MoS_2-decorated CdS nanorods for efficient photocatalytic degradation of organic pollutants

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Experimental section

1. Materials and Methods

Chemicals. Cadmium nitrate tetrahydrate and triethanolamine were purchased from Tianjin Damao Chemical Reagent Factory. Thiourea and ethylenediamine were purchased from Aladdin Reagent Co., Ltd (Shanghai, China). Sodium molybdate, p-benzoquinone(p-BQ), ethanol, and Rhodamine B were purchased from Shanghai McLean Biochemical Technology Co., Ltd. Isopropyl alcohol (IPA) was purchased from Chengdu Kelong Chemical Co., Ltd., China. All chemicals were of analytical grade and were employed without any additional purification treatment. The pH values were adjusted by 0.5 mM NaOH and H_2SO_4. Deionized water (18.2 MΩ) from the Millipore Milli-Q water purification system was used to prepare all the solutions in the experiments.

Synthesis of CdS Nanorods. Dissolve 0.45 g of cadmium nitrate tetrahydrate and 0.35 g of thiourea in 10 mL of ethylenediamine, and stir the mixture for 30 minutes. Then transfer the solution into a Teflon-lined high-pressure reactor and heat it at 200 °C for 24 hours. After the reaction, collect the product by centrifugation, wash it five times with deionized water and absolute ethanol, and dry it under vacuum at 60 °C for 12 hours.

Synthesis of MoS_2/CdS Composites. Disperse 0.5 g of the as-prepared CdS nanorods in 30 mL of deionized water. Add 0.0576 g of sodium molybdate to the suspension, ultrasonicate for 30 minutes, and stir for 6 hours. Then add 0.1064 g of thiourea, ultrasonicate for another 30 minutes, and stir for 1 hour. Transfer the mixture into a 100 mL Teflon-lined high-pressure reactor and maintain it at 210 °C for 24 hours. After the reaction, centrifuge the resulting product, wash thoroughly with water and ethanol, dry under vacuum for 12 hours, and collect the sample, labeled as MC4 (wt%=8). Additionally, by varying the molar ratios of sodium molybdate and thiourea, composite samples labeled MC1, MC2, MC3, and MC5 (wt%=2、4、6、10) were obtained. A physically mixed sample with the same ratio as MC4 was also prepared and labeled as Cd+Mo.

Characterization. The crystal structure, and surface chemical structure of the samples were studied by X-ray diffraction (XRD, MiniFlex 600, Japan). UV-VIS spectrophotometer (UV-VIS DRS, Lambda 1050+, Perkin-Elmer, USA) was used to check the light absorption characteristics. Scanning electron microscope (SEM, SUPRA 55 Sapphire, Carl Zeiss, Germany) and high-resolution transmission electron microscope (HRTEM, JEM 2100F, Japan) were used to observe the surface morphology. X-ray photoelectron spectroscopy (XPS, Scientific K-Alpha, Thermo, USA) was carried out to check the composition of valence states of elements. The dynamics of photogenerated carriers were studied by steady-state photoluminescence (PL, FL-4600, Hitachi, Japan) spectroscopy at a directional wavelength of 350 nm using a fluorescence spectrophotometer. The photoelectrochemical property was carried out by an electrochemical analyzer (CHI660E, Shanghai Chenhua).

Photocatalytic activity tests. The photocatalytic activity of the prepared MoS_2/CdS composites was evaluated by degrading the organic dye Rhodamine B (RhB) and nitenpyram (NTP). 10 mg of the catalyst and 10 mL of a 15 mg/L RhB solution were added to a test tube and stirred in the dark for 30 minutes to establish an adsorption-desorption equilibrium between the catalyst and the RhB solution. After the dark reaction, the sample was ultrasonically dispersed to ensure uniform distribution of the MoS_2/CdS material in the dye solution. A 350 W xenon lamp was used as a light source to simulate visible light irradiation. At specified time intervals, 1 mL of suspension was taken out at regular intervals, and the photocatalyst was separated using a water membrane filter with a pore size of 0.22 μm. The concentration of the RhB solution was measured by using UV-visible spectrophotometry. The degradation efficiency of RhB was calculated using the following formula:

$$\eta = \frac{c_i - c_t}{c_i}$$

where c_i is the initial concentration of the pollutant, c_t is the concentration of the pollutant in the solution at t, and η is the degradation efficiency of the pollutant.

10 mg of the catalyst was ultrasonically dispersed in 10 mL of NTP solution (10 mg/L) and stirred in the dark for 30 minutes to establish adsorption-desorption equilibrium. During visible-light irradiation, 1 mL of the reaction mixture was sampled at specific time intervals and filtered through a 0.22 μm aqueous filter membrane to remove photocatalyst particles. The 350 W Xenon lamp equipped with a UV-cut filter (λ>420nm) was used as the visible light source. The degraded NTP solution was detected by high performance liquid chromatography (Agilent HPLC 1260).

At room temperature, 10 mg of Rhodamine B was weighed and dissolved to prepare a 15 mg/L solution. Four 15 mL test tubes were each filled with 10 mL of the 15 mg/L Rhodamine B solution and 10 mg of MoS_2/CdS composite, followed by ultrasonic dispersion. The mixtures were stirred at 450 $r \cdot min^{-1}$ in the dark for 30 minutes to achieve adsorption-desorption equilibrium. Then, respectively add 1 mL of deionized water (blank control), isopropyl alcohol (IPA, a hydroxyl radical quencher), triethanolamine (TEOA, a hole quencher), and p-benzoquinone (PBQ, a superoxide radical quencher). The four test tubes were placed in a photochemical reactor for photocatalytic reaction at room temperature. Samples were taken at specific time intervals, centrifuged, and the supernatant was analyzed by UV-Vis spectrophotometry to determine the residual concentration of Rhodamine B after reaction.

Electrochemical experiment.

An electrochemical workstation was used to record the photocurrent response (i-t) of the samples. The test was carried out in a traditional three-electrode with platinum wire as the counter electrode and Ag/AgCl (3 M KCl) as the reference electrode. The prepared sample (5 mg photocatalyst, 20 μL Nafion) was coated on 5 × 25 × 1.1 mm ITO conductive glass as the working electrode. The electrolyte is sodium sulfate (Na_2SO_4, 0.5 M). To measure the transient photocurrent of the sample, the xenon lamp was turned on or off every 30 seconds.

Table S1 Comparison with the related photocatalysts on RhB degradation

Sample	Pollutant concentration（mg/L）	Sample concentration（g/L）	Time（min）	removal rate（%）	Source type	Ref.
CZC-LDH	1	0.1	180	60.67	0.0205	[1]
ZnO/CdS	10	0.25	120	80	0.0086	[2]
Zn-doped CdS	10	1.0	135	85	–	[3]
ZnO@NCQD NCs	10	0.5	120	92	–	[4]
CdS/ZnO composites	15	1.0	150	91.5	0.01316	[5]
MC4	15	1.0	90	90	0.02161	**This work**

Table S2 Comparison with the related photocatalysts on NTP degradation

Sample	Pollutant concentration（mg/L）	Sample concentration（g/L）	Time（min）	removal rate（%）	Degradation rate	Ref.
CC2	20	1.0	240	96	–	[6]
Fe3O4@BNPs-ZnS-CdS	10	1.0	90	70.9	0.0136	[7]
TiO_2/rGO/CdS	10	0.5	75	85	–	[8]
G0-MCD-TiO2/CdS	20	1.0	120	83.6	0.0146	[9]
G1-MCD-TiO2/CdS	20	1.0	120	88.5	0.018	[9]
MC4	10	1.0	90	89	0.02686	**This work**

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