

Biomolecule-Assisted Synthesis of Nanocrystalline CdS and Bi₂S₃ for Photocatalytic Hydrogen Evolution

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Abstract

Novel CdS and Bi₂S₃ hollow nanospheres were prepared by simple “one-pot” biomolecule-assisted hydrothermal method using glutathione (GSH) as sulfur source and structure-directing reagents. The single-phase CdS and Bi₂S₃ photocatalysts were capable of evolving H₂ from aqueous solutions containing a sacrificial electron donor, under visible light irradiation ($\lambda \geq 420$ nm) with Pt co-catalyst. A possible formation mechanism of complexation, S-C bond rupture, and spherical aggregate followed isotropic Ostwal ripening or anisotropic Ostwal ripening was proposed in this study.

Keywords: CdS, Bi₂S₃, Photocatalyst, Hydrogen Evolution, Ostwal Ripening

1. Introduction

Since the evolution of hydrogen and oxygen over TiO₂ and Pt counterelectrodes under the irradiation of ultraviolet (UV) light was first reported by Fujishima and Honda [1], photocatalytic water splitting has been received much attention and widely studied for converting solar energy into clean and renewable hydrogen energy. Most of already developed photocatalysts can only take advantage of ultraviolet irradiation accounting for a small fraction 4% of the overall solar energy. Generally, sulfides exhibited good photocatalytic activities under visible light [2]. Among all sulfides, nanocrystalline CdS with unique nanostructure, has been provided with good photocatalytic activity for hydrogen production [3]. Therefore, many investigations have been made in the development of various methods for the design and fabrication of hollow nano- or microspheres [4], nanorods [5], microcages [6], and nanoporous sheetlike/hollow CdS [7] using a template and/or surfactant.

Pt-loaded CdS nanowire arrays with highly ordered crystalline prepared by a hard template of mesoporous silica showed good photocatalytic activity for hydrogen production under visible light irradiation [8,9]. Nanostructured CdS, including nanosheets and hollow nanorods, with diameters of 3 nm exhibited large BET surface area and high hydrogen yield under visible light irradiation ($\lambda \geq 420$ nm) [7]. Some nanostructured CdS with

various morphologies, such as hollow sphere-like [4], rod-like [10], snake-like alignment of nonspherical [11] and microcage-like [6], have been also prepared for photocatalysts.

In present study, CdS and Bi₂S₃ hollow nanospheres were prepared by simple “one-pot” hydrothermal method using glutathione (GSH) as the sulfur source and structure-directing reagents. This paper concerns the synthesis, characterization, photocatalytic activity and the formation mechanism of the novel structural CdS and Bi₂S₃.

2. Experimental Procedures

2.1. Materials and Instruments

All chemicals adopted were of analytical grade. The UV-visible absorption was checked by using a UV-vis spectrophotometer (TU1901, China). The XRD patterns were obtained with a Bruker D8 advance diffractometer using Cu-K α radiation. TEM measurements were conducted using a JEM-2010. FESEM images were obtained on a JEOL JSM-6700 field-emission scanning electron microanalyzer.

2.2. Method of Synthesis

0.99 mmol Cd(NO₃)₂·4H₂O, 0.99 mmol GSH and 45 mL deionized water was added into 80 mL capacity stainless

Teflon autoclave, which gave a GSH/Cd²⁺ molar ratio of 1:1. After stirred for 30 min, the autoclave was heated at 160°C for 24 h. The precipitates were centrifuged and washed using ethanol and deionized, and finally dried at 80°C. With the same method, Bi₂S₃ nanomaterials were prepared at a GSH/Bi³⁺ molar ratio of 3:2.

2.3. Photocatalytic Reaction

Photocatalytic hydrogen evolution was performed in a top-irradiation Pyrex cell. The hydrogen evolved was analyzed by a thermal conductivity detector (TCD) gas chromatograph (MS-5A zeolite column). The detailed experiment was listed in **Figure 4**.

3. Results and Discussion

3.1. Characterization of Materials

The XRD pattern of the prepared CdS microsphere was shown in **Figure 1**. According to its main diffraction peaks at 24.9°, 26.6°, 28.4°, 43.7°, 52.0°, it can be well matched with the standard values (JCPDS Card no 02-0549). The broadness of the diffraction peaks indicates that the dimensions of the CdS nanoparticles are very small. **Figure 1** also shows that all the diffraction peaks of Bi₂S₃ can be indexed to be a pure orthorhombic phase for Bi₂S₃ (JCPDS Card no. 06-0333) with lattice parameters $a = 1.1150$ nm, $b = 1.1300$ nm, and $c = 0.3981$ nm. The intensities and positions of the peaks are

in good agreement with literature values [12].

3.2. SEM and TEM Observations of CdS and Bi₂S₃

The TEM image of CdS shown in **Figure 2(a)** demonstrated that the satisfactorily hollow nanospheres with the size of 100 - 200 nm in diameter were formed. It can be seen that the relative whiter areas in the central area of image and the dark walls of the hollow nanospheres consist of sub-nanocrystallites with the size of about 5 nm in diameter (The inserted TEM amplificatory image). The thickness of their walls is ca. 60 nm. The SEM overview images shown in **Figure 2(b)** indicated that the nanospheres were inhomogeneously dispersed. An open void that evolved from the hollow interior space was present in the

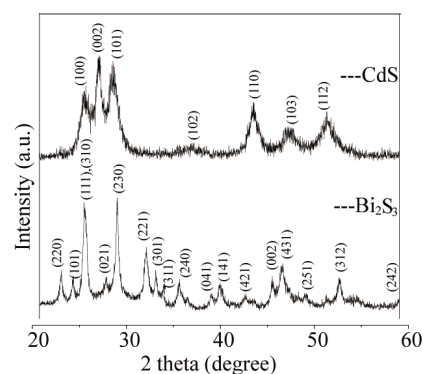


Figure 1. XRD patterns of CdS and Bi₂S₃.

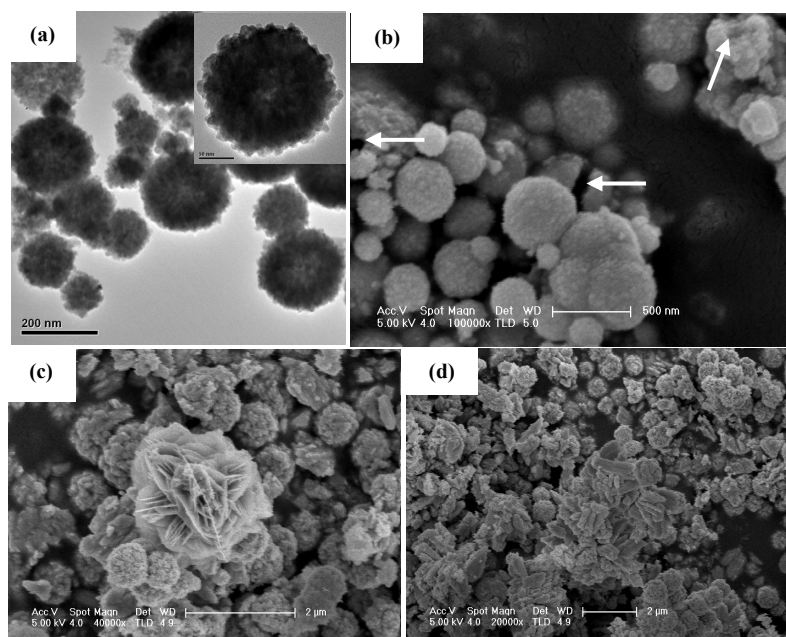


Figure 2. TEM (a) and SEM (b) images of the CdS hollow microspheres. The inset **Figure 2(a)** is the TEM amplificatory image of the corresponding sample. SEM (c, d) images of the Bi₂S₃.

center of the nanospheres, and some of the spheres were broken, confirming their hollow nature as pointed out by the arrow shown in **Figure 2(b)**. The FESEM photographs of Bi_2S_3 shown in **Figures 2(c)** and **(d)** were obviously observed that some of Bi_2S_3 showed coarse spheres and rod-particles, and camellia flower-like agglomerated structure, instead of a uniform hollow sphere structure.

3.3. Photocatalytic Performance

Figure 3(a) shows that the CdS hollow microspheres exhibit an absorption edge of 510 nm. The Tauc plot derived from UV-vis reflectance measurement of CdS hollow spheres indicated a direct band gap of 2.43 eV. It has been reported that the band gap of Bi_2S_3 varies from 1.2 to 1.84 eV depending on the synthesis method [13]. The band gap of Bi_2S_3 prepared in the study is about 1.73 eV according to the result shown in **Figure 3(b)**.

Figure 4(a) shows the time courses of hydrogen evolution over CdS hollow spheres. The initial photocatalytic hydrogen yield attained 67.2 $\mu\text{mol/h}$. **Figure 4(b)** shows the photocatalytic activity of Bi_2S_3 for the hydrogen evolution. The hydrogen yield is ca. 0.75 $\mu\text{mol/h}$, being quite low compared to that of CdS. The activity difference might result not only from the different element component but also from the different apparent structure and the particle size. Future investigation on controlling and influence of apparent structure on photocatalytic activity is being undertaken.

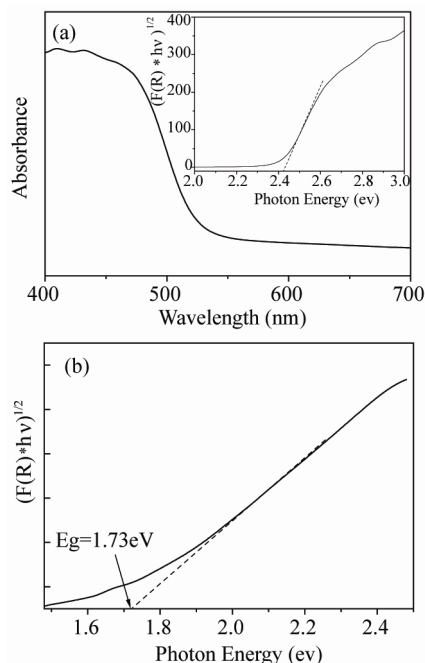


Figure 3. (a) UV-vis spectrum of CdS nanoparticles. The inset curve is the Tauc curve; (b) The Tauc curve of Bi_2S_3 .

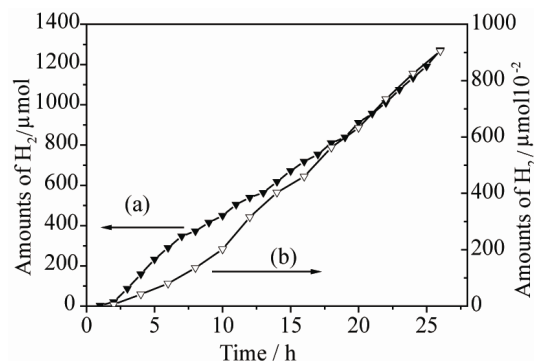


Figure 4. The rate of H_2 evolution on CdS hollow sphere catalysts with loading of 0.5 wt% Pt (a), and Bi_2S_3 catalysts with loading of 0.5 wt% Pt (b) in aqueous solution of 20 ml of 0.35 M Na_2SO_3 , 20 ml of 0.25 M Na_2S and 40 ml deionized water: catalyst, 0.1 g; light source, 300 W Xe lamp with filter ($\lambda \geq 420 \text{ nm}$).

3.4. Formation Mechanism of Hollow Microspheres

It is speculated that the synthesis reaction of CdS hollow microspheres consists of two steps as follows. The first step is GSH-dominated nucleation process which can be formulated:

In this process, glutathione plays the role as sulfur source and structure-directing reagents. First, it could chelate with Cd^{2+} to form initial precursor complexes [Equation (1)], followed by S-C bonds rupturing due to high temperature [Equation (2)]. Second, the excess GSH could be adsorbed on the surface of CdS nanoparticles because S in the glutathione has a strong affinity toward the Cd in the CdS, and small CdS nanoparticles aggregated due to the interaction of H-bond on the surface of GSH. Finally, solid spheres were formed through the progressively developing of its curved faces.

The second step is the Ostwald ripening process. The nanocrystallites located in the inner cores have higher solubilities due to the higher surface energies associated with their larger curvatures, compared with the outer nanocrystallites. As the reaction proceeded, the CdS in the outer layers of the nanospheres grew larger at the expense of the inner ones by the mass transfer between the solid core and outside chemical solution through intercrystallite interstitials of the nanospheres [14], which was accompanied with the formation of the interior space, as shown in **Figure 5(1)**. However, the growth is likely to proceed in two ways, viz. isotropic growth and anisotropic growth. Generally, a reaction is more likely to lead to an anisotropic growth with a relatively slow supply of reaction precursors than that with fast one [15]. As it has been known, the solubility of CdS in aqueous solution is much higher than Bi_2S_3 with their Ksp values at

1.4×10^{-29} and 1.82×10^{-99} , respectively. Thus, camellia flower-like or cauliflower-like hierarchical architectures by anisotropic ripening mechanism were shaped on the surface of Bi_2S_3 spheres shown in **Figure 5(2)**. Moreover, when we substituted Na_2S and thiourea for GSH to perform the preparation, no CdS and Bi_2S_3 nanospheres were found. This result could further indicate that GSH plays an indispensable role in the fabrication of certain three-dimensional nano materials with different morphologies and structures.

4. Conclusions

In summary, the fabrication of uniform CdS hollow nanospheres and Bi_2S_3 nanospheres-based camellia flower-like and/or cauliflower-like hierarchical architectures have been achieved by simple “one-pot” method using a biomolecule-assisted hydrothermal process without any template. A possible formation mechanism concerned complexation, S-C bond rupture, and spherical aggregate followed isotropic Ostwal ripening or anisotropic Ostwal ripening. The as-prepared CdS photocatalyst exhibited higher photocatalytic activity under visible light. The biomolecule-assisted hydrothermal method provides a simple alternative route for the preparation of unique morphology inorganic semiconductor sulfide nanocrystals. The structure and property can be expected to be promoted feasibly by changing preparation conditions for different compounds.

5. Acknowledgements

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6. References

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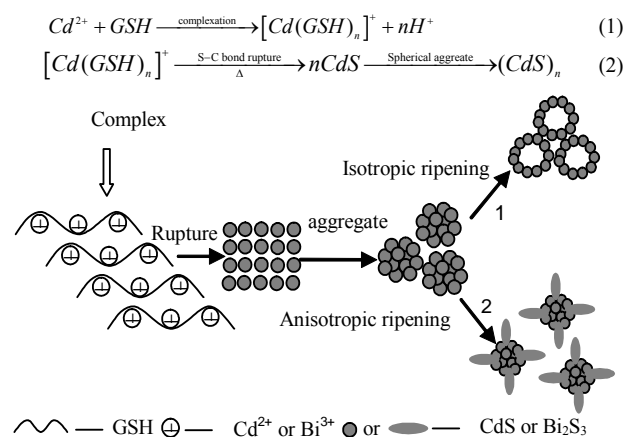


Figure 5. The scheme of the formation process of the CdS hollow microspheres or the Bi_2S_3 nanospheres-based camellia flower-like or cauliflower-like hierarchical architectures.

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