CdS@MoS₂ Hetero-structured Nanocomposites Are Highly Effective Photo-Catalysts for Organic Dye Degradation

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ABSTRACT: CdS@MoS₂ hetero-structured nanocomposites (HSNPs) were successfully synthesized via a hydrothermal approach. The morphology and crystal structure of these composites as well as their ability to act as photocatalysts for the degradation of methylene blue were investigated using scanning electron microscopy, X-ray diffraction, transmission electron microscopy, and UV−vis absorption spectroscopy. The developed CdS@MoS₂ nanocomposites exhibited an 80% degradation rate with 30 min of visible light irradiation. To characterize the basis of the photocatalytic properties of these materials, the transient photocurrent densities were determined for the CdS@MoS₂ HSNPs and pure dendritic CdS nanotrees. The results suggest that the photocatalytic activity may reflect electron transfer between the conduction band maximum of CdS and MoS₂. Additionally, the improved visible light absorption, decreased electron−hole pair recombination, and enhanced surface area for more effective dye absorption likely contribute to improved photocatalytic performance.

INTRODUCTION

With the rapid development of science and technology, the treatment of environmental pollution has become a key issue of social concern. In the field of wastewater treatment, photocatalysis is a promising method that uses light energy to treat organic wastewater.¹,² In recent years, photo-catalytic technology (such as the TiO₂ photocatalyst) has been widely used in wastewater treatment.³ In particular, TiO₂ can significantly promote the decomposition of toxic and harmful organic pollutants to reduce environmental damage.⁴ However, because TiO₂ has a wide band gap (3.2 eV), it can only absorb 4% of the ultraviolet (UV) light in natural light. The UV region accounts for only about 4% of the entire solar spectrum, with visible light as 45% of the total energy, so most solar energy is not utilized by TiO₂ materials due to the limitation of the wide band gap of these materials.⁵ Thus, there is significant interest in the development of new photocatalysts with low band gap and high catalytic activity under visible light.⁶−⁹

Cadmium sulfide (CdS) has a narrow band gap of 2.4 eV at room temperature, which allows for higher and more efficient absorption of visible light.¹⁰−¹² In addition, CdS nanomaterials have a sufficient energy level for various photocatalytic reactions, allowing extensive applications in multiple photocatalytic processes, such as wastewater decomposition,¹³ CO₂ reduction,¹⁴ and organic dye degradation.¹⁵−¹⁷ However, the photocatalytic activity of pure CdS materials is not sufficient to meet the requirements of practical applications.¹⁸ For example, CdS materials generally exhibit lower adsorption capacity for reactants and suffer photo-corrosion and severe aggregation during photocatalysis, which may reduce their surface areas and increase the recombination rate of photo-generated carriers, reducing the overall photo-catalytic activity.¹⁹,²⁰ CdS materials can undergo serious photo-corrosion during photocatalysis because the sulfide anions can be easily oxidized by photo-generated holes, causing the CdS materials to be highly unstable and thus limiting their practical applications as photocatalysts.¹⁹,²¹−²³

Interestingly, these limitations can be partially overcome by combining CdS with molybdenum disulfide (MoS₂), resulting in the material with significantly increased photocatalytic efficiency.²⁴−²⁶ As semiconductor materials, MoS₂-based nanomaterials have a direct band gap of about 1.9 eV. MoS₂ is a transition metal sulfide that is composed of three atomic layers (S−Mo−S) stacked by weak van der Waals interactions, and these materials function as efficient photo-catalysts.²⁷−³¹ MoS₂ nanomaterials are rich in sulfur on the edges of the surface structure, providing sufficient active sites for photo-

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catalytic reactions. In addition, the CdS@MoS₂ composite material can effectively separate charges by coupling two semiconductor materials with matching energy levels and promote the oxidation—reduction reaction in the photocatalytic process.

In this study, the hydrothermal method was successfully used to synthesize dendritic CdS@MoS₂ hetero-structured nanocomposites (HSNPs). The structure and morphology of the obtained CdS@MoS₂ HSNP were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). The CdS@MoS₂ HSNPs prepared using this method showed high adsorption of reactants and high photocatalytic performance for the degradation of organic dyes such as methylene blue (MB).

## RESULTS AND DISCUSSION

The XRD patterns of the obtained pure CdS nanorods and CdS@MoS₂ HSNPs prepared with different MoS₂ contents were determined and are shown in Figure 1. The black line indicates the pure CdS nanorods, and the peaks at 24.8, 26.5, 28.2, 36.6, 47.8, 51.9, and 58.3° were assigned, respectively, to the diffraction of (100), (002), (101), (102), (110), (112), and (202) crystal faces of the hexagonal wurtzite structure of CdS, according to the JCPDS (41-1049). The other lines indicate the results for CdS@MoS₂ HSNPs prepared with different MoS₂ contents and show similar peaks as the red line corresponding to the CdS nanorods. These results show that the obtained pure CdS nanorods and CdS@MoS₂ HSNPs have hexagonal wurtzite structures. However, no diffraction peaks were observed that are associated with MoS₂, which mainly located in the outer layer of the nanocomposites.

The morphology and crystal structure of the CdS@MoS₂(5%) HSNPs were characterized by TEM. As shown in Figure 2a, the HSNP material has a typical branched nanostructure with dendritic CdS branched nanowires as the scaffold and MoS₂ coated on the surface of the dendritic structure. Element mapping patterns of obtained CdS@MoS₂(5%) HSNPs (Figure 2c–f) show the uniform dispersal of Cd in the dendritic CdS branch nanowires and Mo mainly located in the outer layer of the nanocomposites. The EDS mapping further confirmed the structure of the CdS@MoS₂ HSNPs containing dendritic CdS branch nanowires and MoS₂ layers.

Figure 3a shows that pure CdS branch nanowires exhibited a highly uniform dendritic and hierarchical structure, with an average diameter of approximately 50–100 nm. As shown in Figure 3b, the CdS@MoS₂(5%) HSNPs still maintained a nanowire-like morphology after the hydrothermal process. Figure 3c shows a typical high-resolution transmission electron microscopy (HRTEM) image of the CdS@MoS₂(5%) HSNPs, showing a (002) plane of 0.34 nm corresponding to hexagonal CdS. Compared with the well-crystallized CdS branch nanowires, no obvious crystal lattices were observed for the MoS₂ layer, indicating that MoS₂ is amorphous. This result is consistent with the results of XRD, which showed no obvious peaks in the patterns of the CdS@MoS₂ HSNPs. Also shown in Figure 3c, the dendritic CdS branch nanowires were covered by an amorphous MoS₂ layer, which facilitated the formation of a heterojunction between the CdS branch nanowires and MoS₂ layer, improving the separation and transfer of photo-generated charge carriers to eventually enhance the photocatalytic activity of the material.

The chemical composition of CdS and the prepared CdS@MoS₂ HSNPs was investigated by XPS, as shown in Figure 4. Overall, the data showed that the CdS@MoS₂ HSNPs were composed of Cd, S, and Mo elements (Figure 4a). In detail, two peaks attributed to the binding energy of Cd 3d₉/₂ and Cd 3d₇/₂.
Figure 3. (a,b) TEM images of pure CdS branch nanowires and CdS@MoS$_2$(5%) HSNPs and (c) HRTEM image of obtained CdS@MoS$_2$(5%) HSNPs.

Figure 4. XPS spectra of the survey spectrum (a), Cd 3d (b), S 2p (c), and Mo 3d (d) of CdS and CdS@5%MoS$_2$ HSNPs.

Figure 5. UV--vis diffuse reflectance spectra (a) and optical band gap energy (b) of CdS, CdS@2%MoS$_2$ HSNPs, CdS@5%MoS$_2$ HSNPs, and CdS@8%MoS$_2$ HSNPs for the wavelength range of 300–800 nm.
indicating the complete reduction of Mo$_{6+}$ 3d$_{5/2}$ into metallic 8%MoS$_2$ HSNPs, and MoS$_2$ for the wavelength range of 400 values of Mo$_{4+}$ 3d$_{5/2}$ and Mo$_{4+}$ 3d$_{3/2}$ (Figure 4d). There was observed at 228.9 and 232.4 eV, which agree well with the addition to the peaks of Cd 3d and S 2p, doublet peaks were the surface of the CdS nanotree can enhance the absorption of MoS$_2$ HSNPs, and MoS$_2$. The results reveal obviously lower the CdS@2%MoS$_2$ HSNPs cocatalyst to a formation of a heterojunction between MoS$_2$ and CdS, band gap energies of CdS@2%MoS$_2$ HSNPs, CdS@5%MoS$_2$ HSNPs, CdS@8%MoS$_2$ HSNPs, CdS, CdS@2%MoS$_2$ HSNPs, CdS@5%MoS$_2$ HSNPs, CdS@8%MoS$_2$ HSNPs, and MoS$_2$ for the wavelength range of 400–740 nm. Pure CdS shows a significant absorption edge near 519 nm for pure CdS NWs, corresponding to the ~2.38 eV band gap (Figure 5b). Loading of the MoS$_2$ cocatalysts onto the surface of the CdS nanotree can enhance the absorption of catalysts in the visible light region from 510 to 740 nm.

Figure 5a shows the UV–vis diffuse-reflectance spectra of CdS, CdS@2%MoS$_2$ HSNPs, CdS@5%MoS$_2$ HSNPs, CdS@8%MoS$_2$ HSNPs, and MoS$_2$ for the wavelength range of 400–740 nm. Pure CdS shows a significant absorption edge near 519 nm for pure CdS NWs, corresponding to the ~2.38 eV band gap (Figure 5b). Loading of the MoS$_2$ cocatalysts onto the surface of the CdS nanotree can enhance the absorption of catalysts in the visible light region from 510 to 740 nm.

Figure 5b shows the plots of $(ahv)^{1/2}$ versus $hν$ of CdS, CdS@2%MoS$_2$ HSNPs, CdS@5%MoS$_2$ HSNPs, CdS@8% MoS$_2$ HSNPs, and MoS$_2$. The results reveal obviously lower band gap energies of CdS@2%MoS$_2$ HSNPs, CdS@5%MoS$_2$ HSNPs, and CdS@8%MoS$_2$ HSNPs than that of pure CdS, which would promote the excitations of electrons from the valence band to conduction band under visible light irradiation. An indirect band gap of 2.33 eV for the as-prepared CdS@5%MoS$_2$ HSNPs suggests a synergistic effect of the CdS@2%MoS$_2$ HSNPs cocatalyst to affect the red shift.

To demonstrate the potential applicability of as-synthesized CdS and the CdS@5%MoS$_2$ HSNP nanostructures for the photo-catalytic degradation of water pollutants, we investigated the photo-catalytic activity of these materials using the photocatalytic degradation of the organic dye MB as a test reaction. The photocatalytic activity was measured for the pure dendritic CdS nanotrees, pure MoS$_2$ nanosheets, and CdS@5%MoS$_2$ HSNPs by degrading MB under visible light irradiation. As shown in Figure 6a, the photocatalytic activity of pure CdS, pure MoS$_2$, and CdS@5%MoS$_2$ HSNPs prepared with different Mo and Cd molar ratios was studied by the photodegradation of MB. All measurements were performed under the same conditions, and the concentration value of the MB solution ($C_0$) was determined based on its absorption peak at 665 nm. Before irradiation, a certain amount of sample was added to the MB suspension and stirred for 5 min under dark conditions to establish an adsorption–desorption equilibrium between the dye and the photocatalyst. Figure 6a,b shows the degradation performance of the catalyst on MB under UV radiation. As shown in Figure 6, the obtained CdS@5%MoS$_2$ HSNP material has the most outstanding performance among the three samples and has good photocatalytic activity. The degradation process of MB follows first-order reaction kinetics, and the reaction kinetic equation is as follows

$$\ln(C/C_0) = kt$$

where C and $C_0$ are the reaction and the initial concentration of the MB solution, respectively, $k$ is a rate constant, and $t$ is the reaction time.

A linear fit of the data (Figure 6c) was used to investigate the decrease in the concentration of MB solution ($C/C_0$). Obviously, the CdS@5%MoS$_2$ HSNPs showed a stronger adsorption capacity for MB. The adsorption rate of the HSNPs reached 36% in dark conditions, higher than that of pure CdS (10%) and pure MoS$_2$ (16%). The average value of $k$ for the CdS@MoS$_2$ HSNPs was 0.105 min$^{-1}$, much faster than the $k$ values for individual CdS and MoS$_2$ of 0.016 and 0.046 min$^{-1}$, respectively. Based on the above results, the photocatalytic activity of CdS was significantly enhanced by the addition of MoS$_2$ to form the CdS@5%MoS$_2$ HSNPs.

As shown in Figure 7, the apparent photocurrent responses of pure dendritic CdS nanotrees and CdS@MoS$_2$ HSNPs were observed under visible light irradiation. Fast and uniform photocurrent responses of the pure dendritic CdS nanotrees and CdS@MoS$_2$ HSNPs as electrodes were observed with each switch-on and switch-off, indicating good reproducibility of the samples. The pure MoS$_2$ showed a very low photocurrent density, indicating the low quantum efficiency of MoS$_2$. However, the CdS@MoS$_2$ HSNPs showed a higher photocurrent density than that of pure dendritic CdS nanotrees. The photocurrent is mainly determined by the effective separation of photo-generated electrons–hole carriers within the photocathode–electrolyte interfaces, and the electrodes are transported to the back contact. Therefore, when the CdS@MoS$_2$ HSNPs are irradiated with visible light, photo-generated electrons from the
excited CdS are probably transferred to indium tin oxide back contact, and photo-generated holes are transferred to MoS₂ via the heterostructure between the dendritic CdS nanotrees and the MoS₂ layers. Overall, this leads to an effective and rapid separation of photo-generated electrons and holes. The higher photocurrent of the CdS@MoS₂ HSNPs suggests that the heterostructure between the dendritic CdS nanotrees and the MoS₂ layers can facilitate the separation and transport of the photo-generated electrons and holes. Photocurrents may reflect additional p–n junctions forming between MoS₂ and CdS and the possibility of the reverse-biased P region. As the p–n junction forms, the hole–electron pairs, excited by photons, will immediately separate under the force of an internal electrostatic field. For the CdS@MoS₂ HSNPs, Schottky barriers (space charge layers) form at the interfaces of the MoS₂–CdS and probably operate in reverse bias, where an increase in barrier results in improvement in the charge separation efficiency, and thus leading to an increase in the photocurrent.

Stability and repeatability are important components of the performance of photo-catalysts. Therefore, we next studied the stability and reusability of the CdS@5%MoS₂ HSNPs over five cycles. As shown in Figure 8a, very little loss of photo-catalytic activity was observed, likely due to the effective cleaning and collection in each cycle. This indicates that the developed CdS@5%MoS₂ HSNPs have excellent long-term stability. Figure 8b shows the XRD pattern of the CdS@5%MoS₂ HSNPs after five cycles. The characteristic XRD peaks of the CdS@5%MoS₂ HSNPs after five cycles were similar to the peaks for the original CdS@5%MoS₂ HSNPs, further confirming the great stability and reusability of the CdS@5% MoS₂ HSNPs.

CONCLUSIONS

In summary, a hydrothermal reaction was applied to synthesize CdS@MoS₂ HSNPs with branched heterostructures. Under visible light excitation, the obtained CdS@5%MoS₂ HSNPs showed improved adsorption and higher MB photo-degradation compared to that of pure CdS or MoS₂. The matched energy band alignment of the CdS@5%MoS₂ HSNPs may promote the transfer of photo-generated electrons and holes from the CdS nanotrees to the MoS₂ layer. In addition, the MoS₂ layer not only can act as a co-catalyst to provide highly active sites for the reduction of organic dyes but also can act as a sacrificial agent to inhibit CdS corrosion. Overall, the obtained CdS@5%MoS₂ HSNPs showed enhanced photocatalytic property, improved stability, and excellent reusability compared to pure CdS nanomaterials.

MATERIALS AND METHODS

Preparation of CdS Nanostructures. All chemicals used in this study were of analytical grade and used without further...
purification. In a typical procedure,32 0.617 g of cadmium nitrate and 0.152 g of CS(NH2)2 were added to a mixed solution of diethylentriamine and deionized water (2:5 volume ratio). The mixed solution was then transferred to a Teflon-lined autoclave (75% of its total capacity of 100 mL). The autoclave was sealed and kept at 160 °C for 24 h for reaction and cooled to room temperature naturally after the reaction was completed. Subsequently, the solution was filtered, washed with deionized water and absolute ethanol several times, and finally dried at 80 °C under vacuum for 6 h to obtain a CdS precursor.

Preparation of CdS@MoS2 HSNPs. A certain amount of cysteine (C3H7NO2S) and ammonium molybdate (H4Mo,N2O24·4H2O) was measured and dissolved in 40 mL of deionized water to form a clear solution. After 5 min of sonication, 50 mg of the prepared CdS sample was dispersed in the obtained solution. After continuing to stir for 60 min, the resulting suspension was transferred to a 50 mL stainless steel autoclave lined with Teflon and kept at 200 °C for 24 h. The theoretical weight ratios of MoS2 in the CdS nanostructures were 2, 5, and 8 wt % and were obtained by changing the amount of cysteine (C3H7NO2S) and ammonium molybdate (H4Mo,N2O24·4H2O), and the resulting materials were designated as CdS@2%MoS2 HSNPs, CdS@5%MoS2 HSNPs, and CdS@8%MoS2 HSNPs, respectively. The product was separated by centrifugation and washed three times with deionized water and ethanol. The final material was dried in a vacuum oven at 80 °C for 6 h.

Characterization of HSNPs. XRD patterns were obtained on an X'Pert PRO (PAN analytical) with Cu Kα radiation at a range of 3–80°. The morphologies and microstructures of the HSNP samples were observed using a field-emission scanning electron microscope (Zeiss Ultra 55). TEM and HRTEM images were obtained using a Zeiss Libra 200 instrument at an acceleration voltage of 200 kV; EDS was attached to the TEM. The elemental composition was determined by XPS (SSX-100).

Photocatalysis Experiments. MB was selected to evaluate the photocatalytic activity of obtained CdS@MoS2 composites. MB was dissolved in H2O solution (20 mg/L, 50 mL) and added with 4 mg CdS@MoS2 photo-catalyst into an 80 mL quartz photoreactor irradiated by a xenon lamp (500 W) with magnetic stirring. Eventually, the MB solution was separated by centrifugation and kept at 200 °C for 24 h. The absorbance of the suspension was measured at a wavelength (%) of 665 nm.

\[ R(\%) = (1 - C_t/C_0) \times 100\% \]  

where \( C_t \) is the concentration of MB at time \( t \) and \( C_0 \) is the initial concentration of MB.

Preparation of Working Electrodes. To prepare the working electrodes, 50 mg samples of powdered CdS or CdS@MoS2 HSNPs were mixed with 50 μL of acetylacetone, and 150 μL of distilled water was mixed in an agate mortar. The material was subjected to grinding to prepare electrodes on fluorine-doped tin oxide transparent electrodes and subsequently calcined at 373–773 K for 2 h in air.

Photoelectrochemical Characterization. The photoelectrochemical properties of the prepared materials were evaluated using a potentiostat with a three-electrode cell consisting of the working electrode, counter Pt electrode, and saturated reference Ag/AgCl electrode, with 0.1 mol/L of aqueous Na2SO4 solution.

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Notes
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