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CdS nanocrystals/TiO₂/crosslinked chitosan composite: Facile preparation, characterization and adsorption-photocatalytic properties



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ABSTRACT

CdS nanocrystals deposited on TiO₂/crosslinked chitosan composite (CdS/TiO₂/CSC) were prepared in an attempt to photocatalyze decolorization of water soluble azo dye in aqueous solution under simulated solar light irradiation. CdS/TiO₂/CSC was characterized by X-ray diffraction (XRD), energy-dispersive spectroscopy (EDS), and scanning electron microscopy (SEM). The characterization results proved that CdS nanocrystals has successfully been deposited on/in TiO₂/crosslinked chitosan composite. The adsorption ability of CdS/TiO₂/CSC was approximately 2.66 mg methyl orange (a typical water soluble azo dye) per gram. The photocatalytic decolorization of methyl orange solution reached 99.1% by CdS/TiO₂/CSC after simulated solar light irradiation for 210 min. Kinetics analysis indicated that photocatalytic decolorization of methyl orange solution by CdS/TiO₂/CSC obeyed first-order kinetic Langmuir-Hinshelwood mechanism ($R^2 > 0.997$). CdS/TiO₂/CSC exhibited enhanced photocatalytic activity under simulated solar light irradiation compared with photocatalysts reported before and the photocatalytic activity of CdS/TiO₂/CSC maintained at 89.0% of initial decolorization rate after five batch reactions. The presence of NO₃⁻ accelerated the decolorization of methyl orange solution by CdS/TiO₂/CSC, while SO₄²⁻ and Cl⁻ had an inhibitory effect on the decolorization of methyl orange. Therefore, present experimental results indicated to assess the applicability of CdS/TiO₂/CSC as a suitable and promising photocatalyst for effective decolorization treatment of dye-containing effluents.

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1. Introduction

In both developing and industrialized countries, a growing number of organic pollutants are discharged into all kinds of open waters [1]. Among those organic pollutants, soluble organic dyes are one of the major groups of pollutants in the wastewater. In China, over 1.6×10^9 m³ of dye-containing wastewater per year is discharged into aquatic environment either directly or through the sewage treatment plants without proper treatment [2]. Dye-containing wastewater is characterized with high color, fluctuating pH, high chemical oxygen demand (COD), low biodegradability, and containing inorganic salts. The decolorization treatment of dye-containing wastewater is one of the most difficult issues to be solved because of its visibility and toxicity even at the very low concentration of soluble organic dyes. Therefore, great emphasis has

been paid on the effective decolorization treatment of azo effluent by all kinds of methods [3,4].

Recently, heterogeneous photocatalysis based on semiconductor photocatalysts has attracted great attention as an environmentally friendly and cost-effective method for decolorization treatment of organic wastewater [5,6]. Among the semiconductors, nanosized titanium dioxide (TiO₂) is an excellent photocatalyst that can effectively degrade and mineralize all kinds of organic pollutants including soluble organic dyes [7]. However, the photocatalytic efficiency of raw TiO₂ so far is still low for practical application, mainly due to its wide band gap (3.2 eV) and high recombination rate of the photogenerated electron (e^-)-hole (h^+) pairs, which meant that only a small fraction of solar energy (3–5%) can be utilized [8]. In order to control the rate of recombination, the composition of two semiconductors with different band gaps can suppress the recombination of e^-/h^+ pairs, resulting in enhanced photocatalytic performance [9]. Recently, CdS/TiO₂ nanocomposite has shown much prospect as an effective visible light photocatalyst [7,10,11]. In the system of CdS/TiO₂, the photogenerated electrons in CdS are transferred into the TiO₂ particles while the holes remain

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in the CdS particles [11]. However, the use of cadmium sulfide (CdS) as a photocatalyst has been limited due to its photocorrosion [10]. Recent researches indicated organic polymer films, such as chitosan films [12] or cellulose films [13,14], can ensure the stabilization of CdS nanoparticles and also provide an interface for the charge transfer, then correspondingly improve photocatalytic efficiency. In addition, chitosan can decrease the leakage of Cd(II) into the treated water during treatment since chitosan is an effective adsorbent and chelator for Cd(II) in aqueous solution [15,16].

In the present work, CdS nanocrystals deposited on TiO₂/crosslinked chitosan composite films (CdS/TiO₂/CSC in chief) were successfully prepared, in an attempt to photocatalyze decolorization of water soluble azo dyes (methyl orange as a model dye). The CdS/TiO₂/CSC was characterized by energy-dispersive spectroscopy (EDS), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The photocatalytic activities of CdS/TiO₂/CSC under both simulated solar light irradiation and visible light irradiation were evaluated. The effects of inorganic anions, pH and reuse of photocatalyst on photocatalytic decolorization of methyl orange by CdS/TiO₂/CSC were examined. This information will be useful for further applications of CdS/TiO₂/CSC for the effective decolorization treatment of practical dye-containing effluents.

2. Experimental

2.1. Materials

Commercial anatase TiO₂ was purchased from Xiamen Micaren Technology Co., Ltd. (Xiamen, China), which was 10–25 nm in size and 210 ± 10 m² g⁻¹ in specific surface area. Chitosan with 92% of deacetylation degree was purchased from Yuhuan Ocean Biochemical Co., Ltd. (Taizhou, China). CdCl₂ and (NH₂)₂CS were used to prepare CdS nanocrystals. Methyl orange (MO in chief, C₁₄H₁₄O₃N₃Na, C.I.13025) as a model pollutant was obtained from Yongjia Fine Chemical Factory (Wenzhou, China). Other chemicals were of analytical grade from Shanghai Chemical Reagent Co., Ltd. (Shanghai, China). 0.1 mol L⁻¹ NaOH or 0.1 mol L⁻¹ HCl was used to adjust pH value of reaction solution. All reagents were used as received without further purification.

2.2. Preparation of CdS/TiO₂/CSC

Fig. 1 represents schematically the preparation of CdS/TiO₂/CSC by a simulating biomineralization method. Firstly, nanosized TiO₂ powder (0.3 g) and CdCl₂ (0.912 g) were mixed into 100 mL of 2% (w/v) chitosan acetate solution with ultrasonic stirring for 2 h. Subsequently, homogeneous suspension was cast evenly on clean

glass plates. After drying under ambient temperature, thin gel films on glass plates were coagulated into 0.2 mol L⁻¹ NaOH solution. Then, the solidified composite thin films were dipped into an equimolar amounts thiocarbamide aqueous solution in a water bath at 60 ± 0.2 °C in order to form nanosized CdS in the composite films slowly. To enhance water-resistant property, composite films were subsequently crosslinked by immersing into a 100 mL of 0.25% (v/v) glutaraldehyde solution for 30 min. Then the yellow composite thin films were washed using absolute ethanol and double distilled water for 3–4 time, respectively, in order to remove excess glutaraldehyde. Finally, the products (CdS/TiO₂/CSC in chief) were dried at 60 °C under atmospheric condition and cut into flakelets (about 1 × 1 mm²).

2.3. Characterization of CdS/TiO₂/CSC

XRD patterns were obtained using a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation at a scanning rate of 6° 2θ min⁻¹ in the 2θ range from 10° to 75°. The scanning electron microscopy (SEM) analysis was performed and energy-dispersive spectroscopy (EDS) was employed to determine the final actual element amounts with a Hitachi SX-650 scanning electron microscopy.

2.4. Adsorption of dye on CdS/TiO₂/CSC

For adsorption experiments, 50 mg of CdS/TiO₂/CSC was added into 100 mL of dye solution (15 mg L⁻¹). Samples were collected at different time intervals and the dye concentration (C_t) in the supernatant liquid was measured on a Varian UV-vis spectrophotometer (Cary 50, Varian Co. Ltd). The amount of dye adsorbed (q_t) onto the CdS/TiO₂/CSC was calculated as follows:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

where C₀ and C_t are the initial and equilibrium solution concentrations (mg L⁻¹), respectively, V is the volume of the solutions (L) and m is the weight of CdS/TiO₂/CSC used (g).

2.5. Photocatalytic decolorization of MO dye

The photocatalytic activity of the as-prepared CdS/TiO₂/CSC was evaluated by photocatalytic decolorization of MO with a 300 W xenon lamp (PLS-SXE300, Beijing Trusttech Co., Ltd., China) as a light resource at 25 ± 0.5 °C. For visible light irradiation experiment, a UV cutoff filter (λ > 400 nm) only allowing the photons

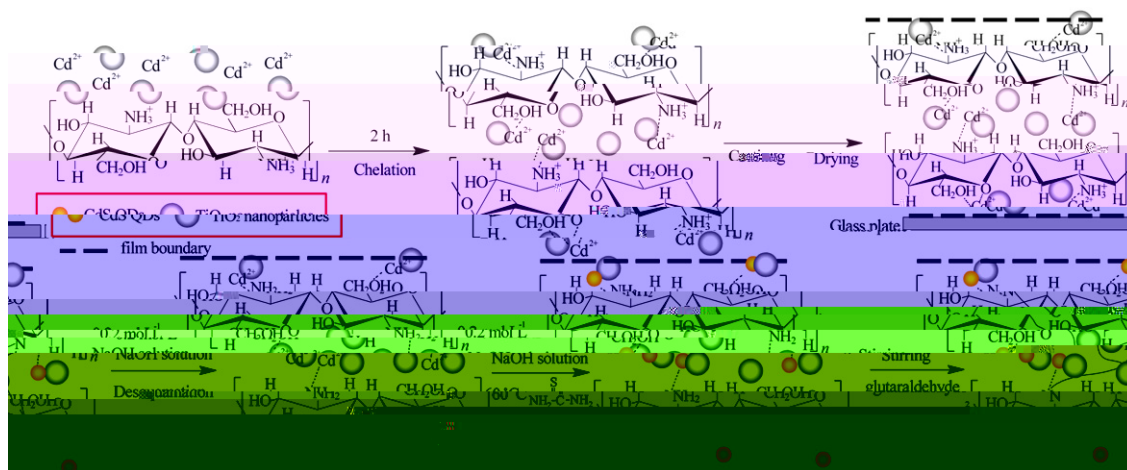
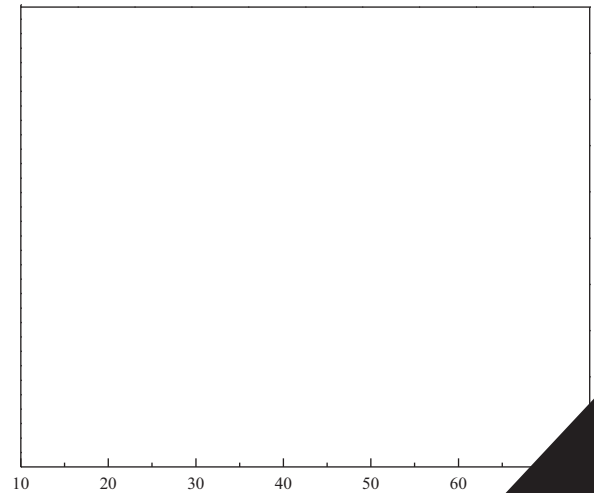


Fig. 1. The schematic mechanism for preparation of CdS/TiO₂/CSC.

to provide visible
maintaining the reac-
tance of suspension
ion intensity was
and 48.8 mW cm^{-2}
of CdS/TiO₂/CSC
(15 mg L^{-1}). Dur-
aqueous suspension
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(about 4 mL) were
rian UV-vis spec-
= 464 nm for MO
e. pH of solution,
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systematically.



2/CSC. For the XRD
1°, 37.89°, 48.09°,
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in Fig. 2b, which

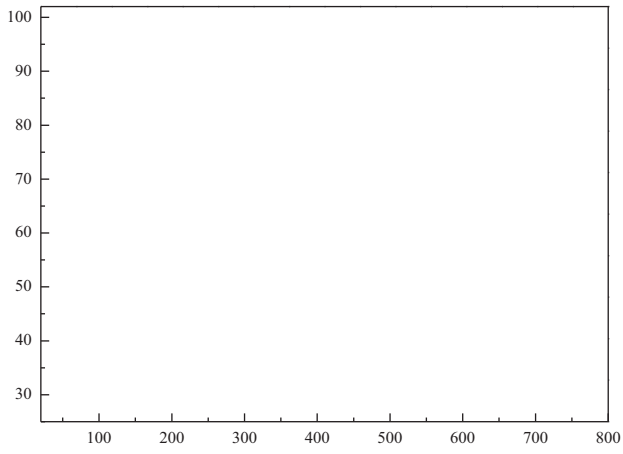


Table 1
Kinetic parameters of MO adsorption on CdS/TiO₂/CSC for 15 mg L⁻¹ initial dye concentration.

Kinetic model	Kinetic parameters				
Lagergren-first-order kinetic model	$q_{e,exp}$ (mg g ⁻¹)	$q_{1e,cal}$ (mg g ⁻¹)	k_1 (min ⁻¹)	R^2	SD (%)
	2.66	2.88	0.010594	0.966	0.077
Pseudo-second-order kinetic model	$q_{e,exp}$ (mg g ⁻¹)	$q_{2e,cal}$ (mg g ⁻¹)	k_2 (g mg ⁻¹ min ⁻¹)	R^2	SD (%)
	2.66	6.36	0.000405	0.650	11.059
Intra-particle mass transfer diffusion model		k_t (mg g ⁻¹ min ^{-1/2})	c (mg g ⁻¹)	R^2	SD (%)
		0.1878	-0.63	0.997	0.054

correlation coefficients ($R^2 = 0.650$) were also found to be lower. These results showed that the pseudo-second-order kinetic model didn't describe the MO adsorption on CdS/TiO₂/CSC. However, the values of the correlation coefficient (R^2) for the Lagergren-first-order kinetic model were ≥ 0.966 and the adsorption capacities calculated by the model ($q_{1e,cal}$) were also closer to that determined by experiments ($q_{e,exp}$). Therefore, it was feasible for the applicability of Lagergren -first-order kinetic model to describe the adsorption process of MO on CdS/TiO₂/CSC. In fact, Lagergren-first-order model has been widely used to define adsorption rates in some cases for the adsorption of dyes by chitosan [23] and chitosan/CNTs hydrogel beads [24].

The rate constant of intra-particle diffusion (k_{id} , mg g⁻¹ min^{-1/2}), which is determined from the slope of the q_t versus $t^{0.5}$ plot, is utilized to determine the rate-determining step of the adsorption process. The linear plot obtained from the initial stage is shown in Fig. 5 c. The high correlation coefficient value ($R^2 = 0.997$ and $SD = 0.054\%$) of the plot indicates that intra-particle diffusion might play a significant role in the initial stage of MO adsorption onto CdS/TiO₂/CSC.

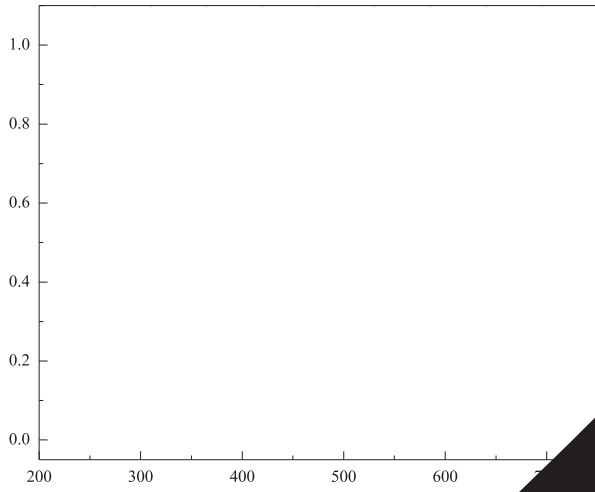


Table 2
Comparison of photocatalytic kinetic parameters of MO solution by different photocatalysts.

Photocatalyst	k_{ap} (min ⁻¹)	Photocatalyst dosage (g ⁻¹)	Light type	C_0 (mg L ⁻¹)	Ref.
CdS/TiO ₂ /CSC	1.20×10^{-2}	0.5	300 W xenon lamp	15	Present study
	5.3×10^{-3}	0.5	Real solar light	15	Present study
AgBr/TiO ₂	8.00×10^{-3}	2.5	1000 W xenon lamp	15	[31]
Pure ZnO nanorods	6.72×10^{-3}	/	365 nm irradiation	15	[30]
Pure ZnO film	2.19×10^{-5}	/	365 nm irradiation	15	[30]
TiO ₂ powder	3.0×10^{-3}	0.5	UVA light	16	[29]

lamp) was higher than the AgBr/TiO₂ under simulated solar irradiation (1000 W xenon lamp) [31] pure ZnO nanorods and Pure ZnO film under 365 nm irradiation [30], TiO₂ powder under UVA light [29], revealing that CdS/TiO₂/CSC was suitable and promising material for the photocatalytic decolorization of dye pollutants from aqueous solutions since it displayed higher photocatalytic activity.

3.5. The reproducibility of CdS/TiO₂/CSC

In view of practical application, the photocatalyst should be chemically and optically stable after several repeated photocatalysis. To investigate the reusability of CdS/TiO₂/CSC in the photocatalytic reaction, the photocatalytic decolorization experiment was repeated five times. For each cycling run, the photocatalyst dosage, initial MO concentration, irradiation time and pH of MO solution were 0.5 g L⁻¹, 15 mg L⁻¹, 300 min and 5.6, respectively. After every decolorization experiment of MO solution, the resulting suspension was filtrated and CdS/TiO₂/CSC was recovered by washing with double distilled water and drying at 80 °C for 1 h. As shown in Fig. 9, after five times of cycle photocatalytic experiment, CdS/TiO₂/CSC did not show a clear decrease in photodecolorization efficiency. The decolorization percent decreased only from 98.4% to 87.6% after five cycles for CdS/TiO₂/CSC, which maintained at 89.0% of initial decolorization rate. Judging from these results, CdS/TiO₂/CSC was regarded to be relatively stable under the experimental condition and owned a better reproducibility of photocatalytic decolorization, which is possible to be used in practical process. Of course, further work is required to better understand factors that affect the decolorization rate of CdS/TiO₂/CSC and to improve further the photocatalyst stability.

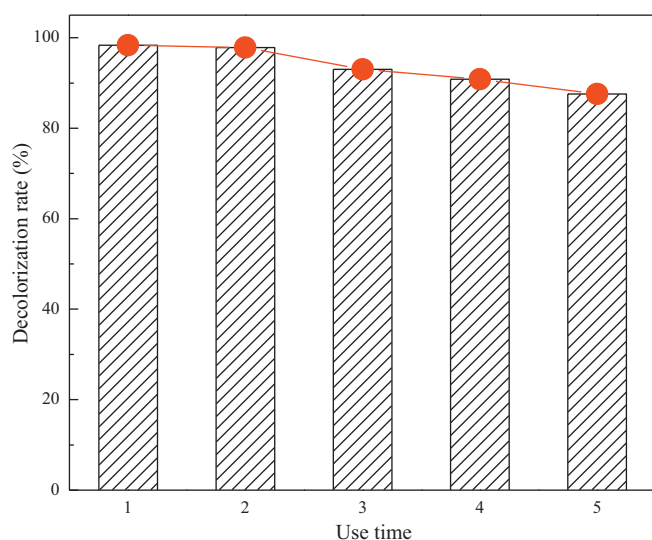


Fig. 9. Cycling runs of MO decolorization in the presence of CdS/TiO₂/CSC. Experimental conditions: [MO]₀ = 15 mg L⁻¹; Photocatalyst dosage: 0.5 g L⁻¹; Air flow rate = 100 mL min⁻¹; pH = 5.6; T = 25 ± 1 °C; Irradiation time: 300 min).

3.6. Effect of solution pH on decolorization

Solution pH is one of dominant parameters controlling photocatalytic decolorization of dye-containing wastewater by photocatalyst. Fig. 10 shows the photocatalytic decolorization of MO solution by CdS/TiO₂/CSC at three pH values. Obviously, increasing pH of dye solution could decrease the decolorization efficiency of MO solution by CdS/TiO₂/CSC. Nearly complete decolorization (99.7%) of MO solution was obtained under simulated solar light irradiation within 150 min at pH 2.0. However, 91.6% and 60.9% color of original MO within 150 min were decolorized when pH of solution increased to 6.0 and 12.0, respectively. High correlation coefficient values ($R^2 > 0.996$) indicated that the decolorization behavior still followed L–H model at different pH values. However, the photocatalytic decolorization rate of MO by CdS/TiO₂/CSC at pH 2.0 is about 4.75 times higher than that at pH 12.0. Similar effect trend of pH were previously observed for the photodecolorization of MO solution by other photocatalyst [26,32]. Firstly, pH changes can influence the adsorption of dye molecules onto the photocatalyst surfaces, an important step for the photocatalytic oxidation to take place [19,33]. Chitosan has primary amino groups with pK_a value close to 6.5 [34]. The point of zero charge of the TiO₂ (Degussa P25) is at pH 6.25; the surface of TiO₂ is positively charged at pH values less than 6.25 [35]. As a result, the surface of CdS/TiO₂/CSC is positively charged at pH values less than 6.5. However, the pK_a of MO is generally reported at pH about 3.46. Therefore, a strong adsorption of MO dye on the CdS/TiO₂/CSC took place in acid solution as a result of the electrostatic attraction of the positively charged CdS/TiO₂/CSC with the MO anions. It



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