Electronic supplementary information

Sunlight activated heterostructure MoS_2/CdS nanocomposite photocatalyst with enhanced photocatalytic activity: Band alignment and mechanism study

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Materials and Methods

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Synthesis of CdS NPs

The CdS nanoparticles were produced utilizing the hydrothermal technique. A solution containing 0.4352 g of cadmium acetate dihydrate ($Cd(OCOCH_3)_2.2H_2O$), 1.5 ml of 80% thioglycolic acid ($HSCH_2COOH$), and 0.1274 g of sodium sulfide (Na_2S) was prepared by mixing them with 50 ml of deionized water. The solution was agitated using a magnetic stirrer for a duration of 30 minutes. Subsequently, the resulting combination was moved to a 100 ml Teflon-lined autoclave made of stainless steel. The autoclave was subjected to thermal treatment in an oven at a precise temperature of 180 °C for 16 hours, after which it was allowed to cool down naturally to the ambient temperature. The reacted products were then centrifuged at 6000 rpm, washed with deionized water, and centrifuged and the procedure was repeated three times. The precipitates were additionally rinsed with absolute ethanol to remove any remaining ions, and the resulting products were dried at 105 °C for 10 hr to obtain yellow-colored CdS nanoparticles. The CdS particles were then subjected to grinding using an agate mortar and pestle and subsequently preserved for future applications.

Synthesis of MoS_2 NPs

The MoS_2 nanoparticles were also synthesized utilizing the hydrothermal method. A total of 0.691 grams of thiourea ($(NH_2)_2CS$) and 0.7182 grams of sodium molybdate dihydrate ($Na_2MoO_4 \cdot 2H_2O$) were combined with 32 milliliters of deionized water. Next, 8 milliliters of pure ethanol were added to the mixture. The mixture was then subjected to sonication for 5 minutes and agitated using a magnetic stirrer at room temperature for 30 minutes until complete dissolution occurred. Subsequently, the solution was transferred into a Teflon-lined autoclave with a volume of 100 cc.

The autoclave was maintained at a temperature of 230 °C for a duration of 16 hours, after which it was allowed to cool naturally to room temperature. The subsequent processing was carried out following the same procedure described for the synthesis of CdS. A similar approach for the preparation of MoS_2 was reported elsewhere [38].

Determination of the point of zero charge

The determination of the point of zero charge (pH_{PZC}) for 5 wt% MC NPs was executed through the pH drift method. [49,50] Initially, eight 100 mL samples of 0.1 M KNO_3 solution were prepared. Subsequently, a 1 M solution of HNO_3 or NH_3 was employed to modify the initial pH values of the 100 mL 0.1 M KNO_3 solutions within the range of 3-10. The function of KNO_3, serving as the background electrolyte, was to ensure that the ionic strength of the solution was consistently maintained at a fixed value of 0.1 M. Following this, 25 mg of 5 wt% MC nanoparticles were added to 100 mL of the pH-adjusted solution. The mixture was then agitated for 24 hours before recording the final pH (pH_f). The point of zero charge was established by analyzing a ΔpH (= pH_i– pH_f) versus initial pH (pH_i) curve, identifying the point where the curve intersects the initial pH line, signifying a ΔpH value of zero.

Results and Discussion

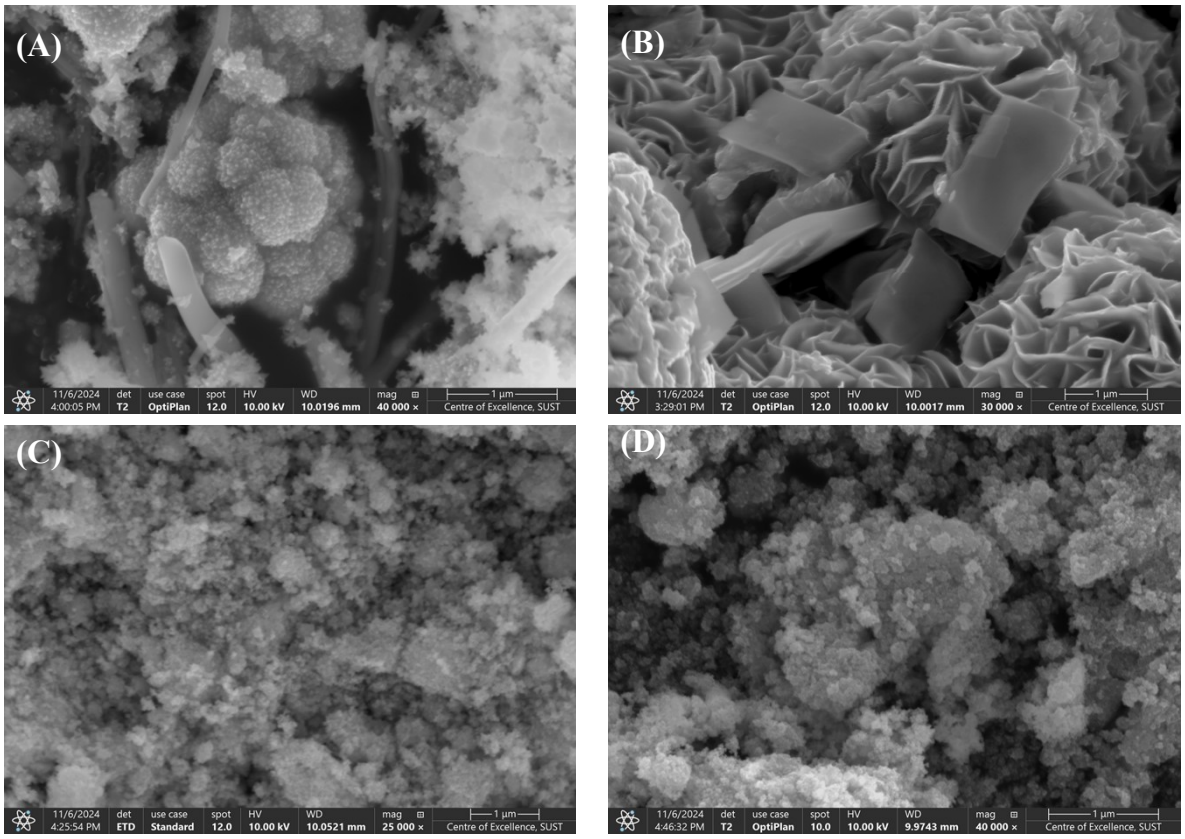

Fig. S1 FESEM image of (A) CdS and (B) MoS_2 (C) 5 wt% MoS_2/CdS and (D) 5 wt% MoS_2/CdS after photocatalytic degradation.

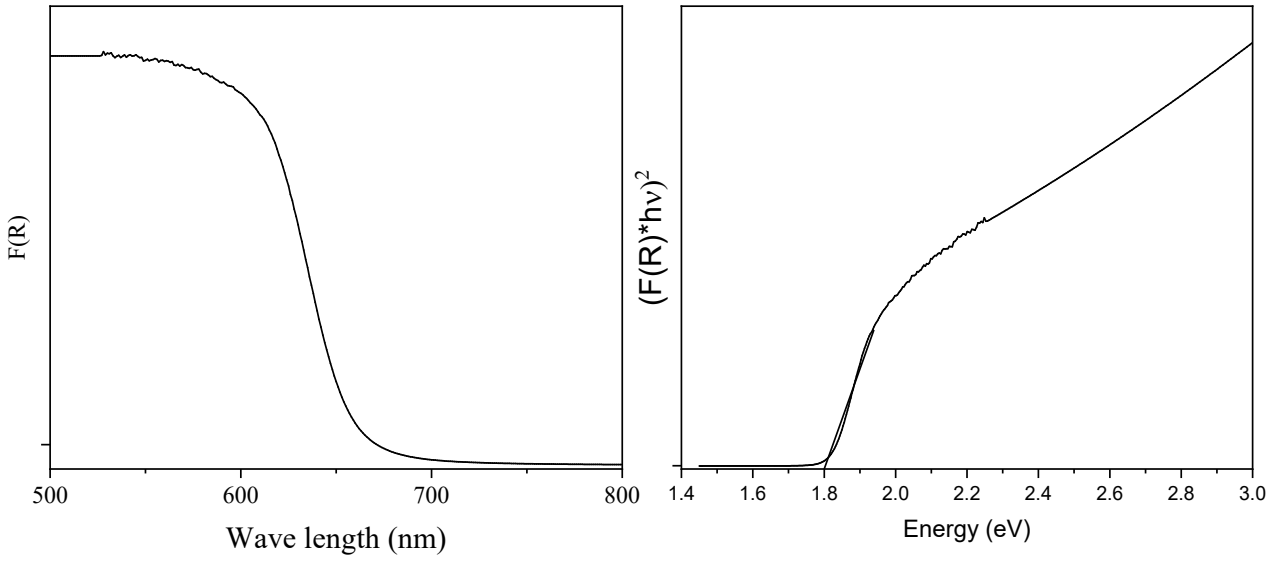

Fig. S2 (A) UV−vis diffuse reflectance spectrum and (B) direct band gap model of MoS_2.

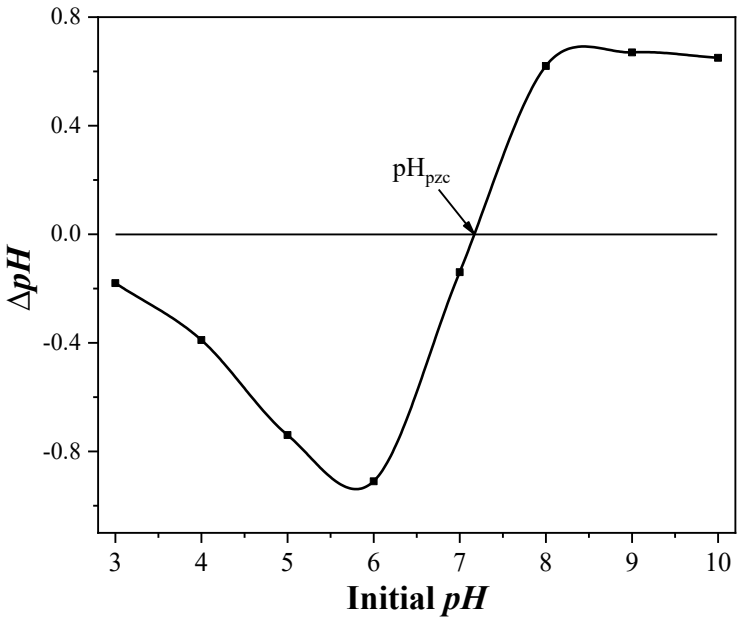

Fig. S3 Determination of point of zero charge of 5 wt% MC by pH drift method.

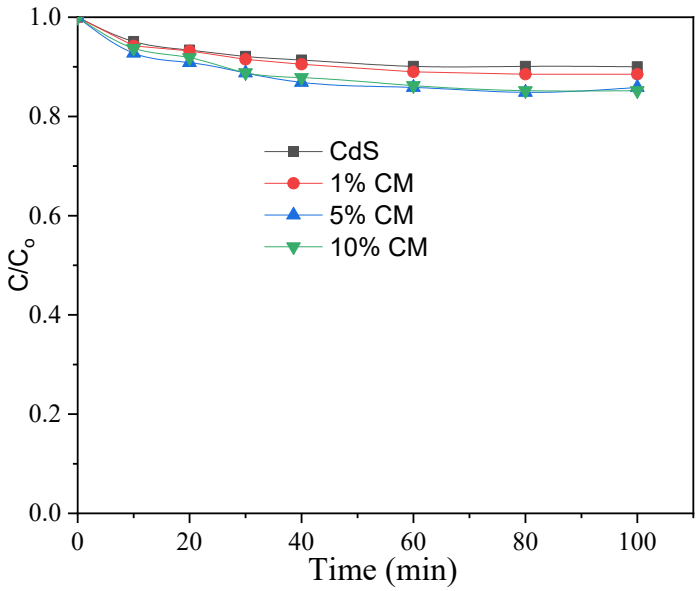

Fig. S4 Effect of contact time on the adsorption of MO dye on 5 wt% MC NC.

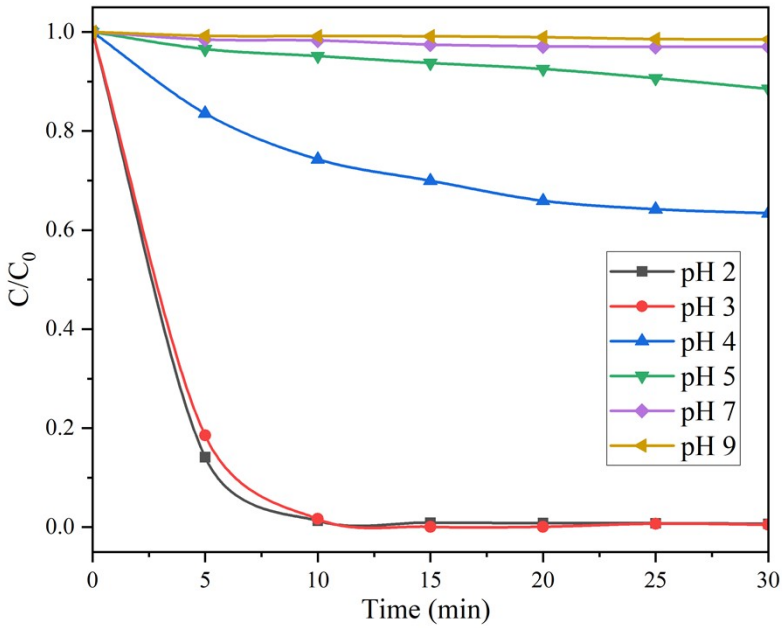

Fig. S5 Effect of pH on the photodegradation efficiency of 5 wt% MC NCs (Catalyst dose = 0.1 g/L; solution volume = 100 mL; initial dye solution concentration = 10 mg/L).

Effect of catalyst dosage on photocatalytic activity

The efficiency of photocatalysis is significantly influenced by the dosage of photocatalyst, as it directly affects the availability of active sites for the process. Therefore, optimizing the photocatalyst dosage can enhance the rate and extent of dye degradation, leading to improved treatment efficiency. Fig. S6 illustrates the influence of the dosage of 5% MC NC on the photocatalytic performance under specific conditions, including a dye concentration of 10 ppm and a pH of 3.0. Fig. S6 shows that the rate of photocatalytic degradation of MO increased significantly as the photocatalyst dosage was increased up to 1 g/L. Further increase in catalyst dosage decreased the degradation efficiency. The improvement in the degradation efficiency of MO dye up to a photocatalyst dosage of 1 g/L results from two primary factors: firstly, increasing the photocatalyst dosage provides more active sites, allowing more dye molecules to interact with the catalyst surface, thus enhancing the degradation rate. Secondly, a higher concentration of photocatalyst improves light absorption, generating more reactive species, which leads to more

efficient dye degradation. The decreased in degradation efficiency at higher dosage was occurred due to light scattering or shielding effects, where excess catalyst particles block light from penetrating the solution effectively or interfere with the interaction between light and the catalyst.[88–90] Hence, optimizing the photocatalyst dosage is essential to attain maximum degradation efficiency.

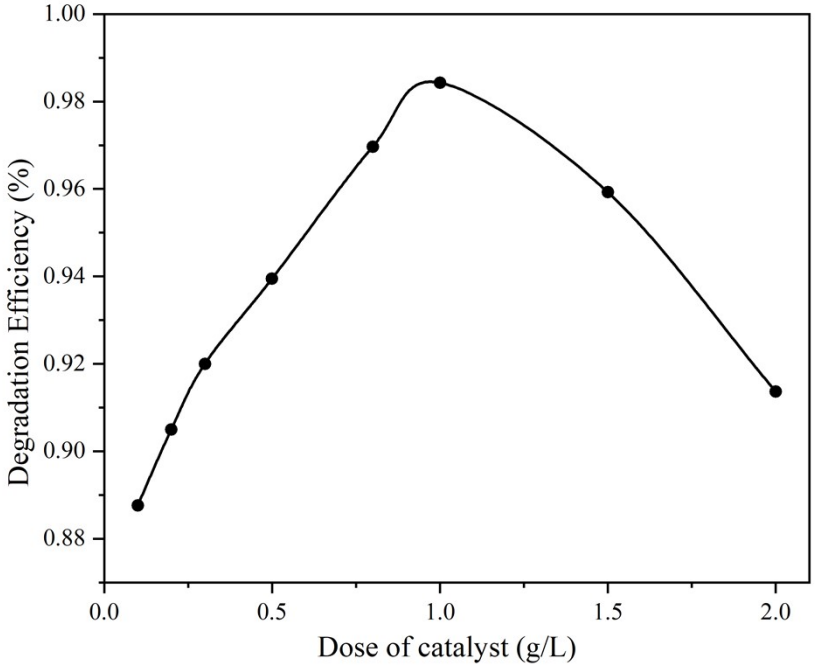

Fig. S6 Effect of dose of 5 wt% MC NCs on MO dye degradation under sunlight (solution volume = 100 mL, solution pH = 3; initial dye solution concentration = 20 mg /L).

Effect of solution concentration on photocatalytic activity

In photocatalytic reactions, the initial concentration of the dye is a crucial factor that can significantly influence the reaction rate and overall efficiency of the process. Therefore, the effect of the initial MO concentration on the degradation efficiency was examined within the range of 10-30 mg/L of MO solution the result is displayed in Fig. S7. Fig. S7 demonstrated that the photocatalytic degradation efficiency of MO decreased with increasing dye concentration. At lower concentrations (10 mg/L), 98% of MO dye was degraded within 10 minutes, whereas at

higher concentrations (30 mg/L), the degradation efficiency dropped to 17%. At higher dye concentrations, the solution may absorb more of the incident light, reducing the amount of light reaching the photocatalyst. This "light shielding" effect can decrease the generation of reactive species, thus lowering the degradation efficiency.[89–91]

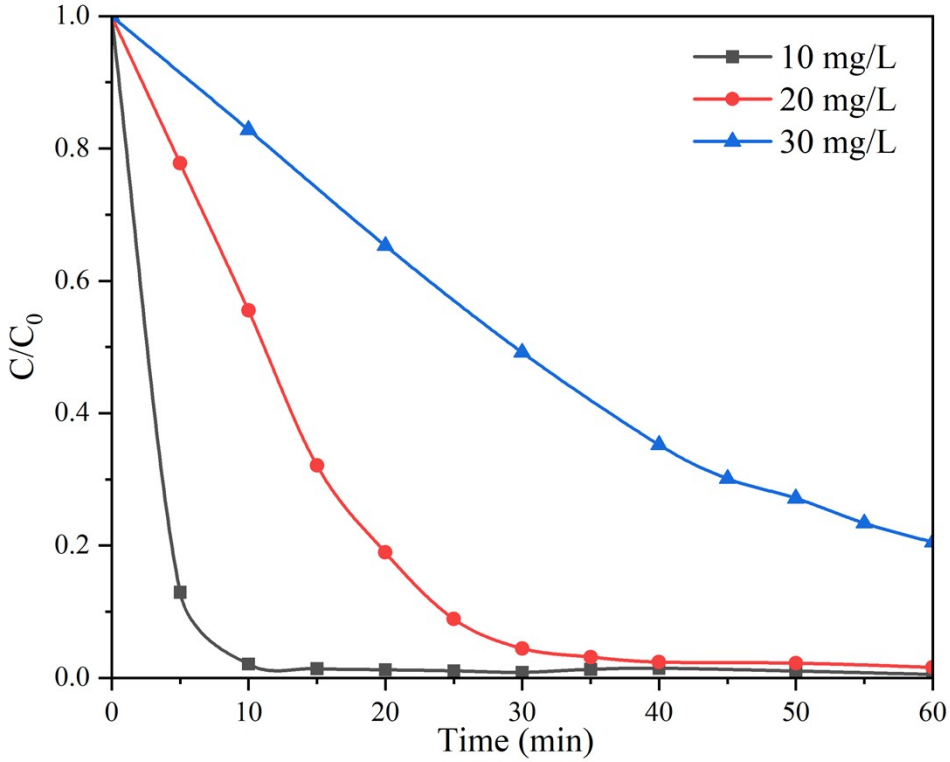

Fig. S7 Effect of initial dye concentration on MO dye degradation (Catalyst dose = 0.1 g/L; solution volume = 100 mL, solution pH = 3).

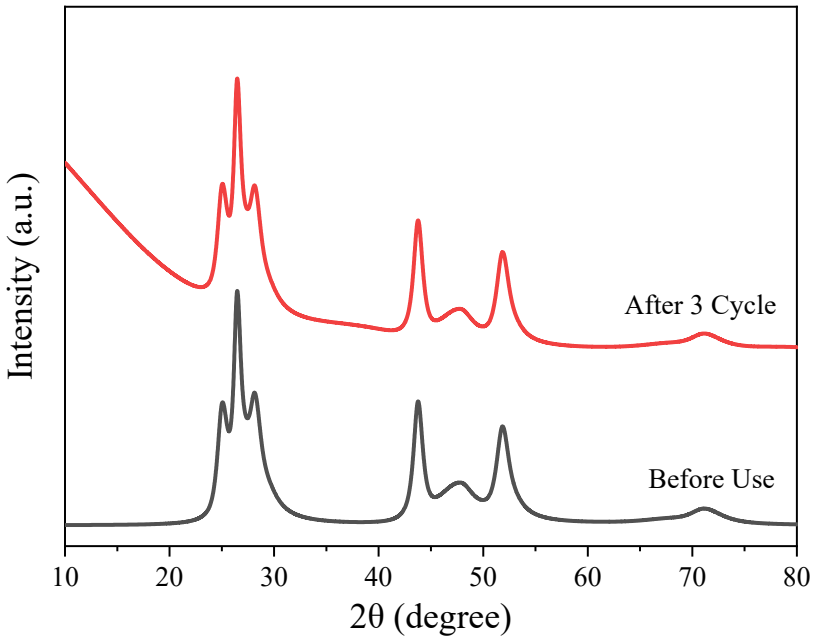

Fig. S8 XRD pattern of 5 wt% MC NCs before and after use for photocatalytic degradation.