

Article

Preparation of Thiadiazole Modified UiO-68-CdS Composites for RhB Degradation under Visible Light Irradiation

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Abstract: In this paper, the photosensitive Zr-MOF material Thiadiazole-modified UiO-68 (UiO-68N₂S) was used to prepare CdS@UiO-68N₂S composites by MOF post-reaction. The chemical composition is characterized using PXRD, FT-IR, XPS, SEM, and TGA. Rhodamine B was used as the model dye for photocatalytic degradation to evaluate the performance of CdS@UiO-68N₂S under visible light irradiation. Experimental results show that the degradation rate of a 25 mg/L RhB solution (10 mL) reached 94% with 10 mg CdS@UiO-68N₂S as a photocatalyst under blue light irradiation in 13 h at room temperature. The mechanism study revealed that O₂^{•−} is the reactive oxygen species for the degradation of Rhodamine B. Recycle experiments showed that CdS@UiO-68N₂S can be reused for three rounds without a significant reduction of its catalytic function.

Keywords: Zr-MOF material; cadmium sulfide; visible photocatalysis; Rhodamine B degradation



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1. Introduction

The degradation of organic pollutants in wastewater by using a semiconductor as a photocatalyst is an efficient method for wastewater treatment [1]. The direct use of visible light to drive catalytic degradation requires an ambient condition with less secondary pollution [2]. Since it has proven to be an effective and green approach, a great deal of research effort has focused on designing efficient photocatalysts, such as titanium dioxide (TiO₂) [3], cadmium sulfide (CdS) [4], and bismuth trioxide (Bi₂O₃), which have been widely studied [5]. CdS is a representative semiconductor with an energy band gap of 2.42 eV, and its excellent photoelectric properties have been widely used [6]. Nevertheless, there are still some problems that limit the use of pure CdS particles, including the tendency for aggregation resulting in a reduction of the surface area [7], the recombination of photogenerated electron-hole pairs [8], and photo corrosion during the photoreaction [9]. Many attempts have been made to improve the activity and stability of CdS, such as embedding CdS particles into polymeric matrices [10], synthesizing CdS quantum dots [11,12], and combining them with other components, such as noble metals [13,14], semiconductors [15,16], and carbon materials [17].

Metal–Organic Frameworks (MOFs) are self-assembled from metal ions and organic linkers, which have physical and chemical properties such as high surface area, structural adaptability, and flexibility [18–22]. MOFs seem to be excellent carriers for CdS particles; it was found that many MOFs, including ZIF–67 [23], MIL–101 [8], UiO–66(NH₂) [24], MIL–53(Fe) [25], MIL–125(Ti) [26], MIL–68(Fe) [27], etc., can utilize their nanosize cavity or specific functional group to anchor the Cd(II) and further give birth to the CdS aggregation in their highly ordered cavity, which helps in affecting its catalytic activity through the interplaying of MOFs and CdS [28,29]. This strategy is now opening up a new avenue for enhancing the light-induced electron transfer between CdS and MOF and improving the efficiency of photocatalysis [30,31].

Zr-MOF possesses a Zr_6 cluster group as a secondary building unit (SBU), and the Zr_6 connection with multi-topic aromatic acid affords the Zr-MOF stable porous coordination networks under a wide range of conditions, making it a potential candidate for nanoparticle carrier [32]. UiO-68N₂S is analogous to UiO-68 [33], and its framework is obtained by linking the thiadiazole-modified tritylene-dicarboxylic acid (H_2 BTDB = 4,7-dicarboxylic acid phenyl-2,1,3-benzothiadiazole) with Zr_6 nodes (Figure 1) [34,35]. H_2 BTDB is a type of linker for photo-sensitive MOF construction [36], and recent research showed that UiO-68N₂S can produce a fluorescence quenching effect toward foreign guest molecules such as aniline and its derivatives; the chemical environment of the thiadiazole group is altered by the hydrogen bonding interaction with amino groups, then generating electron leaps in other pathways [37]. These findings suggest that the thiadiazole group is a good photosensitive group when responding to external stimuli [38]. In addition to the aforementioned photosensitive properties, the thiadiazole group of BTDB²⁻ in UiO-68N₂S contains S and N atoms, which are good binding sites toward Cd(II) ions selectively [39]. Herein, we report for the first time on coupling UiO-68N₂S with CdS through the sequential incorporation of Cd^{2+} and S^{2-} into UiO-68N₂S (Figure 1). Evaluation of the visible-light photoactivity of CdS@UiO-68N₂S through RhB degradation shows improved activity over CdS and UiO-68N₂S and good recyclability.

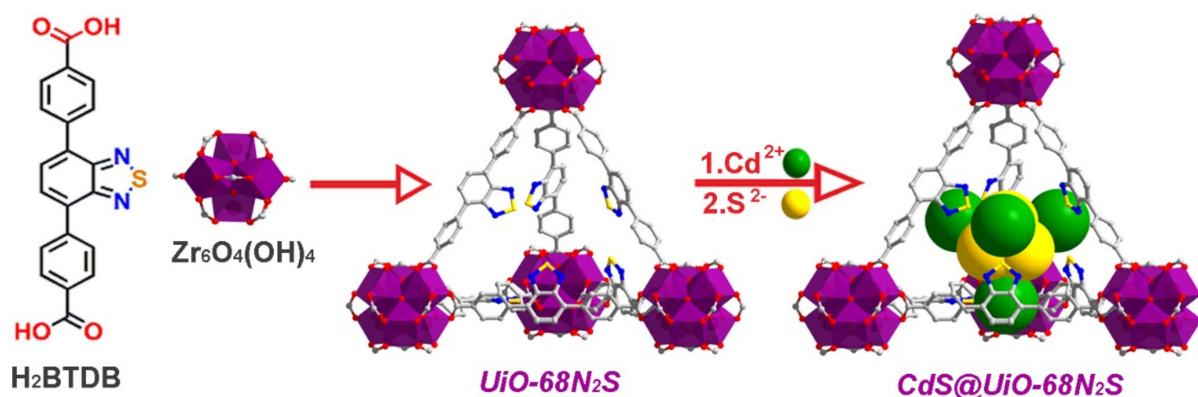


Figure 1. Construction and the pore structure of UiO-68N₂S, as well as the strategy of loading CdS particles.

2. Materials and Methods

2.1. Materials and General Methods

The organic ligand, reagents, and solvents were commercially available and were used as received without further purification. Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku Miniflex600 diffractometer (Rigaku, Tokyo, Japan) with a scanning angle of 3–60° and a scan rate of 5°/min. IR spectra were recorded in the range of 4000–450 cm^{-1} on a Nicolet 6700 FT-IR spectrometer (Thermo Fisher Scientific, Waltham, American) using the KBr disc technique. Scanning electron microscope (SEM) micrographs were obtained using a PhenomTM Pro instrument (Phenom-World, Eindhoven, Netherland) with a 5 kV accelerating voltage. Thermogravimetric analysis (TGA) for the polycrystalline sample was performed on a SEIKO EXSTAR6000 (SEIKO, Kyoto, Japan) under an N₂ atmosphere in the temperature range of 30–800 °C at a heating rate of 10 °C min^{−1}. The X-ray photoelectron spectroscopy (XPS) measurements were recorded on AXIS SUPRA spectrometer (Shimadzu, Kyoto, Japan) using Al K α radiation. Inductively coupled plasma mass spectrometry (ICP-MS) analysis of the digested sample was performed on an Agilent 7700X ICP-MS (Agilent technology, Santa Clara, American). UV-Vis spectra were recorded on an Agilent 8453 (Agilent technology, Santa Clara, American) UV-Vis for the RhB degradation as well as the ultrasonically dispersed samples of the catalyst.

2.2. Synthesis of the Complexes

Synthesis of UiO-68N₂S. H₂BTDB ligand (0.0244 g, 0.065 mmol) was immersed in DMF (N,N-dimethylformamide) containing 6 mL in reaction tubes, and 100 μ L of trifluoroacetic acid (TFA) was added. The solution was stirred magnetically and heated in an oil bath at 120 °C until the ligand was dissolved. Then, ZrOCl₂·8H₂O (0.021 g, 0.065 mmol) and 100 mg (0.82 mmol) of benzoic acid were added. The reaction tube was placed in the oven at 120 °C for 3 days. The obtained yellow precipitates were washed with DMF (10 mL $\times$ 3) and then anhydrous methanol (10 mL $\times$ 3) at room temperature. The supernatant was removed by centrifugation, and the sample was collected and dried at 50 °C to obtain the final product of UiO-68N₂S.

Synthesis of CdS@UiO-68N₂S. UiO-68N₂S (0.03 g, 0.011 mmol) was immersed in a solution containing 0.5 g (1.62 mmol) of Cd(NO₃)₂·4H₂O in 15 mL MeOH and stirred magnetically in an oil bath at 50 °C for 12 h. The obtained precipitate was then washed with anhydrous methanol (10 mL $\times$ 3), centrifuged, and the supernatant removed. The precipitate was immersed in 6 mL of MeOH, and 0.5 mL of ammonium sulfide solution was added dropwise under magnetic stirring in an oil bath at 50 °C for 12 h. The mixture was processed by centrifugation, the supernatant was removed, and the resulting solid was washed with anhydrous methanol (10 mL $\times$ 3) and dried at room temperature to obtain a sample of UiO-68N₂S loaded with CdS (CdS@UiO-68N₂S).

Synthesis of CdS. Cd(NO₃)₂·4H₂O (1.0 g, 3.24 mmol) was dissolved in 50 mL of MeOH in a beaker, and then a solution of ammonium sulfide (1 mL, 14.68 mol/L) was added dropwise under stirring at room temperature; the precipitates were washed with MeOH (10 mL $\times$ 3) and dried at 50 °C to obtain the sample of CdS.

Catalytic reactions. The photocatalyst of CdS@UiO-68N₂S (0.01 g, 0.0027 mmol) was placed in 10 mL of RhB solution at a concentration of 0.025 mg/mL and magnetically stirred under a light-proof environment for about 2 h until the adsorption–desorption equilibrium. The photocatalytic performance experiments were carried out at room temperature with a blue light-emitting diode (LED) lamp (λ = 480 nm, 80 W) as the light source, and the absorbance of the RhB solution was measured at a certain time interval after the start of light exposure to calculate the degradation rate. The photocatalytic activity is reflected by the plots of c/c_0 vs. t (time), where c_0 is the initial RhB concentration and c is the remaining RhB concentration at time t .

Catalyst recovery and reuse. The photocatalyst CdS@UiO-68N₂S was recovered by centrifugation after the photocatalytic reaction, washed repeatedly using methanol, and dried. The photocatalytic experiments were repeated under the same conditions.

3. Results and Discussion

3.1. Characterization

PXRD patterns had been recorded for samples to confirm the crystalline phase of UiO-68N₂S and CdS@UiO-68N₂S composites. Figure 2a shows the PXRD patterns of the UiO-68N₂S, where the diffraction peaks at 2θ of 4.6, 5.3, 7.5, 8.9, and 9.5° correspond to the diffractions of the (111), (200), (220), (311), and (222) planes of UiO-68 [33], suggesting the as-prepared UiO-68N₂S is isostructural to UiO-68. Slight diffraction peaks at 2θ of 24.9, 25.9, 27.6, 43.6, 47.4, and 51.6° were also found in accordance with the diffractions of the (100), (002), (101), (102), (2-10), and (103) crystal planes of CdS (JCPDF 41-1049), suggesting a possible low CdS content in the CdS@UiO-68N₂S sample. The IR spectra of the CdS and CdS@UiO-68N₂S were recorded in the wavelength range of 4000–400 cm^{−1} using KBr compacts. Figure 2b shows the IR spectra of CdS@UiO-68N₂S, where the typical Cd–S bond vibrations at 1012 cm^{−1}, 845 cm^{−1}, and 627 cm^{−1} were found [23,40], further indicating the successful loading of CdS in UiO-68N₂S.

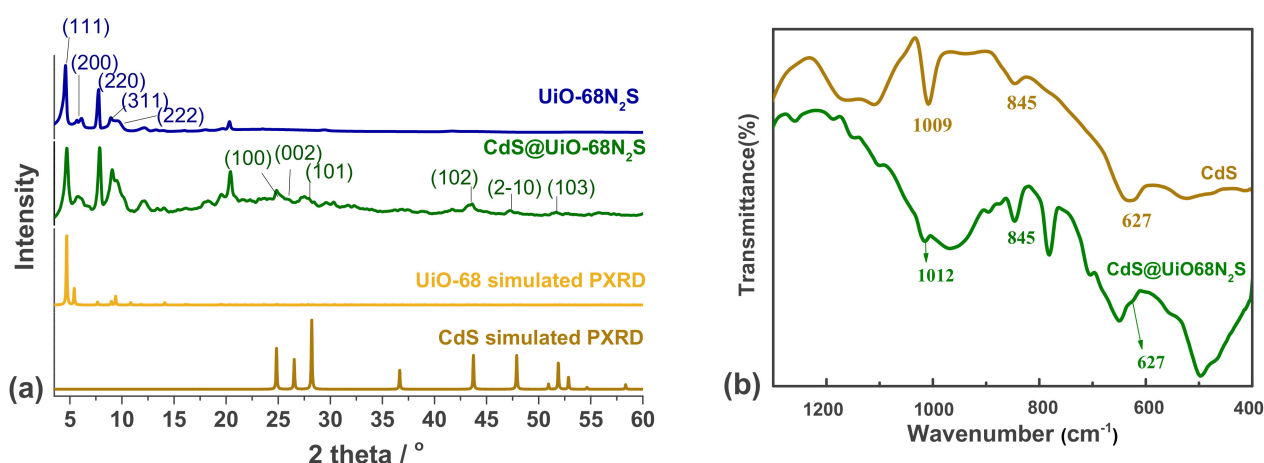


Figure 2. PXRD patterns (a) and IR spectra (b) for CdS@UiO-68N₂S and CdS.

To probe the elemental composition and its relative content in CdS@UiO-68N₂S, we carried out X-ray photoelectron spectroscopy (XPS), as shown in Figure 3. The XPS pattern has strong absorption at an electron binding energy of 183 eV, corresponding to the absorption of 3d electrons of element Zr (Figure 3a) [41], strong absorption at an electron binding energy of 165 eV, corresponding to the absorption of 2p electrons of element S (Figure 3b), and absorption at an electron binding energy of 405 eV, corresponding to the absorption of 3d electrons of element Cd (Figure 3c) [42]. The ratio of Zr/S/Cd of CdS@UiO-68N₂S given by XPS analysis was calculated to be 6.0/4.3/0.11. ICP-MS element analysis was conducted on the digested sample of CdS@UiO-68N₂S, which reveals a precise Zr/Cd ratio of 6/0.21. Using this ratio, the chemical formula of CdS@UiO-68N₂S can be deduced by combination with the chemical formula of UiO-68 as [Zr₆O₄(OH)₄](BTDB)₆(CdS)_{0.21}. It should be noted that the ratio of Zr/S/Cd deduced from the XPS is slightly lower than the theoretical value of Zr/S/Cd = 6.0/6.2/0.21 in CdS@UiO-68N₂S, and this difference is expected to arise from the fact that the signal response of the XPS is mainly derived from the elements on the surface of the sample.

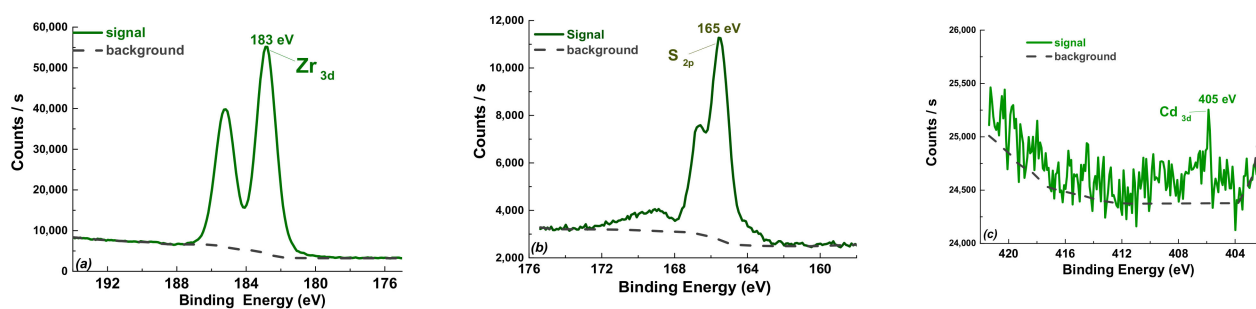


Figure 3. XPS spectra of elements in CdS@UiO-68N₂S: Zr (a), S (b), and Cd (c).

For further analyzing the guest composition of CdS@UiO-68N₂S, the thermogravimetric analysis (TGA) was conducted as shown in Figure 4, where the first mass loss of 20 wt% in the temperature range of 25–250 °C was witnessed for CdS@UiO-68N₂S, which can be attributed to MeOH incorporated during the solvent exchange and CdS incorporation processes. Compared with guest content of 40 wt% in pristine UiO-68N₂S samples, the reduction in guest content is believed to result from the incorporation of CdS, which reduces the space for guest molecules in UiO-68N₂S. After the decomposition of the linker at around 500 °C, the TG curve goes into a mass plateau with the rest mass of 25 wt% and 18.5 wt% for CdS@UiO-68N₂S and UiO-68N₂S, respectively. The increase in the rest mass of CdS@UiO-68N₂S is believed to have arisen from the residue of CdO in addition to ZrO₂.

(ca. 21 wt%). The TG data of CdS@UiO-68N₂S helps in deducing the possible composition of CdS@UiO-68N₂S as [Zr₆O₄(OH)₄](BTDB)₆](CdS)_{0.21}(MeOH)₂₃.

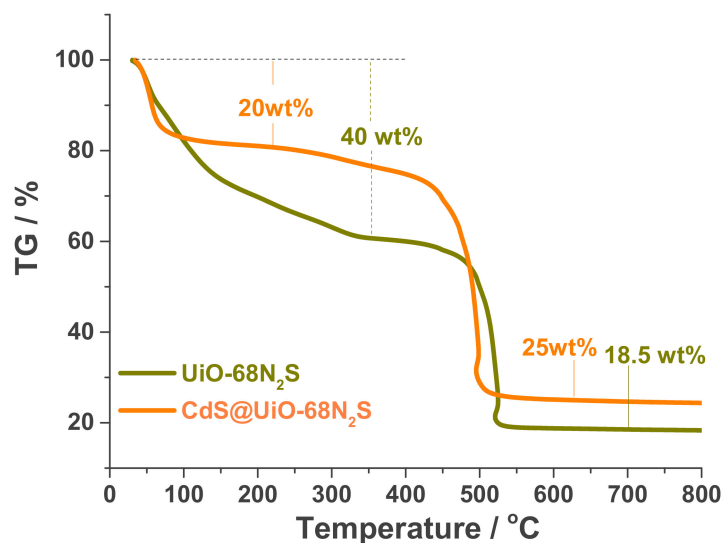


Figure 4. Thermogravimetric analysis of UiO-68N₂S and CdS@UiO-68N₂S.

Scanning electron microscopy (SEM) was used to characterize the morphology of the samples. UiO68-N₂S presents an octahedron morphology (Figure 5), which is similar to that reported for UiO-68 previously [33]. As for CdS@UiO-68N₂S, the morphology did not change significantly after the CdS loading experiment. According to the XPS elemental analysis, the small particle found on the surface of the octahedron mostly came from the partial octahedron that crashed during the mechanical string in the complex preparation.

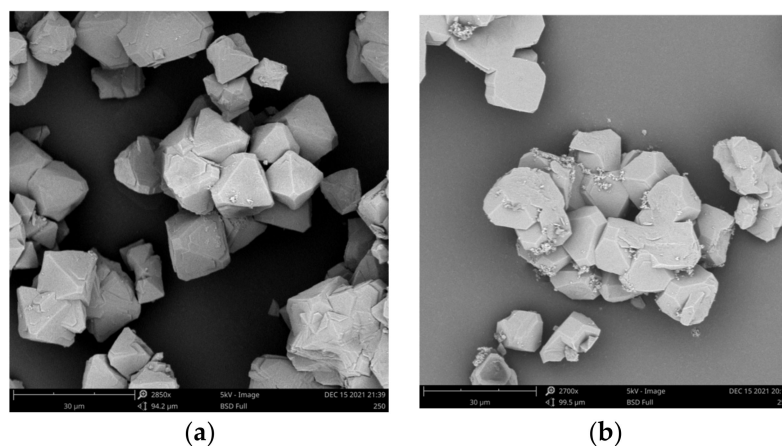


Figure 5. SEM images of (a) UiO-68N₂S and CdS@UiO-68N₂S (b).

The optical absorption properties of UiO-68N₂S, CdS, and CdS@UiO-68N₂S samples were examined by UV-Vis spectrometer after the ultrasonic dispersion in MeOH, and the results are presented in Figure 6. It can be seen that UiO-68N₂S has a significant absorption effect in the ultraviolet region of 292 nm and 394 nm [37], and CdS has a broad absorption band in the region of less than 540 nm. After loading CdS into UiO-68N₂S, the composite shows a better absorption effect in the visible light region around 428 nm. Therefore, the incorporation of CdS made the absorption peak of UiO-68N₂S red-shifted, which obviously broadens the light response range and improves the utilization of visible light. According to the relation $E_g = 1240/\lambda$ [43], the band gap energies of CdS, UiO-68N₂S, and CdS@UiO-68N₂S can be calculated to be 2.3, 3.1, and 2.9 eV, respectively.

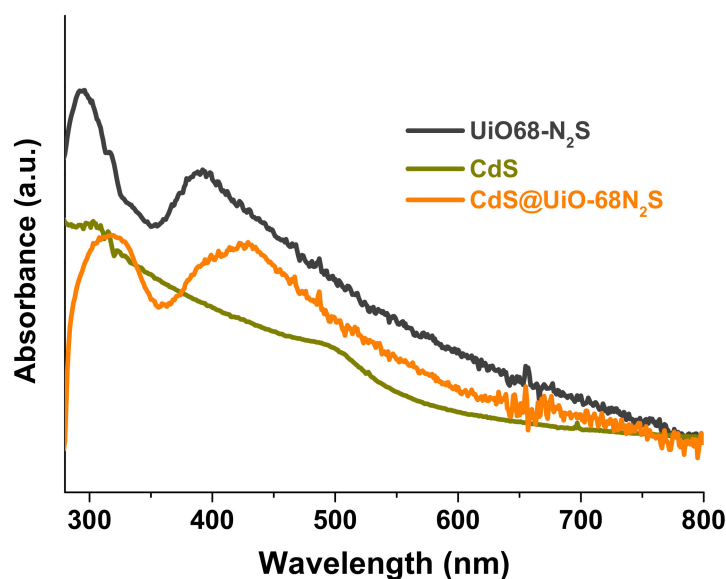


Figure 6. UV-Vis spectra of UiO-68N₂S, CdS, and CdS@UiO-68N₂S.

3.2. Catalytic Experiments

The photocatalytic activity of the CdS@UiO68N₂S catalyst was estimated by means of the oxidation of RhB as a model substrate. The reaction conditions were conducted in the presence of air and CdS@UiO-68N₂S (10 mg) as photocatalysts in a water solution of RhB (25 mg/L, 10 mL) under blue light LED irradiation at room temperature; the degradation of RhB was monitored by the absorbance change at 551 nm through UV-Vis spectrometry (Figure 7a). To our delight, the photocatalytic reactions went smoothly, affording an RhB degradation rate of 94% within 13 h (Figure 7b). To further reveal the kinetics of photocatalytic degradation, the degradation of RhB dye could be applied to a pseudo-first-order kinetic reaction ($\ln(c_0/c) = kt$) due to $R^2 > 0.9$ [44] (Figure S1), where k is the rate constant. The liner fit gave a k value of 0.1636 h^{-1} (or 0.0027 min^{-1}) (Figure 7c).

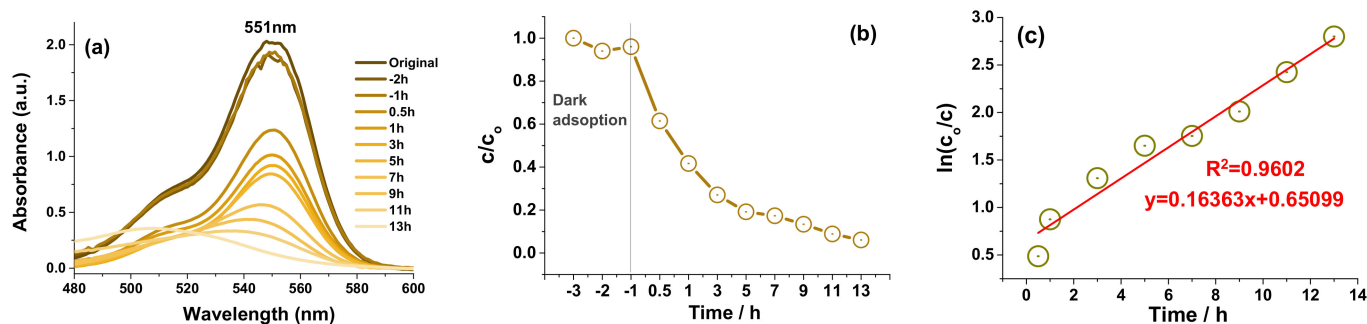


Figure 7. Time-dependent UV-Vis spectra of RhB photodegradation via CdS@UiO-68N₂S (a), the dynamic process of the RhB concentration change (b), and the photodegradation kinetics (c).

To gain further insight into the photocatalytic mechanism, photo-oxidation of RhB was carried out under different conditions. The control experiments revealed that the photocatalyst was required for the RhB degradation (entries 1 and 2, Table 1). It is important to clarify the photocatalytic ability of the individual components in the CdS@UiO-68N₂S. Under the same condition, UiO-68N₂S and CdS showed moderate degradation of 39% and 6%, respectively (entries 3 and 4, Table 1). The result revealed a better photocatalytic ability through the incorporation of CdS into UiO-68N₂S. It is also important to clarify what kind of active species are involved in photocatalytic RhB degradation. Generally, two main active intermediates, such as $\cdot\text{OH}$ and $\text{O}_2^{\bullet-}$, have been proposed for the photocatalytic degradation of RhB [25]. The experiment revealed that only 4% of RhB was degraded when

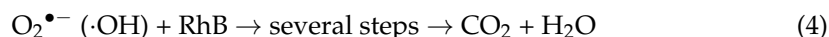
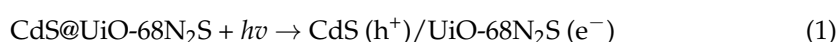
0.37 mmol of benzoquinone was added to the reaction solution as a scavenger of $O_2^{\bullet-}$, ref. [45], indicating that significant suppression of the RhB degradation occurred (entry 5, Table 1) and that $O_2^{\bullet-}$ may be a key participant in the reaction. In contrast, the equal dosage of *tert*-butanol as a scavenger of $\cdot OH$ [46] in the reaction system resulted in only slight suppression of the RhB degradation (entry 6, Table 1).

Table 1. Photocatalytic degradation of RhB under different conditions ^a.

Entry	Catalyst	Additive	Light	Degradation
1	CdS@UiO-68N ₂ S	N.D.	Blue light	94%
2	N.D.	N.D.	Blue light	1%
3	UiO-68N ₂ S	N.D.	Blue light	39%
4	CdS ^b	N.D.	Blue light	6%
5	CdS@UiO-68N ₂ S	Benoquinone ^c	Blue light	4%
6	CdS@UiO-68N ₂ S	<i>tert</i> -butanol ^d	Blue light	86%

^a Condition: RhB solution (25 mg/L, 10 mL), UiO-68N₂S (0.01 g, 0.011 mmol), CdS@UiO-68N₂S (0.01 g, 0.0027 mmol), light (blue LED light: wavelength = 480 nm, power = 80 W), R.T. (30 °C), reaction time: 13 h. ^b CdS (0.01 g). ^c Benoquinone (0.04 g, 0.37 mmol). ^d *tert*-butanol (0.37 mmol) (Figures S2–S6 show the original UV-Vis spectra for entries 2–6, respectively).

Based on the band gap analysis and the controlled experiment, a possible mechanism of charge transfer or reaction mechanism of the photocatalysis system is proposed in Figure 8. As seen first, under visible light irradiation, due to the appropriate band structures, both CdS and UiO-68N₂S can be excited to generate electrons in the CB, leaving holes (h^+) in the VB. The photogenerated electrons can be effectively transferred from the CB of CdS to that of UiO-68N₂S, while the holes remain in the CdS particles [27]. The photogenerated electrons transferred to the surface of the composite could react with the adsorbed dissolved oxygen to produce free radicals, such as $O_2^{\bullet-}$, resulting in the degradation of RhB [47]. At the same time, the remaining h^+ would transfer from the VB of UiO-68N₂S to that of CdS and then be combined with H₂O to produce active $\cdot OH$ radicals, which can directly oxidize RhB to some extent. According to the UV-Vis spectra of the RhB degradation process, a continuous reduction of the absorption peak of RhB without new peaks appeared, suggesting that the RhB decomposes into small molecules and finally CO₂ and H₂O [48]. The major reaction steps in RhB photocatalytic degradation are summarized by the following equations:



The performance of CdS@UiO-68N₂S in photo RhB degradation is compared with the recently reported photosensitive MOFs or CdS-MOFs complex, including Ag/AgCl@CFNMT [44], 1.5-CdS/MIL-53 [48], BiOBr@Bi-MOF [49], Cu(II)-based MOF [50], and CdS/g-C₃N₄/MIL-125(Ti) [51]. Their activity toward RhB photocatalytic degradation is summarized in Table 2. In all these cases, the conjugation of semiconductor particles with MOFs showed enhanced catalytic performance over the single components. In addition to the photocatalyst, the process of RhB photocatalytic degradation is also highly dependent on the power of the light source and the homogeneous state of the oxygen source. In this work, CdS@UiO-68N₂S shows moderate photocatalytic ability with a first-order kinetic constant of 0.0027 min⁻¹. Given the slight difference in dosage and the same oxygen source of air, the power of the LED light would take responsibility for the photocatalytic ability of CdS@UiO-68N₂S. In another aspect, compared to the widely used xenon lamp, the LED

light used in our case suggests that dye photodegradation for wastewater treatment can be performed in a more convenient and economical way.

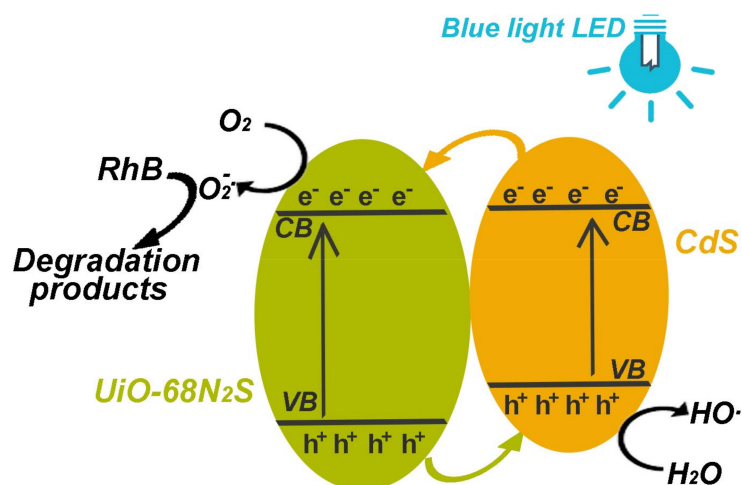


Figure 8. Proposed mechanism of RhB photocatalytic degradation in the presence of CdS@UiO-68N₂S and blue-light LED irradiation.

Table 2. Comparison of RhB photodegradation performance of MOF-based catalysts.

Catalyst	Catalyst Dosage	RhB Concentration	Light Source	Oxygen Source	Catalytic Activity	k^a/min^{-1}
Ag/AgCl@CFNMT ^b [44]	0.08 g/L	20 mg/L	Visible-light LED (100 W)	H ₂ O ₂ (20 uL)	98.8% (10 min)	0.103
1.5-CdS/MIL53 [48]	1.0 g/L	10 mg/L	Xenon lamp (500 W)	Air	86% (1.5 h)	0.0158
BiOBr@Bi-MOF [49]	0.6 g/L	20 mg/L	Xenon lamp (300 W)	Air	99.4% (60 min)	0.07009
Cu(II)-based MOF [50]	30 mg Cat. for 40 ppm RhB		UV light	Air	80% (100 min)	0.01358
CdS/g-C ₃ N ₄ /MIL125(Ti) [51]	N.D.	N.D.	Xenon lamp (300 W, $\lambda > 420$ nm)	Air	90.2% (90 min)	0.0414
CdS@UiO-68N ₂ S [this work]	1.0 g/L	25 mg/L	Blue light LED (80 W, $\lambda = 480$ nm)	Air	94% (14 h)	0.0027

^a First-order kinetic constant, ^b CFNMT = CoFe₂O₄/NH₂-MIL-125(Ti).

3.3. Photocatalytic Recycle Experiments

The recovery and reuse of a heterogeneous catalyst are of great importance from the perspective of wastewater treatment. The high photocatalytic RhB degradation of CdS@UiO-68N₂S under visible light encouraged us to examine its recyclability. After each cycle, CdS@UiO-68N₂S was recovered by centrifugation and washed with H₂O three times. The ICP-MS analysis of the reaction solution showed that only negligible amounts of Zr(IV) and Cd(II) were detected, indicating the reaction was a heterogeneous process. As depicted in Figure 9a, when the recovered catalyst CdS@UiO-68N₂S was subsequently used for another three successive cycles, the RhB degradation was found to be just slightly reduced to 84%, which was believed to result from the mass lost during the centrifugation. PXRD patterns of the reused catalyst showed that the structural integrity of the CdS@UiO-68N₂S framework was still maintained after the first and third recycle reactions (Figure 9b), indicating that the CdS@UiO-68N₂S framework was robust and stable under the reaction conditions.

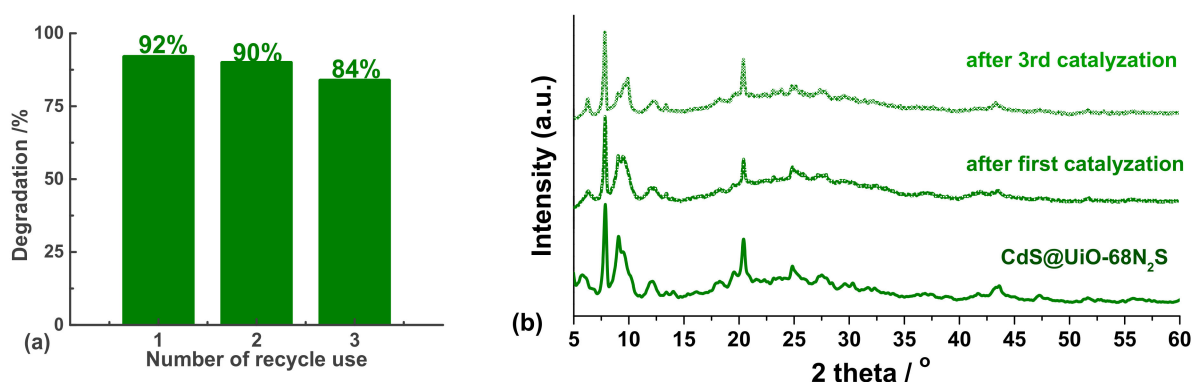


Figure 9. Recycling experiments for photo-degradation of RhB by CdS@UiO-68N₂S (a), PXRD patterns for the pristine and recovered samples of CdS@UiO-68N₂S after the first and third recycle uses (b).

4. Conclusions

In the work, the CdS@UiO-68N₂S complex was successfully constructed through the incorporation of CdS into the cavities of UiO-68N₂S via sequential adsorption of Cd²⁺ and S²⁻, and the conjugation of CdS and UiO-68N₂S with thiadiazole groups helped in improving the visible light absorption. The photocatalytic activity of CdS@UiO-68N₂S was evaluated by the degradation of dye RhB in aqueous solutions under blue light LED irradiation and ambient temperature, which revealed that up to 94% RhB degradation could be achieved under the conditions of 1.0 g/L catalyst dosage and 25 mg/L initial RhB concentration. The photocatalytic activity of CdS@UiO-68N₂S was better than that of the individual components, suggesting efficient charge separation via the conjugation. Besides, the CdS@UiO-68N₂S could be reused for four cycles without a significant decrease in activity, revealing its potential application as a green catalyst for environmental use.

Supplementary Materials: Supplementary data in the following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/cryst13050785/s1>. Figure S1: Kinetic analysis for the RhB photo degradation with CdS@UiO68-N₂S; Figures S2–S6: Photocatalytic degradation of RhB under varied conditions.

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