2           | $\text{Cu}(\text{CH}_3\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ , $\text{NH}_2\text{CSNH}_2$ | Silica gel |
| S3           | $\text{Zn}(\text{CH}_3\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ , $\text{NH}_2\text{CSNH}_2$ | Silica gel |

infrared (FTIR) spectrometer with KBr as diluting agent and operated in the range 738–4 000  $\text{cm}^{-1}$ , a Raman spectrometer using 50 mW Ar laser with  $\lambda=514.5$  nm, and a photoluminescence (PL) spectrometer using 250, 220 and 230 nm excitation wavelengths at room temperature for CdS, CuS-Cu<sub>2</sub>S mixture and ZnS, respectively.

## 3 Results and discussion

### 3.1 XRD analysis

The crystallographic planes of XRD spectra (Fig.1) were indexed using Bragg's law for X-ray diffraction and compared with those of the JCPDS software with reference codes 01-0647, 03-0724, 12-0175 and 01-0792 for CdS (cubic), covellite CuS (hcp), Cu<sub>2</sub>S (cubic) and sphalerite ZnS (cubic), respectively[16]. The products are composed of CdS (cubic) for N1 and S1, a mixture of covellite CuS (hcp) and Cu<sub>2</sub>S (cubic) labeled with the asterisks (\*) for N2 and S2, and sphalerite ZnS (cubic) for N3 and S3. XRD spectrum of silica gel (Fig.1) is also shown for comparison. When silica gel was used, the product spectra still correspond to the same phases as in the template-free solutions did. XRD intensities become higher, showing that silica gel functions as a template to model atoms in more perfect orders. These reflect the degree or extent of the crystals. A small amount of silica



**Fig.1** XRD spectra of different products and silica gel

gel remains in the products although they have been washed out by water. The calculated lattice parameter [17](Table 2) are very close to those of the corresponding JCPDS software[16].

**Table 2** Calculated lattice parameters of products

| Product                   | Silica gel-free |       | Containing silica gel |       |
|---------------------------|-----------------|-------|-----------------------|-------|
|                           | a/nm            | c/nm  | a/nm                  | c/nm  |
| CdS (cubic)               | 0.582           | –     | 0.581                 | –     |
| CuS (hcp)                 | 0.378           | 1.636 | 0.379                 | 1.640 |
| Cu <sub>2</sub> S (cubic) | 0.557           | –     | 0.558                 | –     |
| ZnS (cubic)               | 0.540           | –     | 0.539                 | –     |

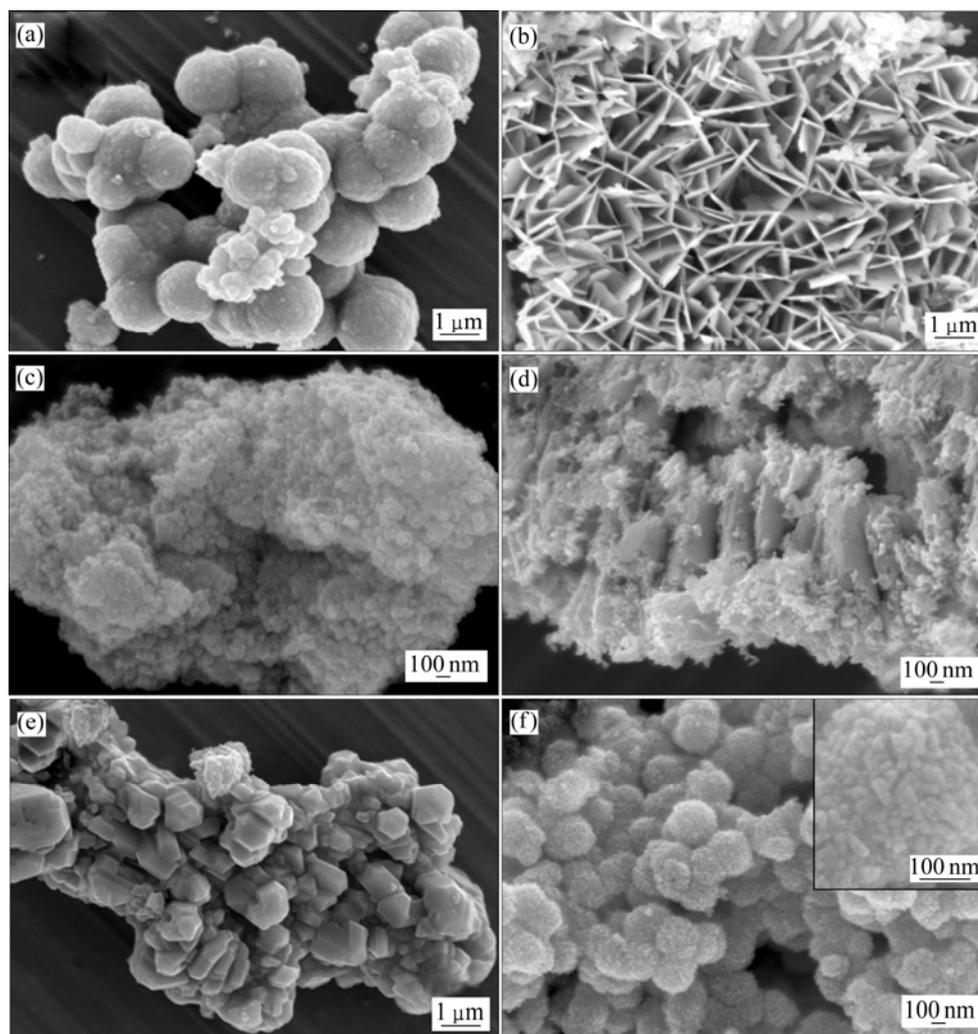
### 3.2 SEM analysis

The SEM images show the change of product morphologies, caused by silica gel. In template-free solutions, N1 (Fig.2(a)) is composed of nanosized spherical particles. Each appears as rough surface. But for N2 and N3 (Figs.2(b) and 2(c)), they are nanoplates in cluster and a bulk of nanoparticles, respectively. When

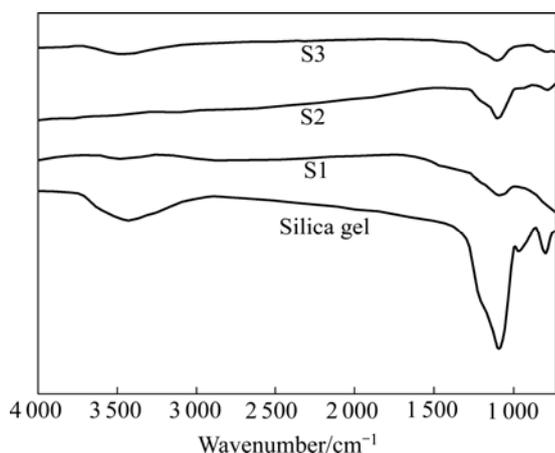
silica gel is added to the solutions, the process is divided into three steps: (1) the template randomly diffuses through the solutions, (2) the 200 °C solvothermal reaction proceeds, and (3) after cooling to room temperature, the template is removed by water. Silica gel functions as a hard template and models the products into some specified morphologies [14–15]. S1, S2 and S3 (Figs.2(d), 2(e) and 2(f)) are composed of elongated particles with clusters of nanoparticles at their tips, hexagonal particles and spherical particles, respectively. At higher magnification, each of the spherical particles (Fig.2(f)) is composed of nanoparticles with different sizes. The results show that silica gel played the role in the product morphologies.

### 3.3 FTIR analysis

The FTIR spectra of silica gel, S1, S2 and S3 (Fig.3) were analyzed using a transmittance mode. For silica gel, its spectrum shows the broad band of stretching vibration of hydroxyl groups on its surface at 3 438 cm<sup>-1</sup>. The bands at 1 098 and 797 cm<sup>-1</sup> are assigned to the Si—O stretching vibration and Si—O—Si bending vibration,



**Fig.2** SEM images of products N1(a), N2(b) and N3(c), and S1(d), S2(e) and S3(f)



**Fig.3** FTIR spectra of silica gel, S1, S2 and S3

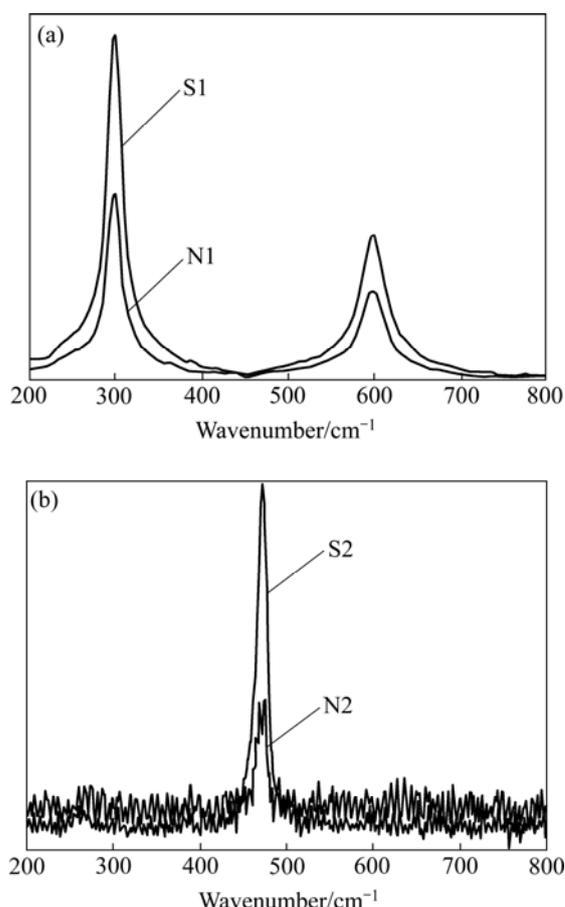
respectively. The band at  $974\text{ cm}^{-1}$  corresponds to the Si—OH stretching vibration[18]. But for S1, S2 and S3, some of the vibration peaks belonging to silica gel no longer exist. The stretching vibration of Si—O still exists but its intensity becomes lower. The analysis shows that silica gel functions as a template which was subsequently washed out by water. Only the residues remain in the products. The results are in accordance with those of the XRD analysis.

### 3.4 Raman spectral analysis

The Raman spectra of N1 and S1 (Fig.4(a)) show two main peaks corresponding to the first and second longitudinal optical (LO) phonon modes, which are polarized in the  $x-z$  face with strong coupling to the exciton along  $c$  axis[1]. The 1LO and 2LO corresponding to the fundamental and overtone modes[1, 19] are detected at  $300$  and  $599\text{ cm}^{-1}$ , respectively. Each of the vibrations is at the same wavenumbers although the products are synthesized with and without using silica gel. They are in accordance with other results[20]. In the solution containing silica gel, atoms are modeled in perfect lattice and the intensity becomes higher. But for those of N2 and S2 (Fig.4(b)), the spectra are very narrow. Their vibrations are in the same wavenumbers at  $474\text{ cm}^{-1}$ , corresponding to lattice vibrations. The present results are in accordance with those of CuS thin films[2]. The intensity of the product synthesized in the solution containing silica gel becomes higher as well. The Raman analysis of ZnS does not show any prominent peaks in the spectra of both N3 and S3.

### 3.5 Photoluminescence (PL) analysis

The PL spectra of CdS, CuS-Cu<sub>2</sub>S mixture and ZnS (Fig.5) were determined at ambient temperature using 250 nm, 220 nm and 230 nm excitation wavelengths, respectively. The distinct PL emissions are detected at 616 nm, 340 nm and 363 nm, which are very close to the

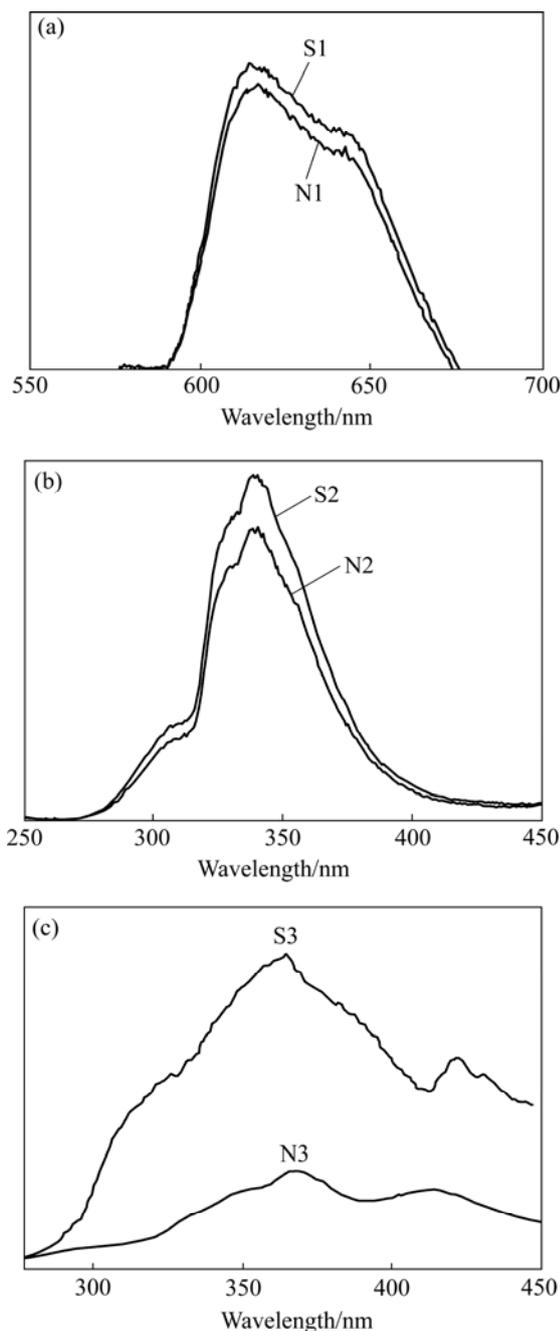


**Fig.4** Raman spectra of N1, S1, N2 and S2

previous reports for CdS[4, 21], CuS[22] and ZnS[9, 23]. Emission caused by defects of ZnS[23] is also detected at 423 nm. For the present analysis, photon energies are lost during the characterization and the emissions of longer wavelengths are detected. Their intensities are influenced by several parameters such as shapes, sizes, and crystallinities, which are controlled by the template. In the solution containing silica gel, atoms are modeled in perfect lattices and higher intensities are clearly detected. These results thus show that silica gel has the influence on PL emissions of the products.

## 4 Conclusions

CdS (cubic), mixed phases of covellite CuS (hcp) and Cu<sub>2</sub>S (cubic), and sphalerite ZnS (cubic) with different morphologies were successfully produced by the solvothermal process with and without using silica gel as a hard template. Their morphologies changed from the spherical particles to elongated particles with clusters of nanoparticles at their tips for CdS, nanoplates in cluster to hexagonal particles for CuS-Cu<sub>2</sub>S mixture, and a bulk of nanoparticles to spherical particles for ZnS by silica gel adding. A small amount of silica gel was also



**Fig.5** PL spectra of CdS(a), CuS-Cu<sub>2</sub>S(b) mixture and ZnS(c)

detected after the products were washed out. Intensities of Raman and photoluminescence spectra were increased by using silica gel as a hard template. But for their wavenumbers and wavelengths, they remained at the same values.

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