SDS-assisted hydrothermal synthesis of porous CdIn$_2$S$_4$ microspheres

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Abstract: The porous CdIn$_2$S$_4$ microspheres were synthesized via a sodium dodecyl sulfate (SDS)-assisted hydrothermal technology. The as-prepared CdIn$_2$S$_4$ products were characterized by X-ray diffraction, field emission scanning electron microscopy and UV-Vis diffusive reflectance spectroscopy. The results showed that hydrothermal time and the surfactant addition had great effect on the structure, morphology and optical property of CdIn$_2$S$_4$ products.

1. Introduction

CdIn$_2$S$_4$ has been studied as an important semiconducting photocatalytic material due to its chemical stability, photocatalytic activity [1] and optoelectronic property [2-3], especially its applications in photovoltaic conversion, photocatalytic hydrogen production and light-emitting diodes [4]. CdIn$_2$S$_4$ with cubic spinel structure has narrow band gap and strong absorption in the visible light region, which largely improve the efficiency of light utilization. Kale synthesized CdIn$_2$S$_4$ nanotubes and “marigold-like” structure by controlling hydrothermal conditions [5]. Zhou prepared CdIn$_2$S$_4$ nanosheets with cubic spinel phase and high crystallinity in the mercaptoacetic acid-assisted hydrothermal process without the help of templates or surfactants. The nanosheets obtained a quasi-rounded morphology with the diameter of about 80 nm [6]. Guo synthesized CdIn$_2$S$_4$ hollow spheres with typical opening hollow architecture via a facile hydrothermal process without any template or surfactant [7].

In this study, a series of porous CdIn$_2$S$_4$ microspheres were prepared by hydrothermal method using sodium dodecyl sulfate (SDS) as template. The influences of hydrothermal time, concentration of SDS on the morphology and photocatalytic properties of CdIn$_2$S$_4$ were studied in detail.

2. Experimental section

2.1. Preparation of materials
All chemical materials were analytical grade without further purification. In a typical procedure, Cd(NO$_3$)$_2$·6H$_2$O (2 mmol), In(NO$_3$)$_3$·4H$_2$O (4 mmol), thioacetamide (TAA, 16 mmol) and different amounts of SDS were added and dissolved in 75 ml of distilled water. The as-prepared solution was then transferred into a Teflon-lined autoclave (100 ml). The autoclave was sealed and controlled at 160°C for a certain time, and then naturally lowered to room temperature. The CdIn$_2$S$_4$ product was obtained by centrifugation then washed with ethanol and deionized water for several times.

2.2. Characterization

The structure, morphology and optical property of as-prepared porous CdIn$_2$S$_4$ microspheres were characterized by XRD (Bruker D8 Advance X-ray diffractometer) using Cu irradiation ($\lambda=0.15418$ nm) with 0.5°/s scanning speed from 10° to 70° (2θ), SEM (HITACHI S-4800) with accelerating voltage was 30 kV and UV-Vis-DRS (Shimadzu UV-2450 spectrophotometer).

3. Results and discussion

3.1. Effect of the hydrothermal time

A series of porous CdIn$_2$S$_4$ microspheres were prepared in aqueous solution with the same amount of SDS at 160°C for different hydrothermal reaction time. The structure and optical property of above-prepared products were characterized by XRD and UV-Vis-DRS. The results showed in Figure 1 (a-e) and Figure 2.

![Figure 1. XRD patterns of CdIn$_2$S$_4$ prepared for 0 h (a); 1 h(b); 6 h(c); 12 h(d); 24 h(e)](image)

![Figure 2. UV-Vis-DRS of CdIn$_2$S$_4$ prepared for 0 h (a); 1 h(b); 6 h(c); 12 h(d); 24 h(e)](image)

It was revealed from Figure 1 that there are ten characteristic diffraction peaks at 20-values of 14.13°, 23.18°, 27.25°, 28.48°, 33.00°, 40.74°, 43.32°, 47.41°, 55.51°, 66.12°, which corresponded to (111), (220), (311), (222), (400), (422), (511), (440), (533), (731) crystal faces of pure cubic spinel phase of CdIn$_2$S$_4$ (ICSD-JCPDS card No.27-0060). It could be seen that hydrothermal time affected the crystalline of the products. With the hydrothermal time prolonging, the diffraction peak intensities were enhanced. However, the apparent broadening peaks of the precipitate without hydrothermal treatment indicated the absence of products with highly crystalline. As shown in Figure 2, the maximum absorption edge of CdIn$_2$S$_4$ prepared for 1 h was located at 560 nm corresponding to about the band gap of 2.21 eV. With the hydrothermal time prolonging, the maximum absorption edges of CdIn$_2$S$_4$ samples showed red shift to 610 nm corresponding to 2.03 eV.
In order to describe the producing process of the CdIn$_2$S$_4$ microspheres, the morphologies of the products prepared for different hydrothermal treating-time were respectively determined by SEM measurement (Figure 3(a-e)).

**Figure 3.** SEM images of CdIn$_2$S$_4$ prepared for 0 h (a); 1 h(b); 6 h(c); 12 h(d); 24 h(e)

As shown in Figure 3, unique flower-like CdIn$_2$S$_4$ microspheres with the average diameter of about 5 μm could be obtained. The formation of microspheres during hydrothermal process could be divided into several obvious growing stages. It was found from Figure 3(a) that mass ruleless dollops without pore structure were produced without hydrothermal treatment, and obvious aggregation of particles could be observed, which indicated that the self-assembly growth of crystallites was educed and accelerated by hydrothermal reaction. However, as shown in Figure 3(b), abundant floss-like spheres with rough surface were formed under this condition, and the size of the loose spheres was about 1-3 μm. With prolonging hydrothermal time to 6 h, the microspheres became tight and developed swelled in size. It could be seen from Figure 3(c) that flower-like CdIn$_2$S$_4$ microspheres composed of numerous flakes were produced through self-assembly growth process. Many slit-like pores were formed among these curved nanosheets and the inside of petals because of the flakes interconnected with each other. Figure 3 (d) showed the morphology of the product treated for 12 h, the microspheres were dispersed with good monodispersion and uniform diameter, and the size of microsphere remained unchanged. Surprisingly, some opening hollow microspheres were obtained during this stage. When hydrothermal time was 24 h, mass microspheres with particular surface consisted of pyramids were produced, as shown in Figure 3(e).

### 3.2. Effect of SDS assistance

A series of porous CdIn$_2$S$_4$ microspheres were prepared in aqueous solution with the different adding amount of SDS at 160℃ for 12 h. The structure and optical property of above-prepared products were characterized by XRD and UV-Vis-DRS. The results showed in Figure 4(a-d) and Figure 5.

**Figure 4.** XRD patterns of CdIn$_2$S$_4$ prepared with different adding amount of SDS 0 g(a); 0.16 g(b); 0.57 g (c); 1.14 g (d)

**Figure 5.** UV-Vis-DRS of CdIn$_2$S$_4$ prepared with different adding amount of SDS 0 g(a); 0.16 g(b); 0.57 g (c); 1.14 g (d)
As shown in Figure 4, with the amount of SDS increasing, the crystallinity of products remained similar, and all the diffraction peaks revealed pure cubic spinel phase of CdIn$_2$S$_4$. The results indicated that the concentration of SDS hardly affected the crystal structure of CdIn$_2$S$_4$ products. As shown in Figure 5, the UV-Vis-DRS showed that the absorption edges of samples displayed blue shift from visible region with the increasing of SDS concentration. This phenomenon was attributed to the difference on structure and morphology of SDS-assisted CdIn$_2$S$_4$ products. The addition of SDS could lead to the formation of small crystallitic particles, which made the absorption edges blue shift. The maximum absorption edge of CdIn$_2$S$_4$ prepared without SDS was located at 550 nm corresponding to band gap of about 2.25 eV; while the absorption edges of SDS-assisted hydrothermal products were located from 540 nm to 520 nm corresponding to band gaps from 2.30 to 2.38 eV.

In order to describe the producing process of the CdIn$_2$S$_4$ microspheres, the morphologies of the products prepared for different adding amount of SDS at 160°C for 12 h were respectively determined by SEM measurement Figure 6(a-d).

![Figure 6](image)

**Figure 6.** SEM images of CdIn$_2$S$_4$ prepared with different adding amount of SDS
0 g(a); 0.16 g(b); 0.57 g (c); 1.14 g (d)

As shown in Figure 6(a), a large amount of variform floss-like spheres with rough surface were obtained under hydrothermal condition without any template. With the amount of SDS increasing, the aggregation of flakes tended to self-organized into regular flower-like microspheres with an average diameter of 3-5 μm. Moreover, the gaps between petals became smaller, and many compact and dense microspheres were formed. It revealed that the SDS-assisted CdIn$_2$S$_4$ nanosheets were prone to self-organized into flower-like microspheres. The adding amount of SDS played a key role on the morphology by the formed different micelle shape. When the adding amount of SDS in aqueous solution was 0.57 g (2.8×10^{-2} mol/L), the spherical micelle could be helpful for the formation of the microspheres with regular slit pore. With the amount of SDS increasing, spherical micelle further transformed into claval micelle, which hindered the formation of even granular microspheres.

4. Conclusions

In summary, porous CdIn$_2$S$_4$ microspheres had been prepared through SDS-assisted hydrothermal technology. The results showed that hydrothermal time and the surfactant addition had great effect on the structure, morphology and optical property of CdIn$_2$S$_4$ products, respectively. The possible mechanism for the formation process of CdIn$_2$S$_4$ porous microspheres had been related with the self-assemble growth of CdIn$_2$S$_4$ crystals.
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