Photocatalytic Penicillin Degradation Performance and the Mechanism of the Fragmented TiO₂ Modified by CdS Quantum Dots

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ABSTRACT: In this study, a novel method was adopted to construct a CdS−TiO₂ heterostructure to degrade penicillin under sunlight. A potato extract was used during the synthesis process of CdS QDs as a stabilizer and a modifier. The CdS−TiO₂ composite with a heterostructure delivers high photocatalytic degradation efficiency. In detail, 0.6 mg/mL of CdS−TiO₂ can successfully decompose penicillin after 2 h, and 5‰ CdS−TiO₂ shows the optimal degradation efficiency with the degradation rate reaching 88%. Furthermore, the underlying mechanisms of the penicillin decomposition reaction were investigated by the EPR test and trapping experiment. It was found that the high photocatalytic degradation efficiency was attributed to the hetero-junction of CdS−TiO₂, which successfully suppresses the recombination of the conduction band of CdS and the valence band of TiO₂. Moreover, it was confirmed that the reaction is the O₂-consuming process, and introducing O₂ can greatly accelerate the generation of a superoxide radical during the photocatalytic degradation process, which eventually improves the degradation of penicillin and shortens the degradation time. Finally, this work provides the possible penicillin degradation pathways, which will inspire the researchers to explore and design novel photocatalysts in the field of wastewater treatment in the future.

1. INTRODUCTION

Antibiotics are extensively utilized to improve the economic development and people’s livelihood including industrial, medical, veterinary, and agricultural field due to their ability to inhibit the human and animal infections. However, the antibiotics abuse would widely cause the surface water pollution, which has already been considered as the common and inevitable harm to the environment. At present, antibiotics have been extensively detected in the surface water, soil, aquatic animals, and plants, which could result in the drug resistance of pathogenic bacteria and then cause greater damage to the aquatic organisms and even human health. Penicillin, a β-lactam water-soluble antibiotic with the highest antibacterial activity, has been widely used to prevent the peptidoglycan generation and destroy the bacterial cell wall formation in curing human and animal diseases. When penicillin is discharged into water, it is difficult to be degraded and removed through traditional water treatment methods. More importantly, it could cause unexpected damage to the organisms due to its biological toxicity, which eventually causes dramatically serious harm to the ecological environment and human health. Therefore, it is urgent to explore novel and effective methods to remove penicillin from the water environment.

For this purpose, a variety of treatment methods have been developed to remove penicillin, including biological, physical, and chemical oxidation. The chemical oxidation methods attract researchers’ attention because they can completely degrade the pollutants and avoid the generation of drug-resistant bacteria. The photocatalytic technology is one of the common methods to fulfill the chemical oxidation that removes pollutants by adopting redox reactions such as ozone oxidation, the Fenton reaction, and photocatalysis. Since Fujishima and Honda first discovered that TiO₂ can successfully realize the water decomposition under visible light in 1972, the photocatalytic degradation technology has received extensive attention. Compared with other semiconductor photocatalysts, such as ZnO, CdS, and CuS, and...
so forth, TiO$_2$ can be considered as the rapidly emerging water decomposition catalyst due to its advantages including nontoxicity, chemical stability, high photocatalytic activity, and low cost. However, owing to a large band gap ($E_g = 3.2$ eV) and wavelength (387 nm), the current TiO$_2$ photocatalyst is largely limited by the inefficient utilization of solar energy and the rapid recombination rate of photo-generated electron−hole pairs, which eventually lead to lower photocatalytic degradation efficiency of TiO$_2$. Therefore, varieties of strategies have been developed to improve the photocatalytic degradation efficiency of TiO$_2$, including metal or nonmetal doping, noble metal deposition, pigment sensitization, high-energy crystal plane exposure, and semiconductor doping. Adopting appropriate chemical or physical methods to combine multiple semiconductors is an effective method to greatly improve the photocatalytic activity of TiO$_2$. Such a hybrid semiconductor can largely maintain the properties and activity of the individual component, leading to a corresponding synergistic effect.

Cadmium sulfide quantum dots (CdS QDs) are a desired semiconductor for the modification of TiO$_2$, which has an $E_g$ of 2.4 eV and has a higher absorption coefficient in the visible light region. Chen et al. found that CdS could be added to successfully construct a CdS/TiO$_2$ heterojunction, which promotes the separation of electrons and holes and eventually improves the photocatalytic performance of the CdS/TiO$_2$ composite. During the synthesis process of CdS QDs, special surfactants or plasticizers are extensively utilized to introduce additional active functional groups to facilitate the formation of an interface, which even strengthens the bonding of the CdS/TiO$_2$ composite. It is well known that biomass is widely used in the synthesis of nanomaterials containing a large number of organic modification groups. Kamran et al. used rice husks and coconut husks to prepare honeycomb biomass charcoal materials, and MnO$_2$ was loaded on these charcoal materials to prepare composite materials. Cinnamon bark extracts were used to prepare manganese nanoparticles and were applied to dye degradation and in antibacterial fields.

We found that the various organic groups and starches existing in potato extracts can provide a more stable synthesis environment for CdS synthesis, while realizing the surface modification to achieve the cost saving and reduce toxicity.

Herein, we successfully added a potato extract into the synthesis process of CdS QDs as a stabilizer and a modifier, which was subsequently loaded on the TiO$_2$ substrate to decompose penicillin. The synthesized CdS/TiO$_2$ composite with a heterostructure delivers high photocatalytic degradation efficiency, which was attributed to the CdS/TiO$_2$ heterojunction formed that successfully suppresses the recombination of the conduction band (CB) of CdS and the valence band (VB) of TiO$_2$. Furthermore, the penicillin decomposition reaction was confirmed as the O$_2$-consuming process. The introduction of O$_2$ could greatly accelerate the generation of superoxide radicals during the photocatalytic degradation process, which eventually improves the degradation of penicillin and shortens the degradation time. This work will inspire the researchers to explore and design novel photocatalysts in the field of wastewater treatment in the future.

## 2. RESULTS AND DISCUSSION

### 2.1. Characterization of the Synthesized CdS/TiO$_2$ Composite

The crystal phase of the prepared CdS/TiO$_2$ composite was characterized by XRD patterns. As shown in Figure 1, after comparing with the standard PDF card of anatase TiO$_2$ (JCPDF no. 99-0008), it was found that the prepared CdS/TiO$_2$ composite mainly contains the anatase TiO$_2$ phase. As for the CdS phase, the corresponding diffraction peak intensities were too weak to be detected when the loaded molar ratio was 1 and 5‰, which was due to the smaller size and a lower content of CdS. When the ratio increased to 1%, the CdS generation was confirmed from the XRD patterns. When the loaded molar ratio increased to 5%, the characteristic peaks corresponding to CdS became more obvious, the main peaks at 20° of 26.5, 30.7, 44, 52.1, 70.5, and 72.6° could be attributed to the (111), (200), (220), (311), (331), and (420) crystal planes of cubic phase CdS (JCPDF Card No. 04-004-0784).
this observation proves that the synthesized CdS/TiO2 composite contained the CdS and TiO2 phases, and the anatase TiO2 phase maintains throughout the whole preparation process regardless of the CdS content.

UV−vis absorption spectrum of CdS/TiO2 was obtained, as shown in Figure 2, and CdS/TiO2 exhibited stronger visible-light absorption as the CdS QD content increased from 1 to 5%. The absorption edge shifted to 550 nm, indicating that the CdS/TiO2 heterojunction could greatly enhance the absorption to visible light.

The morphologies and structures of CdS QDs and CdS/TiO2 can be observed in the TEM and HRTEM images. As shown in Figure 3, the individual CdS QDs present a spherical shape with a diameter of around 5 nm and exhibit good dispersibility. The spacing of the lattice fringes of CdS QDs was measured to be 0.336 nm (Figure 3b), corresponding perfectly to the (111) crystal plane of CdS.40−42 After loading TiO2, the CdS/TiO2 composite could be obviously observed as shown in Figure 3c, which stacked in the fragments with well dispersion. The corresponding spacings of the lattice fringes of 0.352, 0.238, 0.336, and 0.206 nm were further measured and confirmed as shown in Figure 3d, which correspond to the (101) and (004) planes of TiO2 and the (111) and (220) planes of CdS, respectively.41,42,50 Meanwhile, it was observed that most of the sheet-like lattices were TiO2, and only a small amount of CdS lattices was found to be stacking or intersecting with the TiO2 lattice. Therefore, it could be preliminarily concluded that CdS was successfully doped into the TiO2 sheet in the CdS/TiO2 composite.

The SEM images of CdS QDs and TiO2 are shown in Figure 4. It could be clearly seen in Figure 4a that the synthesized cadmium sulfide quantum dots have a small particle size and are uniformly dispersed in the form of small spherical particles. The synthesized TiO2 shown in Figure 4b is stacked in sheets with organic coatings on the surface.

The elemental distribution of CdS/TiO2 was further investigated by SEM−EDS mapping. As shown in Figure 5, the CdS/TiO2 composite exhibits a multilayer flake morphology with small protrusions on the surface, which was similar to cauliflower. Moreover, the EDS analysis revealed the uniform distribution of existing Ti, Cd, and S elements of the CdS−TiO2 composite, which further demonstrates that CdS was uniformly distributed on the TiO2 substrate.

XPS was utilized to further explore the surface chemical composition and the bonding environment of CdS/TiO2. Figure 5 shows the characteristic peaks of O, Cd, Ti, and S elements. According to the integral calculation of the XPS spectra, it was found that the oxygen element, titanium element, sulfur element, and cadmium element in the sample account for 45.56, 43.79, 1.73, and 8.92%, respectively. Observed from the high-resolution Cd 3d XPS spectrum (Figure 6a), two peaks at 411 and 404.3 eV correspond to Cd 3d3/2 and Cd 3d5/2, respectively.50−52 The peaks at 162.4 and 161.7 eV (Figure 6b) can be attributed to S 2p1/2 and S 2p3/2, respectively, while the peak at 161.7 eV is attributed to sulfide,49 further confirming the formation of CdS. The peak at
162.4 eV indicates the existence of sulphydryl groups on the surface.53 As for the Ti 2p spectrum (Figure 6c), the peaks at 464.0 eV and 458.3 could be attributed to Ti 2p1/2 and Ti 2p3/2, respectively, confirming the presence of Ti4+ in samples.54 Figure 6d presents the O 2p spectrum, which could be divided into two peaks, indicating the existence of an oxygen lattice (529.5 eV) and hydroxyl groups (530.9 eV), respectively.55,56

In order to further confirm the functional groups existing on the CdS/TiO2 surface, the FTIR analysis was carried out (Figure 7). The broad peak at 3271 cm−1 corresponds to the O–H stretching vibration of the surface water molecules.
however, the N–H stretching vibration of the organic matter introduced by the organic matter of the potato extract is also within this range, which may be hidden by the O–H stretching vibration of the water molecules. The peak at 1632 cm⁻¹ corresponds to the tensile vibration of aromatic C–N and the symmetric contraction of carboxyl groups, respectively, and the peak at 1045 cm⁻¹ corresponds to the tensile vibrations of C–O. The last peak at 625 cm⁻¹ corresponds to the stretching vibration of Ti–O, which proves the successful synthesis of TiO₂.

Measurements of nitrogen sorption isotherms were used to obtain the Brunauer–Emmett–Teller (BET) specific surface area of synthesized pure TiO₂ nanomaterials and CdS/TiO₂ loaded with CdS (QDs), respectively. The results are shown in Figure 8. The adsorption performance of the two materials for nitrogen increases linearly with the increase of pressure, showing the trend of a typical type II isotherm. The calculated specific surface areas are 225 and 229 m²/g, respectively, indicating that the prepared TiO₂ nanomaterials have a relatively high specific surface area. After loading a small amount of CdS (QDs) on the surface, the specific surface area slightly increases. Therefore, the prepared CdS/TiO₂ composite material has excellent surface properties.

2.2. Photocatalytic Performance. The photocatalytic activities of the as-prepared CdS/TiO₂ were evaluated by the penicillin concentration variations under visible-light irradiation. As shown in Figure 9. The CdS QDs and TiO₂ standards exhibited specific photocatalytic activities, which deliver a penicillin degradation rate of 68% (TiO₂) and 37% (CdS QDs) after 2 h, respectively. The presence of TiO₂...
nanocomposites enhanced the penicillin degradation. Specifically, the degradation rate of penicillin was found lower than that of TiO2 as the CdS QD content was 1 and 5%, which due to the insufficient utilization of the photons produced from CdS/TiO2 caused by the excessive. When the CdS QD content decreased to 1 and 5%, the corresponding penicillin degradation rates increased to 81 and 88%, respectively, which were much higher than those of individual CdS QDs or TiO2, indicating that the successfully constructed CdS/TiO2 heterostructure could suppress the recombination of photogenerated electron−hole pairs prolonging the life of the photocatalytically active charge carrier.

Subsequently, deactivation measurements were carried out to investigate the durability of CdS/TiO2 for PG degradation, as shown in Figure 10. In this experiment, after 2 h of irradiation, the CdS/TiO2 suspension was further filtered (0.45 μm filter paper), washed, and collected for reuse. After five times of reuse, the penicillin degradation rate decreased from 100 to 94% at the end of the experiment (2 h). The results indicated that the prepared CdS/TiO2 composite exhibited good reusability and stability.

2.3. Proposed Mechanism for the Enhanced Photocatalytic Activity. The electron paramagnetic resonance (EPR) measurements were conducted to identify *O2−, *OH, and h+, in DMPO solution with the CdS/TiO2 photocatalyst, as shown in Figure 11a−c. The potentials of the conduction band (E_{CB}) and the valence band (E_{VB}) of CdS and TiO2 were −0.65 and +1.75 eV as well as −0.44 and +2.76 eV, respectively. The E_{CB} of CdS is less positive than that of TiO2, therefore, CdS and TiO2 would form CdS/TiO2 heterostructures. Obviously, in the absence of light irradiation, no characteristic peaks attributed to DMPO−*O2− (*OH, and H+) could be observed in the EPR spectra, indicating no reactive radical generation in the absence of light irradiation. After light irradiation for 1 min, the corresponding peaks were apparently observed in the EPR spectrum. The peak intensity gradually increased with prolonging irradiation time, demonstrating the generation and enrichment of *O2−, *OH, and h+ in DMPO with CdS/TiO2 during the photodegradation experiment. Trapping experiments were conducted to determine the primary reactive species in the photocatalytic degradation (Figure 11d). When EDTA-2Na, p-BQ, and IPA were added, the degradation rate of penicillin declined to 35, 55, and 82%, respectively. These results indicate that h+ was the dominant active specie and played a major role in the photocatalytic reaction, followed by *O2− and *OH.

PL emission spectroscopy measures the recombination of electrons and holes under light, which is useful to illustrate the behavior of carrier migration and separation in photocatalysts. Therefore, the PL spectra of synthesized TiO2, CdS QDs, and CdS/TiO2 were measured, as shown in Figure 12. TiO2 and CdS QDs had obvious emission peaks at 362 and 379 nm, respectively, and the peak intensities were close to each other. The peak intensity of CdS QDs was weaker than that of TiO2. The emission peak of CdS/TiO2 appears at 375 nm, which was due to the shift of the emission peak caused by the competition of the composite material for electrons. By comparison, it could be clearly seen that the peak intensity of CdS/TiO2 was significantly weaker than that of TiO2 and CdS QDs. It was revealed that the loading of CdS QDs on TiO2 enhanced the separation ability and transfer of photogenerated electrons in the system, promoted the transfer of photogenerated electrons, and delayed the recombination time between excited electrons and holes, further proving the successful construction of a heterostructure.
The possible mechanism of photo-generated charge transfer in the CdS/TiO2 composite under visible light irradiation is illustrated in Figure 13, and the relevant reactions have been listed in eqs 1–8. When the absorption energy on the surface of CdS/TiO2 is higher than 2.4 eV, the electron would excite from the VB to the CB of CdS because of its lower $E_g$ than that of TiO2. Because the CB of CdS QDs is more negative than that of TiO2, the photogenerated electrons would migrate from the CB of CdS (−0.65 eV) to that of TiO2 (−0.44 eV). Moreover, $h^+$ would stay in the VB of CdS, because the VB of CdS QDs (+1.75 eV) is less positive than that of TiO2 (+2.76 eV), which would thus suppress the electron–hole recombination. The excited electrons in the CB of CdS would probably react with dissolved O2 in solution to produce $O_2^−$ (eq 4) and then finally form $OH^−$ (eqs 5–7). The photogenerated holes would transfer from the VB of TiO2 to the VB of the CdS and oxidize the hydroxyl groups into.

Figure 11. EPR spectra of radical adducts with DMPO in the CdS/TiO2 system at different irradiation times and trapping experiments. (a) $O_2^−$, (b) $OH^−$, (c) trapping holes, and (d) trapping experiments.

Figure 12. Photoluminescence (PL) spectra of TiO2, CdS QDs, and CdS/TiO2 under 330 nm excitation.

CdS·TiO2 + $h^+$ → CdS($e_{CB}^− + h_{VB}^+$)·TiO2

(1)

CdS($e_{CB}^− + h_{VB}^+$)·TiO2 → CdS($h_{VB}^+$)·TiO2($e_{CB}^−$)

(2)

TiO2 + $h^+$ → TiO2($e_{CB}^− + h_{VB}^+$)

(3)

e_{CB}^− + O2 → $O_2^−$

(4)

$O_2^− + H_2$O$^\cdot$HO2 + OH$^−$

(5)

$^\cdot$HO2 + $H_2$O$^\cdot$OH + H2O2

(6)

H2O2 → 2$^\cdot$OH$^−$

(7)

$h^+ + OH^− → ^\cdot$OH

(8)
hydroxyl radicals (eq 8). Under these strong oxidizing free radical ions, penicillin was degraded into small molecules.73−75

After confirming the optimal CdS QD content (5‰), the O2 concentration variation during the reaction and its effect on the photocatalytic reaction were further investigated, as shown in Figure 14a. During the whole photocatalytic degradation process, oxygen, air, and nitrogen were separately added to the solution at a rate of 0.8 mL/min to investigate the influences of O2 on the photocatalytic degradation process derived from the degradation rate. There was no obvious change of the degradation rate when introducing air into the solution, and the degradation rate at the end of process was 87%. In addition, the results also showed that introduction of N2 greatly inhibited the degradation process, the degradation rate declined to 20% at the end of the reaction, which was due to that the surface of CdS/TiO2 tends to adsorb a large amount of N 2 in the N 2 environment. Therefore, the photogenerated electrons could not react with O2 to produce •O2−, eventually resulting in the stagnation of the degradation reaction. Surprisingly, after adding O2 into the solution, the degradation rate dramatically increased to 100% in 1 h, indicating O2 would greatly improve the photocatalytic efficiency. This was mainly due to that O2 could greatly accelerate the generation of a superoxide radical during the photocatalytic degradation process, which eventually improves the degradation efficiency and shortens the degradation time. This work will inspire the researchers to explore and design novel photocatalysts in the field of wastewater treatment.

3. CONCLUSIONS

In this study, a novel method was used to synthesize a CdS/TiO2 composite with a heterostructure to decompose penicillin. A high photocatalytic degradation efficiency has been achieved with the CdS/TiO2 composite. Subsequently, the corresponding mechanism has further been systematically studied. It was demonstrated that the high photocatalytic degradation efficiency was attributed to the heterojunction of CdS/TiO2, which successfully suppresses the recombination of the CB of CdS and the VB of TiO2. Furthermore, the penicillin decomposition reaction was confirmed as the O2-consuming process, and thus O2 could greatly accelerate the generation of a superoxide radical during the photocatalytic degradation process, which eventually improves the degradation efficiency and shortens the degradation time. This work will inspire the researchers to explore and design novel photocatalysts in the field of wastewater treatment.

4. EXPERIMENTAL SECTION

4.1. Synthesis of Catalysts. 4.1.1. Synthesis of CdS QDs.

A certain amount of potato (Solanum tuberosum L.) was boiled in deionized water for 0.5 h, which was then filtered by eight layers of gauze to obtain the potato extract as the stabilizer and...
modifier for the next procedure. Thioacetamide (TAA, Macklin, analytical grade) and cadmium sulfate octahydrate (3CdSO₄·8H₂O, Macklin, analytical grade) were added into the above potato extract with a molar ratio of Cd²⁺/S²⁻ = 1:30. After reacting in an electronic steam sterilizer for 20 min (121 °C, 102 kPa), the aqueous CdS QD solution was finally obtained.

4.1.2. Synthesis of TiO₂ Loaded with CdS QDs. 15 mL of glacial acetic acid (Macklin, analytical grade) and 34 mL (10 mmol Ti) of butyl phthalate (analytical grade) were added to the beaker, with vigorous stirring to form a homogeneous solution A. Meanwhile, 50 mL of the prepared CdS QD solution was added to 200 mL of ethanol (Macklin, analytical grade) to form solution B. Subsequently, the Solution A was added to the solution B with stirring until homogeneous solution formation, which was then placed in the autoclave. After reacting at 121 °C for 20 min, the as-obtained residue was washed several times, and dried at 60 °C. The molar ratio

Figure 15. Schematic diagram of total ion current and degradation pathways of penicillin products, (a) total ion current, (b) compound b m/z = 180, (c) compound c m/z = 136, (d) compound d m/z = 246, (e) compound e m/z = 274, and (f) degradation pathways of penicillin.
of Cd to Ti in the prepared CdS/TiO₂ composite was set to be 1, 5%, 1, and 5% (1, 5%, 1, 5% CdS/TiO₂), respectively.

4.2. Characterizations of Synthesized Samples. The phases of the samples were determined by XRD measurement (TongDa, Cu Kα radiation, k = 0.1542 nm 40 kV, 100 mA). The morphology, size, and dispersion of the samples were characterized by TEM (JEOL2100) and SEM (HITACHI SU8020). The element composition and chemical valence of the samples were analyzed by X-ray photoelectron spectroscopy and FT-IR (XPS, Thermo Escalab 250Xi, FTIR Bruker TENSOR 27). The UV-visible DRS of the samples were measured using a spectrophotometer (PERSEE, T9) operating in the diffuse mode. The BET surface area of the catalysts was determined using a nitrogen adsorption apparatus (MICRO-MERITICS, ASAP 2020, U.S.A.) in a relative pressure (P/P₀) from 0.05 to 0.3. The PL spectra were obtained on a Hitachi F-7000 spectrophotometer.

4.3. Photocatalytic Degradation Experiment. Photocatalytic degradation experiments were conducted on a cylindrical photochemical reactor using a 300 W xenon lamp as the simulated sunlight. The reactor was kept at a constant temperature (25 °C) by circulating cool water. In each batch, 40 mg of catalysts were added into a 100 mL of penicillin solution (100 mg/L). Before irradiation, the solution was stirred in the dark for 30 min to achieve equilibrium. One mL of the suspension was transferred for centrifugation at regular intervals. A certain amount of supernatant was selected and filtered with a 0.45 μm filter membrane, and then transferred for the high-performance liquid chromatography and liquid chromatography–mass spectrometry (LC–MS) measurements to detect the concentration of penicillin and degradation products, respectively.

During the photocatalytic degradation process, isopropanol (10 mmol/L), ethylenediaminetetraacetic acid disodium salt (EDTA-2Na, 10 mmol/L), and p-benzoquinone (p-BQ, 10 mmol/L) were added to the solution to capture hydroxyl radicals (•OH), holes (h+), and superoxide radicals (•O₂⁻), respectively. The dominant free radicals could be confirmed by comparing the degradation of penicillin with and without these reagents. A mass spectrometer was placed at a certain distance from the surface of the reaction solution with a detection molecular mass of 32, and the O₂ concentration could be detected according to the change of the electrical signal intensity.

The LC–MS measurements were conducted with the Hypersil BDS C18 column, using a mixture consisting of 50 vol % ultrapure water (containing 0.1% formic acid) and 50% acetonitrile as the mobile phase. The flow rate was controlled as 1 mL/min, the column temperature was 30 °C, and the injection volume was 20 μL. During the test, the mass spectrometer was connected with an electrospray ionization source and operated in the negative ion mode. The ratio of mass to charge (m/z) of the scan was 50–500.

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Notes

The authors declare no competing financial interest.

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