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Article

Surface treatment effect on the photocatalytic hydrogen generation of CdS/ZnS core-shell microstructures

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ABSTRACT

CdS/ZnS core-shell microparticles were prepared by a simple two-step method combining ultrasonic spray pyrolysis and chemical bath deposition. The core-shell structures showed enhanced photocatalytic properties compared with those of CdS or ZnS spherical particles. CdS/ZnS photocatalysts with different amount of ZnS loaded as shells were prepared by adjusting the concentrations of Zn and S precursors during synthesis. The optical properties and photocatalytic activity for hydrogen production were investigated and the amount of ZnS loaded as shell was optimized. Thermal annealing and hydrothermal sulfurization treatments were applied to the core-shell structure and both treatments enhanced the material's photocatalytic activity and stability by eliminating crystalline defects and surface states. The result showed that thermal annealing treatment improved the bulk crystallinity and hydrothermal sulfurization improved the surface properties. The sample subjected to both treatments showed the highest photocatalytic activity. These results indicate that CdS/ZnS core-shell microspheres are a simple structure that can be used as efficient photocatalysts. The hydrothermal sulfurization treatment may also be a useful surface treatment for metal sulfide photocatalysts. The simple two-step method provides a promising approach to the large-scale synthesis of core-shell microsphere catalysts.

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1. Introduction

Semiconducting photocatalytic materials with high photocatalytic activity and stability have received considerable attention for their potential applications in solar-hydrogen production [1]. Colloidal semiconductor photocatalysts are of particular interest owing to their tunable physical and chemical properties as well as recent advances in their synthesis methods. There remains a need to design and develop photocatalysts with high photocatalytic efficiency, good stability, and low cost. CdS is regarded as a promising low-cost semiconductor

because of its optimal band gap and the favorable position of its conduction band and valence band edge for water splitting. Thus, CdS has been widely investigated as a photocatalyst for visible-light-driven H₂ evolution [2–5]. However, its instability in aqueous solution due to self-photocorrosion through reactions of photogenerated holes has limited its applications in photocatalysis. Recently, attention has been devoted to modification and hybridization of CdS with other materials to improve its photocatalytic performance and stability [6–10]. Nanoporous CdS nanosheets and hollow nanorods have been synthesized by a two-step aqueous route that consisted of an

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initial precipitation of nanoporous $\text{Cd}(\text{OH})_2$ followed by ion-exchange to form CdS nanostructures [11]. The obtained CdS nanostructures showed an apparent photoluminescence (PL) quantum yield of about 60.34% measured at 420 nm. CdS nanocrystals with different phase structures have been synthesized by a simple cadmium–thiourea complex thermolysis route [12]. The mixture of cubic and hexagonal CdS that was obtained showed higher photocatalytic activity compared with that of pure cubic or hexagonal CdS. A $\text{C}_3\text{N}_4/\text{CdS}$ nanocomposite [13] and carbon-coated CdS nanoparticles [14] have been synthesized by template-free one-step calcination and one-step hydrothermal carbonization routes, respectively. Both structures showed improved photocatalytic activity and stability compared with those of bare CdS. A composite photocatalyst (Pt-PdS/CdS), which achieved a high QE of up to 93% in photocatalytic H_2 production in the presence of sacrificial reagents under visible light irradiation, has also been reported [15]. However, the use of the expensive noble metal Pd in that work limited its potential for large scale applications. A long range ordered $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ twin-homojunction structure has been reported, which had improved charge carrier separation and achieved efficient photocatalytic hydrogen production without the use of any noble metals [16]. ZnS is a semiconductor with wide band gap (3.6 eV) [17,18] and can be used to form solid solutions with CdS and tune its band gap and conduction band energy level [19–21]. Multi-component CdS/ZnS core-shell nanostructures with ZnS as a protective shell around the CdS core have been synthesized and applied as efficient photocatalysts. The ZnS shell can passivate surface defects of the CdS core, which lead to non-radiative recombination, by reducing the number of dangling bonds on the particles surface, considerably improved the activity and photostability of the particles [22–25].

Depending on their relative band edge positions, CdS/ZnS core-shell heterojunction possess a straddling gap (type I) structure, with the conduction and valence band of ZnS straddling those of the CdS core. Within this structure, both electrons and holes are confined to the core [26]. Owing to the charge carrier confinement, type-I CdS/ZnS core-shell structures show unique optical and electrical properties that have drawn much attention for potential applications in optoelectronic devices such as QD-LEDs and for biological fluorescence labeling [24,27–33].

It has been reported that CdS/ZnS core-shell structures exhibit high stability and high activity in photocatalytic solar energy conversion applications [24,28]. Little et al. [27] demonstrated that the thickness of the ZnS shell had a great influence on the optical and morphological properties of CdS/ZnS heterostructures owing to a large lattice mismatch of 7.5% between CdS and ZnS. For example, it has been reported that the thickness of the ZnS shell has a great influence on the PL quantum yield of the CdS/ZnS core-shell microstructures [29,30]. Many other factors such as the electronic properties of the shell, size of the core, and post treatments can substantially influence the performance of the core-shell structure.

In this work, CdS/ZnS core-shell micro-structures were prepared by a simple two-step method combining a simple

ultrasonic spray pyrolysis with chemical bath deposition (CBD) steps. In the first step, CdS microparticles (MPs) as the core material were prepared by ultrasonic spray pyrolysis (USP). In the second step a ZnS shell was grown on the surface of the CdS particles by CBD. Through these two steps, type-I core-shell CdS/ZnS MPs were synthesized. Photocatalytic characterization showed that the type-I CdS/ZnS MPs had much higher photocatalytic activity and stability than that of the CdS particles. By adjusting the concentrations of the ZnS precursor, we obtained CdS/ZnS core-shell MPs with different amount ZnS loaded as shell and studied the effects of different amounts of ZnS on their optical or photocatalytic properties. We also used a heat treatment under a nitrogen atmosphere to improve the crystallinity of the materials, which also increased the photocatalytic activity. Furthermore, we used a hydrothermal sulfuration treatment of the CdS/ZnS MPs in Na_2S aqueous solution to eliminate surface oxide impurities and other surface defects to further improve the photocatalytic activity of the materials. The two-step synthesis method used in this work provides a simple approach to large-scale and low-cost synthesis of core-shell microsphere catalyst for photocatalytic applications. We also demonstrated that the hydrothermal sulfuration treatment is a simple and effective surface treatment for improving the photocatalytic performance of metal sulfide photocatalysts.

2. Experimental

2.1. Synthesis of CdS and ZnS particles

USP was used to prepare spherical CdS and ZnS MPs. The particle sizes, which ranged from sub-micrometer to micrometer particle diameters, were controlled by adjusting the molar concentrations (0.1, 0.5, and 1.0 mol/L) of the precursor solutions used for spray pyrolysis. In a typical procedure, a 100-mL aqueous solution containing metal nitrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ or $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) and $\text{SC}(\text{NH}_2)_2$ (purchased from Sinopharm Chemical Reagent Co. Ltd, used as received) with a concentration of 0.5 mol/L was prepared. This aqueous solution was then transferred to an ultrasonic nebulizer (operating at a frequency of 1.72 MHz), where it was atomized into micro-droplets and carried to a temperature-controlled tube-furnace by a nitrogen gas flow. The pyrolysis reaction transformed the micro-droplets to CdS or ZnS microspheres at 500 °C. A schematic diagram of the ultrasonic spray pyrolysis system is shown in Fig. 1. The resulting CdS or ZnS particles were collected from the quartz tube.

2.2. Synthesis of CdS/ZnS core-shell structures

The CdS/ZnS core-shell structures were prepared by a two-step method. The first step was USP deposition of the CdS powder as described above (with a precursor concentration of 0.5 mol/L) followed by dispersion of a 0.2-g portion of the obtained CdS powder in a CBD precursor solution consisting of 100 mL of aqueous $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{SC}(\text{NH}_2)_2$ at concentrations of 0.5 and 1.0 mol/L, respectively. For optimization of the

Fig. 1. Schematic illustration of ultrasonic spray pyrolysis system.

ZnS shell deposition, the amount of the ZnS loaded as shell was adjusted by setting the concentrations of the CBD precursor to 0.2, 0.3, and 0.5 mol/L, while maintaining the Zn to S molar ratio at 1:2. The mixed solutions were transferred to a 150 mL round-bottom flask and maintained at 60 °C with stirring for 2 h for the CBD. After the reaction, a light-yellow powder was collected from the flask and washed with deionized water three times and then dried at 70 °C in a vacuum oven for 6 h.

2.3. Surface treatment for CdS/ZnS core-shell microparticles

To eliminate surface defects and improve the crystallinity of the obtained CdS/ZnS core/shell structures, the micro-particles were transferred to a quartz tube furnace for annealing at 350 °C for 0.5 h in a nitrogen atmosphere.

Another surface treatment involved hydrothermal sulfuration. For this method, 0.5 g of the CdS/ZnS powder was dispersed in 60 mL aqueous Na₂S solution (0.2 mol/L). After stirring for 15 min, the suspension was transferred to a 100 mL Teflon-lined autoclave. The sulfuration treatment was performed at 180 °C for 10 h in an oven. After the hydrothermal treatment, the autoclave was allowed to cool to room temperature naturally. The obtained yellow powders were washed

with distilled water three times then dried at 70 °C in a vacuum oven for 6 h.

2.4. Characterization

The structural and optical properties of the CdS, ZnS and CdS/ZnS core-shell particles were systematically examined by scanning electron microscopy (SEM, model JSM-6700), X-ray fluorescence spectrometry (XRF, 4 kW, Bruker, Rh K_{α}), UV-visible spectrophotometer (CHTACHI U-4100), X-ray diffraction (XRD, Cu K_{α} , 40 kV, 40 mA, PANalytical) and photoluminescence (PTI QuantaMaster™ 40). All measurements were conducted at room temperature.

The photocatalytic hydrogen evolution experiments were performed in a reactor with a side irradiation Pyrex cell maintained at 35 °C. A 12.56-cm² side window of the cell was irradiated with visible light obtained from a PLS-SXE300/300UV Xe lamp with a cutoff filter ($\lambda > 430$ nm, $T = 65\%$). A 0.2-g portion of photocatalyst powder was dispersed with magnetic stirring in a cell filled with 200 mL of aqueous Na₂SO₃ (0.25 mol/L) and Na₂S (0.35 mol/L) as a sacrificial electron donor. The amount of H₂ evolved was determined by sampling from the cell and testing with thermal conductivity detector (TCD) gas chromatography (Beifen-Ruili SP-2100, NaX zeolite column, nitrogen as a carrier gas). Blank experiments revealed that no hydrogen was produced without catalyst added or under no light irradiation. The evaluation of photocatalytic activity followed reports of Zhang [19].

3. Results and discussion

3.1. CdS, ZnS and core-shell CdS/ZnS microspheres

Fig. 2(a) and (b) show SEM images of the spherical CdS and

Fig. 2. SEM images of CdS (a), ZnS (b) and CdS/ZnS core-shell microspheres (c) prepared by USP at starting-solution concentrations of 0.5 mol/L and their corresponding XRD patterns (d), UV-vis spectra (e) and hydrogen evolution rate (f).

Fig. 3. SEM (a), TEM (b) and HRTEM images (g) of CdS/ZnS core-shell spherical particle and corresponding EDS elemental mapping of Cd (c), Zn and Cd (d), S (e), and Zn (f).

ZnS microspheres formed by USP with precursor solution concentrations of 0.5 mol/L at 500 °C. The surface of the CdS particles was rough owing to fast nucleation of CdS primary particles in a single droplet and their subsequently aggregation. The surface of the ZnS microspheres was smooth, which could be attributed to slow nucleation and formation of a single ZnS particle in each droplet.

The sizes of the CdS and ZnS microspheres were found to range from 600 to 1000 nm. The broad size distribution of the CdS or ZnS particles was likely caused by collisions and merging of droplets under the deposition conditions that led to the formation of the CdS or ZnS particles. However, the average particle size could be controlled by changing the concentration of the starting solution used for pyrolysis [34]. The CdS/ZnS core-shell MPs were synthesized by further deposition of a ZnS shell on the CdS MPs by a CBD method with a Zn precursor concentration of 0.5 mol/L. The particles formed are denoted as CdS/ZnS-0.5. The SEM image in Fig. 2(c) shows the CdS/ZnS core-shell MPs. The CBD treated MPs possessed a smoother surface after the ZnS layer was coated on to the CdS spherical particles. The XRD results shown in Fig. 2(d) indicated that the

ZnS particles formed with hexagonal ZnS (JCPDS 00-001-0677) and the CdS particles were composed of hexagonal CdS (JCPDS 00-006-0314). The as-prepared CdS/ZnS-0.5 contained peaks from hexagonal CdS, ZnS, and cadmium zinc sulfite (JCPDS 00-011-0284). As shown in Fig. 2(e), the absorption edge of CdS is 562 nm corresponding to a band gap of 2.2 eV. The ZnS particles showed an absorption edge of 391 nm, corresponding to a band gap of 3.17 eV. When the CdS particles were covered by the ZnS shell the absorption edge of the resulting CdS/ZnS particles blue shifted to 536 nm (corresponding to an energy of 2.31 eV). The hydrogen production activity shown in Fig. 2(f), indicates that the formation of the CdS/ZnS heterojunction considerably improved the photocatalytic activity of CdS MPs. The ZnS particles showed the lowest activity owing to the large bandgap of this material.

To elucidate the microstructure of the CdS/ZnS core/shell, we conducted a detailed investigation using a field-emission transmission electron microscope (FE-TEM) as shown in Fig. 3. The broader distribution of Zn over the particles surface compared with that of Cd suggested coverage of ZnS over the CdS core and successful fabrication of a spherical core/shell structure. An HRTEM image of a heterojunction in the CdS/ZnS core-shell structure is shown in Fig. 3(g). We observed clear lattice planes with fringe spacings of 0.206, 0.245, and 0.329 nm corresponding to the (110) and (102) planes of hexagonal CdS (JCPDS 00-006-0314) and the (100) plane of hexagonal ZnS (JCPDS 00-001-0677), respectively.

3.2. Optimization of shell deposition for CdS/ZnS core-shell structure

To better understand the effects of the ZnS precursor solution concentration on the optical and photocatalytic properties of CdS/ZnS core/shell structure, two more CdS/ZnS core-shell microparticle samples (CdS/ZnS-0.2 and CdS/ZnS-0.3) were prepared with Zn precursor concentrations of 0.2 and 0.3 mol/L, respectively. The shell thickness of the core-shell MPs was difficult to determine from TEM images (Fig. 3(b)). Thus, we applied XRF analysis to determine the amount of ZnS covering the CdS particles, and the results are shown in Table 1. We found that the amount of ZnS in the particles increased with increasing concentration of the Zn precursor solution.

Fig. 4 shows the UV-vis absorption and PL spectra of CdS and CdS/ZnS core/shell structures, which were formed with different Zn and S precursor concentrations. The obtained core-shell structures showed a similar absorption edge to that of the CdS particles, which could be attributed to the low thickness of the ZnS shell. Furthermore, no notable changes were observed with different Zn precursor solution concentra-

Table 1

XRF analysis data of CdS/ZnS core-shell structure with different concentrations of Zn source in precursor solution.

Sample	Cd		S		Zn		Zn/Cd ratio	
	wt%	mol%	wt%	mol%	wt%	mol%	wt%/wt%	mol%/mol%
CdS/ZnS-0.2	18.2	8.4	31.6	51.4	50.2	40.2	2.7	4.7
CdS/ZnS-0.3	9.8	4.4	32.6	51.2	57.6	44.4	5.8	10.1
CdS/ZnS-0.5	6.48	3.1	30.4	51.0	55.8	45.9	8.6	14.8

Fig. 4. UV-vis absorption (a) and PL spectra (b) of CdS and CdS/ZnS core-shell particle formed with Zn precursor solution concentrations of 0.2, 0.3, and 0.5 mol/L. Inset: PL spectra (500–900 nm) of CdS particle. All samples were heat-treated.

tions. In the PL spectra, the peak centered at 540 nm derived from the band edge emission of CdS microspheres. The intensity of this peak was clearly enhanced as the concentration of the Zn precursor was increased. This could be attributed to passivation of CdS surface defects by the ZnS shell [24]. It has been observed that the photoluminescence quantum yield of CdS/ZnS core-shell structures can be improved through passivation of non-radiative recombination sites on the CdS surface upon shell growth [35–38]. New emission peaks appeared at 480 nm, which could be identified as arising from ZnO [39] in the CdS/ZnS core-shell MPs. The presence of ZnO likely originated from oxidation of the ZnS shell during the heat treatment.

Fig. 5 shows the H_2 evolution with time for CdS/ZnS core-shell MPs prepared with the different concentrations of Zn source precursor under visible light irradiation. The hydrogen production rate of the heat-treated CdS/ZnS core-shell particles prepared with the highest Zn precursor concentration showed the highest initial hydrogen production rate. The hydrogen production rate of the CdS/ZnS-0.3 sample exhibited an increase over time and became the highest after 6 h. This effect may be attributed to stripping of the surface layer, which had a high density of defects.

Fig. 5. Hydrogen evolution rate of bare CdS and CdS/ZnS core-shell structures prepared with Zn precursor concentrations of 0.2, 0.3, and 0.5 mol/L. All samples were heat-treated.

3.3. Surface treatments for CdS/ZnS core-shell microspheres and their photocatalytic activities

It is widely recognized that surface treatments play an important role in modifying the physical and chemical properties and photocatalytic performance of photocatalysts [40]. The shell of these CdS/ZnS particles was deposited by CBD at a relatively low temperature, which may have resulted in poor crystallinity and a high density of surface defects. Therefore, to improve the crystallinity of the particles and reduce interfacial defects between the CdS core and ZnS shell, we applied a heat treatment under a N_2 atmosphere. During the heat treatment, the photocatalyst surface may have been partially oxidized. To address this issue, a hydrothermal sulfurization step was performed to improve the surface properties of the particles and thus enhance the photocatalytic activity of the CdS/ZnS core-shell particles.

To investigate the effects of surface properties on photocatalytic performance, the CdS/ZnS-0.3 sample was selected and either heat treated and subjected to a hydrothermal sulfurization step, heat treated only, or treated only by the hydrothermal sulfurization step. We obtained four different samples based on the different treatment procedures, as listed in Table 2.

The optical properties of the samples subjected to different treatment procedures were measured. As illustrated in Fig. 6 (a), all four CdS/ZnS core-shell samples showed the same absorption edge at 540 nm, which revealed that no change occurred to the CdS core after different surface treatments. The

Table 2
Four treatment procedures for CdS/ZnS-0.3 samples.

Sample label	Treatment procedure
A	Non-treatment
B	Thermal heat treatment
C	Hydrothermal sulfurization
D	Thermal heat treatment followed with hydrothermal sulfurization

Fig. 6. UV-vis absorption (a) and PL emission spectra (b) (excitation wavelength 340 nm) of CdS/ZnS-0.3 core-shell structured samples **A**, **B**, **C** and **D**, as labeled in Table 2.

absorption spectrum for the core-shell structure was a superposition of absorption response of CdS core and ZnS shell. A difference in the absorption response was observed in the range 320–420 nm, which could be attributed to differences in the absorption edge of the ZnS shell in the treated samples. A blue shift of the absorption edge in samples **C** and **D** was found compared with that of the samples **A** and **B**. This could be caused by a reduction of surface defect states, which induced a narrowing of the bandgap in samples **C** and **D** after the hydrothermal sulfurization. In sample **B**, the thermal annealing may have oxidized the surface leading to a red shift of absorption edge compared with that of the untreated sample **A**.

The PL emission spectra were recorded at room temperature to reveal the effect of surface treatment on the band structure of sample CdS/ZnS-0.3, as shown in Fig. 6(b). The edge band emission peaks of CdS at about 570 nm was observed for all the samples. Unlike the spectra of samples **A** and **B**, a relatively strong peak at about 720 nm was found in the spectra of samples **C** and **D**. This peak can be attributed to defect emission from the ZnS shell. It has been reported that different intrinsic defects including sulfur vacancies (V_s), zinc vacancies (V_{zn}) and interstitial sulfur (I_s) exist in ZnS crystals and that the localized acceptor states of V_{zn} and I_s are above the valence band of ZnS [28,41]. Therefore, the emission occurring from electronic transitions between intrinsic defects and the conduction band of ZnS lead to these visible emission peaks. The emission peak centered at 428 nm can be regarded as arising from luminescence of self-activated centers [41].

Fig. 7 displays the XRD patterns for the CdS/ZnS-0.3 core-shell particles subjected to different surface treatments. For the untreated sample **A**, a complex XRD pattern was observed, which included contributions of diffraction peaks of $Cd(OH)_2$ (JCPDS 00-012-0062), $Zn(OH)_2$ (JCPDS 00-012-0142), CdS (JCPDS 01-080-0006) and ZnS (JCPDS 03-065-0309). This result indicated that multiple compounds were present in sample **A**. After the thermal heat treatment, diffraction peaks from ZnO (JCPDS 00-005-0664) and CdS were found in sample **B**. This result suggested that during the thermal treatment, surface $Zn(OH)_2$ decomposed to ZnO and that ZnS was oxidized to ZnO. The samples **C** and **D** showed similar XRD patterns with

intense peaks from CdS and ZnS, indicating good crystallinity of the CdS core and ZnS shell. This result suggests that the hydrothermal sulfurization converted the oxidized surface back to ZnS.

Structural characterization of the samples subjected to different treatments was performed with a TEM as shown in Fig. 8. The as-prepared sample possessed a relatively smooth surface, with large ZnS crystals attached to the spherical particles, as also shown in Fig. 3. After being subjected to thermal annealing, the surface of the shell became rough as grains formed due to recrystallization and partial oxidation of ZnS. The hydrothermal sulfurization treatment reduced the grain size on the shell of the as-prepared and thermally annealed samples.

Fig. 9 shows the photocatalytic performance of the CdS/ZnS-0.3 core-shell structured particles subjected to different surface treatment procedures. The thermally annealed sample **B** showed better photocatalytic activity than that of the as-prepared sample **A**, despite the partial surface oxidation that occurred during the thermal annealing. Samples **C** and **D**, which were treated by hydrothermal sulfurization, showed improved the photocatalytic activity, which could be attributed to improved surface properties. Sample **D**, which was subjected to both heat-treated and hydrothermal sulfurization, showed

Fig. 7. XRD patterns of CdS/ZnS-0.3 core-shell particle samples **A**, **B**, **C** and **D** subjected to four different surface treatments.

Fig. 8. TEM images of CdS/ZnS-0.3 core-shell particle samples **A**, **B**, **C** and **D** subjected to four different surface treatments.

the highest hydrogen production rate ($55.5 \mu\text{mol g}^{-1} \text{h}^{-1}$), which can be ascribed to a combination of improved bulk crystallinity and a decrease in surface defects. The stability of sample **D** was further tested over four separate runs as shown in Fig. 9(b), demonstrating the relatively good stability and reusability of this catalyst. Although this activity was not as high as that reported for CdS/ZnS composites loaded with noble metal co-catalysts [42,43], the low cost of our approach in terms of both materials and the synthesis method indicate that our catalysts may be promising candidates for large-scale photocatalytic applications.

Photogenerated electron and hole pairs at type-I core-shell structures are confined within the core owing to the type I band structure [44,45]. Thus, excitons generated in the core may not be able to move to the surface and enable water reduction. A charge transfer process through the shell material by a tunneling effect has been reported for CdSe-ZnS core-shell na-

noparticles [46]. However, in our case the ZnS shell was relatively thick so that photogenerated charges must have leak directly to the surface. This indicates incomplete coverage of the ZnS shell in our catalyst. Thus, the ZnS shell deposition improved the photocatalytic activity compared with that of the bare CdS. This effect may be explained by passivation of surface states on the CdS surface which reduced charge carrier recombination at the surface to facilitate the photocatalytic reactions [24]. A hydrothermal sulfurization treatment further improved the surface properties of the ZnS shell by reducing the non-radiative defects, as confirmed from the PL results.

4. Conclusions

CdS MPs were prepared by ultrasonic spray pyrolysis and type-I CdS/ZnS core-shell structures were fabricated by epitaxial growth of a ZnS shell onto the CdS core particles by CBD. Our results showed that the CdS/ZnS core-shell structures had higher photocatalytic activities than that of the bare CdS cores. The enhanced photocatalytic performance of the CdS/ZnS core-shell structure for hydrogen production may be related to surface modification of the CdS core by the ZnS shell and hydrothermal sulfurization treatment, which helped to passivate surface states of the CdS core. CdS/ZnS core-shell structures with different amounts of ZnS loaded as shell were prepared by adjusting the concentrations of the Zn precursor in aqueous solution. Thermal annealing, hydrothermal sulfurization and a combination of these steps were applied to CdS/ZnS-0.3 core-shell particles and we studied the influence of these procedures on the optical, structural and photocatalytic properties of the materials. We found that samples treated with both treatments had the highest photocatalytic activity owing to both improved bulk crystallinity and surface properties. This work demonstrates a method for combining ultrasonic spray pyrolysis, CBD, and hydrothermal sulfurization to generate core-shell structures with improved photocatalytic performance as metal sulfide photocatalysts. The photocatalytic activities of the core-shell structures demonstrated that the CdS/ZnS core-shell particles were suitable for application as efficient photocatalysts.

Fig. 9. (a) Hydrogen production amount for CdS/ZnS-0.3 core-shell structured samples **A**, **B**, **C** and **D** subjected to four different surface treatments over a time course; (b) Repeated photocatalytic hydrogen production measurements from sample **D**.

Graphical Abstract

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CdS/ZnS core-shell heteromicrostructures with optimized amount of ZnS loaded as shell were synthesized by a simple two-step method. Surface treatments further improve their photocatalytic activities and stabilities. This method demonstrates a promising low-cost synthesis of core/shell microstructures.

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核壳结构CdS/ZnS微米球表面处理与光催化制氢性能的关系

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摘要: 具有高活性和稳定性的半导体光催化材料是太阳能光催化制氢领域的研究热点, 其中CdS胶体颗粒催化剂因其合适的禁带宽度和带边位置以及较低的原料价格而广受关注. 但它在水溶液中不稳定, 易受光腐蚀, 因而限制了其应用. 目前人们致力于用各种方法提高其稳定性, 包括各种纳米结构的应用、复合其他催化剂材料以及不同晶相结构复合. ZnS是一种宽禁带半导体, 禁带宽度为3.6 eV, 常被用来与CdS形成固溶体调控其能带结构, 从而提高其性能和稳定性. 其中核壳结构CdS/ZnS异质结具有跨越型(I型)能带结构, 具有特殊的光学和电学性质, 在量子点LED和量子点生物荧光显示剂方面获得关注和应用, 同时也显示了良好的光催化性能. 研究人员对核壳结构CdS/ZnS异质结材料中ZnS壳层厚度对其光学性能包括荧光效率等的影响进行了研究, 然而ZnS壳层厚度、颗粒尺寸及其表面处理对光催化性能影响方面的报道很少.

本文发展了一种简易的两步法, 制备了核壳结构CdS/ZnS微米球光催化剂. 首先采用超声喷雾热分解法制备CdS微米球, 然后以水浴法在CdS微米球上生长ZnS壳层. 采用扫描电镜(SEM)、X射线衍射(XRD)、紫外-可见吸收光谱(UV-vis)和透射电镜(TEM)对所得样品进行了表征. SEM和TEM结果显示, 所得微米球为完整包裹的球形核壳结构; XRD表征证实CdS核与ZnS壳层皆为六角相晶型; 光催化性能表征结果显示, 该样品的光催化制氢性能远高于单独的CdS微米球以及同法所制的ZnS微米球.

通过改变前驱液浓度(Zn源浓度分别为0.2, 0.3和0.5 mol/L)获得了三种不同厚度的核壳结构CdS/ZnS微米球, X射线荧光光谱结果证实了其壳层厚度成功调控. UV-vis结果发现, 其吸收边由内核CdS决定, 受壳层厚度的影响不大. 光致荧光发射光谱分析发现, 随着壳层厚度的增加, 其540 nm处的CdS带边发射峰强度逐渐增大. 这可能是由于ZnS壳层对CdS表面缺陷的钝化作用降低了其非辐射复合过程, 从而提高了荧光发光效率. 光催化制氢性能结果表明, 前驱液浓度为0.3 mol/L时合成的核壳结构CdS/ZnS微米球的产氢效率最高.

为了进一步提高其光催化效率, 采用氮气中高温热处理、水热二次硫化法以及两者共用三种方式对性能最优的微米球进行改性, 获得了三种核壳结构CdS/ZnS样品. 结果发现, 这些改性方法未影响其吸收边, 但水热二次硫化法处理以及两者共用处理的样品在540 nm处的光致荧光发射峰强度明显高于未处理的和高温热处理的样品, 证实水热二次硫化法处理可以有效地消除其表面缺陷, 减少非辐射复合. XRD结果表明其晶型没有发生变化. TEM表征发现, 经高温热处理后其壳层发生重结晶, 形成颗粒包裹形貌, 而经水热二次硫化法处理后其壳层同样发生重结晶, 但包裹颗粒的尺寸明显更小. 光催化性能测试表明, 处理后样品的光催化性能皆优于未处理样品, 其中两者共用法处理的样品产氢性能和稳定性最高.

关键词: 核壳结构; 光催化; 表面处理; 制氢; 低成本合成

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