Graphical Abstract

**Degradation of Refractory Pollutants under Solar Light Irradiation by a Robust
and Self-Protected ZnO/CdS/TiO₂ Hybrid Photocatalyst**

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Abstract

Photocatalyst plays a vital role in the photochemical water treatment. To improve the visible-light photoactivity of TiO_2 for refractory pollutant degradation, CdS/TiO_2 hybrids with different nanostructures have been prepared, but usually suffer from a low photocatalytic degradation efficiency and a rapid photocorrosion. In this work, we developed a synergistic $\text{ZnO}/\text{CdS}/\text{TiO}_2$ hybrid, which could act as a robust and self-protected photocatalyst for water purification without additional sacrificial reagents. This was attributed to the two different junction mechanisms in one single hybrid. Photons were selectively adsorbed by ZnO and CdS , then, the electrons with a low reductive activity in ZnO recombined directly with the holes with a low oxidative activity in CdS , whereas the holes with a high oxidative activity in ZnO and the electrons with a high reductive activity in CdS were captured for catalytic reaction. The superiority of the novel $\text{ZnO}/\text{CdS}/\text{TiO}_2$ hybrid over the traditional CdS/TiO_2 hybrid in both photocatalytic activity and anti-photocorrosion capacity was demonstrated in the degradation of Atrazine and Rhodamine B, two typical refractory organic pollutants, and the treatment of real textile wastewater under solar light irradiation. The developed $\text{ZnO}/\text{CdS}/\text{TiO}_2$ hybrid exhibited an excellent potential for the degradation of refractory pollutants, and provided a new way to advance intrinsically solar-susceptible catalyst for photochemical wastewater treatment.

Keywords: Photochemical wastewater treatment; CdS ; anti-photocorrosion; catalytic performance; Atrazine

1. Introduction

TiO₂ is recognized as the most important semiconductor photocatalyst for water purification (Chong et al., 2010; Hernández-Alonso et al., 2009). Due to the intrinsic atomic and electronic structures, two main barriers largely limit its environmental applications under solar irradiation: wide band-gap (3.0~3.2 eV) and low charge-mobility (Grätzel et al., 2001; Steven et al., 2010; Sun et al., 2008). To overcome these two barriers, a combination of TiO₂ with a narrow band-gap semiconductor is of considerable interests for practical application at a low cost (Li et al., 2009). CdS, owing to its narrow band gap (2.2~2.4 eV), high absorption coefficient and suitable conduction band (-0.5~0.6 eV), is preferably used to sensitize TiO₂ for the visible-light photoactivity (Daskalaki et al., 2010; Gao et al., 2009; Grätzel et al., 2001; Hernández-Alonso et al., 2009; Lee et al., 2008; Li et al., 2009; Li et al., 2011; Tada et al., 2006; Zhu et al., 2010). To further improve photon conversion efficiency as well as apparent catalytic performance, the CdS/TiO₂ hybrid based on the highly ordered, vertically oriented nanotube arrays has attracted increasing interest due to their enhanced charge transfer (Gao et al., 2009; Steven et al., 2010; Sun et al., 2008; Zhu et al., 2010). But this hybrid is largely limited by its intrinsic photocorrosion behavior in practical pollutant degradation, especially when used in aqueous solutions under solar light irradiation (Daskalaki et al., 2010; Kenneth et al., 1977; Meissner et al., 1998; Reber et al., 1986). This drawback can be overcome by scavenging the corrosive holes in CdS with sacrificial reagents

(Daskalaki et al., 2010; Lee et al., 2008; Tsuji et al., 2004), such as $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$ (Daskalaki et al., 2010), $\text{S}^{2-}/\text{SO}_3^{2-}$, I^-/I_3^- , $\text{Co}^{2+}/\text{Co}^{3+}$ (Sapp et al., 2002), $\text{Fe}^{2+}/\text{Fe}^{3+}$ (Tian et al., 2005), ethanol (Daskalaki et al., 2010), lactic acid (Li et al., 2011), triethanolamines (Sheeney-Haj-Ichia et al., 2004), ascorbic acid (Wang et al., 2009) and mixed redox couples (Cazzanti et al., 2006). In principle, the sacrificial reagent, as an electron donor, should possess a sufficiently low potential and can be readily oxidized by the holes with a low capacity ($E^\circ = 1.38 \text{ V}$) in CdS, then the oxidized CdS is regenerated and recycled. However, these sacrificial reagents are not appropriate for practical applications owing to their high cost, large consumption, side reaction and secondary pollution (Daskalaki et al., 2010; Janga et al., 2007). Thus, solid sacrificial reagents with large environmental superiorities are highly desired.

Recently the hybrids based on the direct Z-scheme junction mechanism are proposed to solve the above problem (Chen et al., 2012; Sayama et al., 2002; Tada et al., 2006). In such hybrids, there is a rapid recombination between the holes with a low oxidative activity and electrons with a low reductive activity at the hybrid interface, while holes with a high oxidative activity and electrons with a high reductive activity are utilized effectively. Thus, no additional sacrificial reagent is needed in this case (Liu et al., 2010; Sayama et al., 2011). A CdS/ZnO hybrid can effectively construct such a direct Z-scheme and exhibit a high efficiency for catalytic reaction (Wang et al., 2009; Wang et al., 2010; Wang et al., 2011). In this hybrid, CdS is usually deposited on ZnO, and solar light irradiates along CdS to ZnO. However, this configuration might lead to the limited activation of ZnO and thus deteriorate the

overall performance of the Z-scheme junction, because of the dominant adsorption of both UV and visible photons by CdS. Thus, if ZnO is deposited on CdS to form a ZnO/CdS hybrid, and solar light irradiates along ZnO to CdS, the activation of ZnO and the overall performance of the hybrid could be significantly improved because of the selective adsorption of UV by ZnO and visible photons by CdS, respectively. Moreover, the sufficiently activated ZnO could provide a solution to overcome the photocorrosion of CdS without the use of any additional sacrificial reagents.

Therefore, in this work we designed and prepared such a ZnO/CdS/TiO₂ hybrid for photochemical pollutant degradation. Within this hybrid, the inner TiO₂ nanotube provided a large surface area, strong light-harvesting capability, convenient charge-transfer way and high charge-collection efficiency to improve photocatalytic activity, while the outer ZnO acted as a solid sacrificial reagent for the middle CdS to improve the anti-photocorrosion capacity. After its preparation, this material was characterized in terms of morphology, catalytic ability and stability, and further used to degrade two typical organic pollutants, Rhodamine B (RhB) and Atrazine, and treat real textile dyeing wastewater under solar light irradiation. In this way, a novel photocatalyst ZnO/CdS/TiO₂ with a high visible-light photocatalytic activity and stability for the degradation of refractory organic pollutants was developed.

2. Materials and methods

2.1. Preparation and characterization of the ZnO/CdS/TiO₂ hybrid

As illustrated in [Scheme 1](#), the TiO₂-NT scaffold (2 cm × 3 cm) was prepared by

anodic oxidation, in which a two-electrode configuration was comprised of a Ti foil as the anode and another Ti foil as the cathode. Briefly, a 0.30 mm Ti foil was burnished and immersed in polishing solution with $\text{HF}:\text{HNO}_3:\text{H}_2\text{O} = 1:1:2$ (volume ratio) to remove oxide layer and blot, and cleaned with soap, acetone and isopropanol before and after chemical polishing. Later, anodization was undertaken in a stirring solution of 0.09 M NH_4F in de-ionized water and ethylene glycol. The water content in the supporting electrolyte and the anodic voltage were in a range of 1-10 vol % and 30-90 V, respectively. The electrochemical treatment included potential ramp from the open-circuit potential to the end potential, followed by holding the potential constant for several days at 15-25 °C.

CdS NPs were deposited onto the TiO_2 NTs using a chemical bath containing CdCl_2 , triethanol amine, ammonium hydroxide and thiourea. 8 ml of 0.1 M CdCl_2 , 4 ml Triethanol amine (50%), 4 ml of NH_4OH (15 M) and 8 ml of 1 M Thiourea were added sequentially into a 80 ml beaker and stirred, followed by dose of 54 ml hot water (70 °C). The TiO_2 -NT was immersed vertically in the bath at 70 °C. The yellow-colored thin films obtained after 5-min deposition were uniform and bright. Then, the hybrid was dried in vacuum oven at 60 °C for 0.5 h.

To prepare the ZnO NPs/CdS NPs/ TiO_2 NTs, firstly, 50 ml of ethanol containing 1.46 g zinc acetate dehydrate was placed into a distillation apparatus and heated to 80 °C for 4 h before the ZnO precursor was obtained; Later, ZnO precursor was immediately diluted to 70 ml with ethanol and cooled rapidly in ice water bath; Thereafter, 0.29 g of lithium hydroxide power was added into the diluted and cooled

the ZnO precursor, the mixture was then hydrolyzed at 0 °C under ultrasonic irradiation for 1 h. For anchoring ZnO NPs to CdS NPs/TiO₂ NTs, the scaffold was dipped into the cooled ZnO precursor for a sufficiently long period, then dried in vacuum oven at 60 °C for 3 h and calcinated in Ar atmosphere at 500 °C for 1 h.

Morphology and structure were imaged by field-emission scanning electron microscope (FESEM, SIRION200, FEI Co., the Netherlands), high-resolution transmission electron microscope/selected area electron diffraction/energy dispersive X-ray spectroscopy (HRTEM/SAED/EDX, JEM-2100, JEOL Co., Japan) and scanning transmission electron microscope (STEM, JEM-ARM200F, JEOL Co., Japan). Crystal structure was characterized by X-ray diffraction (XRD, X'Pert, PANalytical BV, the Netherlands). Diffuse reflectance spectra was measured on a UV/Vis spectrophotometer (DRS, UV 2550, Shimadzu Co., Japan), chemical composition was analyzed by X-ray photoelectron spectroscopy (XPS, PHI 5600, Perkin-Elmer Inc., USA).

2.2. Photocatalytic degradation tests

The photochemical properties of the hybrid were measured by transient photocurrent response and HO^{*} generation. The photocatalytic activities were measured for the decomposition of RhB, a typical azo dye widely used in industries, and Atrazine, a typical herbicide widely found in water environments, and the treatment of real textile dyeing wastewater in a custom-made 60-ml photoreactor under solar irradiation (300-770 nm) at ambient temperature (Scheme S1). The light

source was a 350 W Xe arc lamp (PLS-SXE350, Beijing Trusttech Co., China) equipped with a 10 cm IR water filter. For each experiment, 30 ml solution and 2×3 cm photocatalyst film were used. The organics were allowed to reach adsorption-desorption equilibrium on the catalyst before irradiation. One-ml sample was regularly taken and filtered by $0.45 \mu\text{m}$ membrane filter before analysis.

The raw textile dyeing wastewater was collected from a local plant in Hefei City, China, and stored in a 4°C refrigerator to keep its characteristics unchanged. The initial pH varied from 6.8 to 7.5 and the ionic conductivity was in a range of $1.37 \sim 2.00 \text{ mS cm}^{-1}$, with an initial chemical oxygen demand (COD), total kjeldahl nitrogen (TKN), ammonium-N, sulfate and chlorides of approximately 7850, 1240, 920, 280 and 610 mg L^{-1} , respectively. The raw textile wastewater was diluted appropriately with distilled water to obtain a constant initial concentration, and Na_2SO_4 was added to keep the conductivity.

2.3. Analysis

Optical absorbance of RhB and textile dyeing wastewater was determined with a spectrophotometer (UV-2401PC, Shimadzu Co., Japan), Atrazine was measured using a high-performance liquid chromatography (HPLC-1100, Agilent Inc., USA) with a Hypersil-ODS reversed-phase column and detected at 254 nm using a VWD detector. The mobile phase was a mixture of water and methanol (40:60) delivered at a flow rate of $1 \text{ mL} \cdot \text{min}^{-1}$. SO_4^{2-} was determined by ionic chromatography (ICSS-2000, Dionex Inc., USA). Intermediates from the Atrazine degradation were identified by

liquid chromatography mass spectrometer (LC-MS, LCMS-2010A, Shimadzu Co., Japan) (see *Supplementary data* for details). COD was determined by following the Standard Methods (APHA, 1998). Total organic carbon (TOC) was measured to determine the mineralization efficiency (TOC-V_{CPN} analyzer, Shimadzu Co., Japan). The Cd element analysis in the CdS-based hybrids and treated aqueous solutions before and after the photocatalytic degradation tests was carried out by using inductively coupled plasma atomic emission spectrometry (ICP-AES) on a Hitachi 850 Fluorescence Spectrometer. For ICP analysis, the Cd remaining in the CdS-based hybrids was completely extracted by dissolving samples in HCl aqueous solution (10 ml, 20 vol.%); the released Cd into the treated solution was analyzed directly.

3. Results and discussion

3.1. Structure and properties of the ZnO/CdS/TiO₂ hybrid

The hybrid preparation process is illustrated in [Scheme 1](#). The as-prepared highly ordered, upright oriented TiO₂ NTs were uniquely found to have large tube diameter, wide inter-tube gap and sufficient tube length to geometrically favor the subsequent loading of photo-sensitizer ([Fig. 1a and b](#)). After the CdS deposition, the nanotubular scaffold remained intrinsically unchanged, and both the interior and exterior surfaces of NTs became much rough with a thicker wall and a smaller diameter ([Fig. 1c and d](#)). These results indicate no any damage to the 1D ordered structure of the scaffold and the uniform deposition of the sensitizer. Also, even after the ZnO deposition, the 1D tubular architecture still remained recognizable from their cross-sectional view, and

both the interior and exterior surfaces became further rougher (Fig. 1e and f). Unlike most of previous works, the depositions of sensitizer exhibited two significant features due to the unique characteristics of the scaffold: 1) mainly locating along the TiO₂ NTs but not at the tubes' entrance; and 2) not only locating outside the TiO₂ NTs, but also within the tubes. As a result, without blocking the tubes' entrance, CdS and ZnO were uniformly deposited on the exterior and interior surfaces along the entire TiO₂ NTs scaffold (Fig. S1), which is essential for the efficient catalytic applications.

The EDX spectra indicate that the hybrid was mainly comprised of Zn, Cd, Ti, O and S, and the elemental maps further illustrate the hierarchical and uniform distribution of ZnO and CdS over the entire TiO₂ NTs (Fig. 2). These results indicate the successful construction of the ZnO/CdS/TiO₂. Moreover, the HRTEM, XPS, XRD and DRS results further demonstrate that the hybrid was comprised of ZnO, CdS and TiO₂, as evidenced by their characteristic lattice fringes (Fig. 2), binding energies (Fig. S2), diffraction peaks (Fig. S3a) and optical adsorption spectra (Fig. S3b). In the DRS spectrum of the ZnO/CdS/TiO₂ hybrid, two sharp absorption steps were clearly observed, one was intrinsically for the upper ZnO and another for the middle CdS. Furthermore, the post-deposition of ZnO onto the CdS/TiO₂ hybrid could significantly improve the optical adsorption in both UV and visible ranges (Fig. S3b). In principle, the enhanced UV absorption of the ZnO/CdS/TiO₂ hybrid might be attributed mainly to the higher charge mobility and more rapid charge separation in ZnO than those in CdS (Sun et al., 2008). The enhanced visible absorption could be ascribed to the high light-harvesting efficiency from the increased optical path and additional light

trapping by reducing reflection and multi-scattering, geometrically resulting from the much more rough surface and larger surface area after ZnO post-deposition (Figs. 1 and S1) (Gao et al., 2009; Steven et al., 2010; Zhu et al., 2010). The DRS results clearly demonstrate that, under the UV-Vis irradiation, the bottom TiO₂ was not thermodynamically activated, but both the upper ZnO and middle CdS were simultaneously activated by the UV and visible photons, respectively, which could be mainly attributed to the excellent transparency of ZnO thin film (Wang et al., 2009; Wang et al., 2010; Wang et al., 2011). Moreover, the DRS results further suggest the unique synergistic mechanism in the ZnO/CdS/TiO₂ hybrid: all of the observed photocatalytic activity was originally derived from both upper ZnO and middle CdS, rather than the bottom TiO₂.

To examine the photochemical properties of the hybrid, its transient photocurrent response and HO^{*} were measured under solar light irradiation. The short-circuit photocurrent on the ZnO/CdS/TiO₂ was much higher and more stable than that on the CdS/TiO₂ (Fig. 3a). This indicates the excellent photocatalytic activity and enhanced anti-photocorrosion capacity were attributed to the synergistic effects of the novel hybrid. Moreover, the semi-quantitatively measured HO^{*} also exhibited a similar trend. The fluorescence signal intensity of HO^{*}-mediated 2-hydroxyterephthalic acid generated on the ZnO/CdS/TiO₂ was much more stronger than that on the CdS/TiO₂ (Fig. S4, see *Supplementary data* for details), which didn't exhibit any signal in 20 min (Fig. 3b), implying a significantly higher HO^{*} intensity and a better photochemical activity of the hybrid under the same conditions (Fig. 4).

3.2. Degradation of RhB and Atrazine and treatment of textile wastewater by the ZnO/CdS/TiO₂ hybrid

To evaluate its application potential, the photocatalytic RhB degradation test was firstly carried out. The CdS/TiO₂ exhibited a RhB removal efficiency of only ca. 20% within 2-h solar irradiation, but the ZnO/CdS/TiO₂ had a nearly 4 times higher RhB removal efficiency (ca. 90%) under the identical conditions (Figs. 4a and S5a and b). Within 2 h, the absolute RhB removal quantities by per cm² electrode surface were ca. 7.5 and 30 µg/cm² for the CdS/TiO₂ and ZnO/CdS/TiO₂, respectively (Fig. 4b).

Such an activity difference was even enlarged for Atrazine degradation (Table 1). The CdS/TiO₂ did not show any obvious photocatalytic activity in the absence of sacrificial reagent (Figs. 4c and S5c). Even after 0.1 M Na₂S and 0.01 M Na₂SO₃ were added, there was no obvious photocatalytic activity for Atrazine degradation (Fig. 5a). In comparison, the ZnO/CdS/TiO₂ exhibited a higher efficiency than all other counterparts. Within 3-h reaction, more than 80% of Atrazine was removed, much higher than those for all the other photocatalysts (Figs. 4c and S5d). The highest absolute Atrazine removal quantity by per cm² electrode was approximately 25 µg/cm² for the ZnO/CdS/TiO₂, while 14.5, 13.9, 14 and 10 µg/cm² only for the ZnO/TiO₂, ZnO/CdS, TiO₂ and ZnO, respectively (Fig. 4d). In addition, for Atrazine at 20 mg L⁻¹, the ZnO/CdS/TiO₂ even exhibited a nearly 5-times higher efficiency than that of the CdS/TiO₂ (Fig. S6). These results clearly demonstrate that the photocatalytic activity of the CdS/TiO₂ was drastically improved after the upper

deposition of ZnO. The main degradation intermediates were identified by LC-MS, and its degradation pathway is illustrated in Scheme S2. Also, for the textile wastewater, both its photochemical decoloration and mineralization efficiencies on the ZnO/CdS/TiO₂ hybrid were much higher than those on the CdS/TiO₂ hybrid (Figs. 4e and f and S7). Within 6 h treatment, the chromophoric absorbance of the real textile wastewater at 475 nm was reduced by ca. 60%, and its TOC was substantially removed by 55.9% on ZnO/CdS/TiO₂, in comparison with ca. 40% and 9.9% on CdS/TiO₂ under the identical conditions.

It should be noted that the TiO₂ exhibited a higher activity than the CdS/TiO₂ for the degradation of both RhB and Atrazine as well as the treatment of real textile wastewater. Such a superiority of TiO₂ over the CdS/TiO₂ hybrid seemed to be strange, which might be attributed to the following three reasons: the unique light source, the different photocatalytic oxidation mechanisms and no dose of sacrificial chemical reagents. First, compared to only the activated CdS in CdS/TiO₂ hybrids under visible light source ($\lambda > 420$ nm) in previous studies, both CdS and TiO₂ were activated simultaneously under UV-Vis light ($\lambda > 300$ nm) in this study (Fig. S8). Also, the charge mobility and charge separation efficiency were significantly much higher in TiO₂ than those in CdS (Daskalaki et al., 2010; Grätzel et al., 2001; Lee et al., 2008; Tada et al., 2006), resulting in a higher quantum efficiency for TiO₂. Secondly, for the CdS/TiO₂, only the electron indirect oxidation occurred for pollutant degradation and the transferred holes with a reduced oxidative potential corrosively oxidized the lattice sulfur species, S²⁻ (Daskalaki et al., 2010; Li et al., 2009). This

was because the typical type-II band gap alignment between CdS and TiO₂ in the CdS/TiO₂ hybrid could greatly lower the redox potentials of the transferred electrons and holes by invalidly releasing a fraction of potential energies (Liu et al., 2010). The reduced redox potentials could change the photochemical mechanism and further inhibit its photochemical performance. In comparison, both hole and electron indirect oxidations simultaneously occurred on the TiO₂ to synergistically generate a large number of active oxygen species for pollutant degradation because of the high oxidative potential of the non-transferred holes (Hernández-Alonso et al., 2009; Liu et al., 2010). Lastly, no any sacrificial reagent, e.g., the typical S²⁻/SO₃²⁻ redox mediators (Sapp et al., 2002), was dosed in this study. Thus, CdS/TiO₂ was corroded severely under UV-Vis irradiation in aqueous solution (Daskalaki et al., 2010; Li et al., 2009), while the photocatalytic stability of TiO₂ was much higher than that of the CdS/TiO₂ under the identical conditions, which could also contribute to the higher photocatalytic activity of TiO₂ reference.

In addition to the substantially increased photocatalytic activity, the novel ZnO/CdS/TiO₂ hybrid further had a much better anti-photocorrosion capacity than the traditional CdS/TiO₂ analogue. In the five cyclic Atrazine degradation tests, the ZnO/CdS/TiO₂ exhibited an excellent stability with an average Atrazine removal efficiency of 80 ± 5.0%; in comparison, the CdS/TiO₂ exhibited much poorer stability with a final removal efficiency of only ca. 40% (Fig. 5a). It was noted that the increased photoactivity of the CdS/TiO₂ should be mainly attributed to the gradual exposure of TiO₂, and it finally exhibited a slightly higher activity (48%) than the

pure TiO₂ (40%) due to the synergistic effects between TiO₂ and residual CdS (Daskalaki et al., 2010; Li et al., 2009; Steven et al., 2010).

A quantitative analysis of both Cd and S contents in the two CdS-based hybrids and their treated solutions before and after 5-run cyclic photocatalytic test further validated the above Atrazine degradation results (Fig. 5b and c). The initial Cd contents in the ZnO/CdS/TiO₂ hybrid and the CdS/TiO₂ hybrid were almost identical, 886.0 and 900.0 µg, respectively. However, after 15-h continuous photocatalytic degradation under simulated sunlight irradiation, the Cd contents remaining in the ZnO/CdS/TiO₂ hybrid and in the CdS/TiO₂ hybrid were 845.0 and 48.0 µg, respectively. After 5-run cyclic photocatalytic test, the cumulatively released Cd contents in the treated solutions were 0.24 and 37.6 mg L⁻¹, respectively (Fig. 5b). The released S²⁻ from the two CdS-based hybrids was mainly transformed to SO₄²⁻ at a level of 0.27 and 35.5 mg L⁻¹, respectively (Fig. 5c), due to the strong oxidative photochemical environment. These quantitative results indicate the superior structural, chemical and catalytic stabilities of ZnO/CdS/TiO₂ for photochemical wastewater treatment over the CdS/TiO₂ under the identical conditions.

To take more insights into the anti-photocorrosion performance of the two CdS-based catalysts, the SEM imaging, DRS measurements and XRD patterns were further carried out before and after cyclic degradation tests for Atrazine degradation (Figs. 6, S9 and S10). A drastic morphological change of the CdS/TiO₂ was observed after only two cyclic degradation tests, implying the serious chemical dissolution of CdS under solar irradiation, while the ZnO/CdS/TiO₂ remained intrinsically

unchanged even after five cyclic degradation tests (Fig. S9). Moreover, the used ZnO/CdS/TiO₂ did not exhibit any obvious DRS change after five cyclic tests, suggesting the excellent chemical and photochemical stabilities as well as the anti-photocorrosion capacity (Fig. 6a); in comparison, the used CdS/TiO₂ exhibited an obvious DRS change, and the optical properties of the bottom TiO₂ layer appeared remarkably after only two cyclic tests, implying the substantially damaged exposure of the bottom TiO₂ due to the chemically oxidative decomposition of the upper CdS (Fig. 6b). Also, the XRD results show the middle CdS layer was dominantly remained in the ZnO/CdS/TiO₂ hybrid after five photocatalytic tests (Fig. S10), while the CdS layer was drastically photocorroded in the CdS/TiO₂ hybrid after only two photocatalytic tests under the identical conditions ($\lambda > 300$ nm, in aqueous solution).

All the experimental results from the anti-photocorrosion characterization agree well with the RhB and Atrazine degradation behaviors and the photocurrent response and fluorescence spectra measurements (Figs. 3-5 and S4-6). This provides more direct evidence for the much improved photocatalytic activity and anti-photocorrosion capacity of the ZnO/CdS/TiO₂ hybrid. In this hybrid, the upper ZnO acted as a robust and clean solid sacrificial reagent to capture the corrosive photo-generated holes in the middle CdS. However, the released high-toxicity Cd²⁺ contents, 0.01 ~ 0.09 mg L⁻¹ (Fig. 5b), from the ZnO/CdS/TiO₂ hybrid were still higher than its permission values in drinking water, i.e., World Health Organization (0.003 mg L⁻¹), United States (0.005 mg L⁻¹), European Union (0.005 mg L⁻¹) and China (0.005 mg L⁻¹). Thus, further improvements are needed.

3.3. Mechanism of the ZnO/CdS/TiO₂ hybrid under solar light irradiation

The working principle of the ZnO/CdS/TiO₂ was based on the two junction mechanisms of both CdS/TiO₂ and CdS/ZnO (Fig. S11a and b). First, when the ZnO/CdS/TiO₂ was irradiated by solar light, the UV photons were selectively absorbed by the outer ZnO, while the visible photons passed through the outer ZnO onto the middle CdS and were completely absorbed by the middle CdS (Fig. S3b). Such a selective absorption made the outer ZnO activated by UV (Reaction 1-1) and the middle CdS activated by visible light (Reaction 1-2), while the bottom TiO₂ remained inactivated as no photons were available (Fig. 7). Then, e⁻_{CB} in ZnO with a low reduction activity could directly recombine with h⁺_{VB} in CdS with a low oxidation activity (Reaction 2-1), and e⁻_{CB} with a high reduction activity in CdS were transferred to TiO₂ scaffold (Reaction 2-2) (Fig. 7). Lastly, h⁺_{VB} in ZnO with a high oxidation activity could decompose pollutant (≡C-OH) directly and indirectly via the formation of HO^{*} from H₂O/OH⁻ oxidation due to their sufficiently high oxidative potentials (Reactions 3-5). Simultaneously, e⁻_{CB} in TiO₂ with a high reduction activity could react with oxygen to form active oxygen species (Reactions 6 and 7), which were indirectly responsible for pollutant degradation (Reaction 8). Therefore, both the direct and indirect oxidations occurred synergistically on the ZnO/CdS/TiO₂, and a significantly enhanced photocatalytic activity and anti-photocorrosion performance were achieved (Figs. 3-6, S4-7, S9, S10 and Table 1).

366 In comparison, for the CdS/TiO₂ alone, under solar irradiation, an electron-hole
 367 pair was formed within CdS only (Reactions 1-2), then electrons were transferred to
 368 the conductance band of TiO₂, leaving the holes on the surface and/or valance band of
 369 CdS (Reaction 9) (Fig. S11a).

371 Then, e⁻_{CB} in TiO₂ with a high reduction activity could react with oxygen to form
 372 active oxygen species (Reactions 6 and 7), which were indirectly responsible for
 373 pollutant degradation (Reaction 8). However, h⁺_{VB} in CdS with a low oxidation
 374 activity could not decompose pollutant directly and indirectly via the formation of

HO^{*} from H₂O/OH⁻ oxidation. This was because h⁺_{VB} in CdS could not react with OH⁻ (or H₂O) thermodynamically to produce HO^{*} due to their low oxidation potential (+1.2~1.5 eV) than that of HO^{*}/H₂O (+2.27 eV) (Lin et al., 2009; Wang et al., 2009; Wu et al., 2006). h⁺_{VB} could be readily captured by sacrificial reagents, or corrode CdS when scavenger was absent. Therefore, only the indirect oxidation occurs on the CdS/TiO₂, resulting in its relatively poor photocatalytic activity and anti-photocorrosion capacity.

The mechanism was proposed mainly based on our experimental results and the results reported in references. Two reasons were responsible for the transfer of electrons from the middle CdS to the bottom TiO₂. One was that the more positive CB of the bottom TiO₂ than that of the upper ZnO might thermodynamically make the electrons in the middle CdS be transferred to the bottom TiO₂ more readily (Wang et al., 2001). Another was the more intimate contact between the bottom TiO₂ nanotubes and the middle CdS nanoparticles than that between the upper ZnO nanoparticles and the middle CdS nanoparticles in the ZnO/CdS/TiO₂ hybrid might make the electrons in the middle CdS be transferred to the bottom TiO₂ more readily (Wang et al., 2008). Also, the electron injection efficiency from CdS into ZnO is much less efficient than that from CdS into TiO₂ (Spanhel et al., 1987).

Furthermore, e⁻_{CB} in the outer ZnO was transferred to the middle CdS because of the two reasons. One was the observed excellent anti-photocorrosion performance and good structural, chemical and catalytic stabilities of the middle CdS in the ZnO/CdS/TiO₂ hybrid in the 5-run cyclic degradation test (Figs. 5, 6, S9 and S10).

This observation was unique and contradictory to most of the previously reported results (Tada et al., 2006; Sun et al., 2008; Steven et al., 2010; Zhu et al., 2010; Li et al., 2011; Daskalaki et al., 2014). Another was the well-documented fact that the corrosive photo-generated holes in VB of CdS could be directly and in-situ consumed by the reductive e^-_{CB} from the CB of activated ZnO through a well-known direct Z-scheme charge transfer mechanism (Wang et al., 2009; 2010; 2011).

4. Conclusions

In order to enhance the overall application potential of the well-known CdS/TiO₂ hybrid for refractory pollutants degradation, we propose the direct utilization of e^-_{CB} with a low reductive energy from ZnO as a solid sacrificial reagent to effectively capture h^+_{VB} with a low oxidative energy from CdS. The experimental results demonstrate that this well-designed and accurately-prepared ZnO/CdS/TiO₂ hybrid exhibit a substantially enhanced photocatalytic activity than the typical CdS/TiO₂ analogue in the degradation of the targeted RhB and Atrazine and the treatment of textile wastewater under solar light irradiation, without any additional sacrificial reagents. Moreover, the intrinsic photocorrosion of the typical CdS/TiO₂ hybrid in aqueous solution under solar light irradiation is substantially reduced and its apparent anti-photocorrosion capacity is largely improved. Due to the both much enhanced catalytic activity and stability, this novel ZnO/CdS/TiO₂ hybrid might be of interest and provide a new chance to advance the catalyst for photochemical applications.

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426 **Appendix A. Supplementary material**

427 Supplementary data related to this article can be found online.

428

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Table 1 - Pollutants degradation and textile wastewater treatment kinetic constants on different photocatalysts. Photocatalytic degradation conditions: solution (30 ml artificial or real wastewater), concentration (5 mg L⁻¹ for RhB and Atrazine, 80 mg L⁻¹ TOC for real wastewater), UV-Vis intensity (350 W xenon lamp), effective electrode area (6 cm²), pH (natural), temperature (ca. 20 °C), magnetic stirring rate (500 rpm) and reaction time (2, 3 or 6 h).

Photocatalyst	Pollutant		Textile wastewater	
	RhB ($\times 10^{-2} \text{ min}^{-1}$)	Atrazine ($\times 10^{-2} \text{ min}^{-1}$)	Abs ₄₇₅ ($\times 10^{-2} \text{ min}^{-1}$)	TOC ($\times 10^{-2} \text{ min}^{-1}$)
TiO ₂	0.91	0.33	0.26	0.09
ZnO	/	0.23	/	/
CdS/TiO ₂	0.23	0.002	0.16	0.02
ZnO/CdS	/	0.28	/	/
ZnO/TiO ₂	/	0.34	/	/
ZnO/CdS/TiO ₂	1.78	0.76	0.22	0.18

/: Not determined.

Scheme 1 - Schematic diagram for the preparation of the ZnO/CdS/TiO₂ hybrid.

Figure Captions

- Fig. 1** SEM images of TiO₂ NTs (a and b), CdS NPs/TiO₂ NTs (c and d) and ZnO NPs/CdS NPs/TiO₂ NTs (e and f).
- Fig. 2** STEM images (a-f), EDX spectra (g) and HRTEM image (inset) of the ZnO/CdS/TiO₂.
- Fig. 3** Short-circuit photocurrent response at +0.30 V (versus SCE) (a) and fluorescence intensity at 423.5 nm (b) of the TiO₂, CdS/TiO₂ and ZnO/CdS/TiO₂ under solar light irradiation. Measurement conditions: short-circuit photocurrent response (supporting electrolyte: 30 ml of 0.1 M Na₂SO₄, anodic potential: +0.3 V/SCE, UV-Vis intensity: 350 W xenon lamp, effective electrode area: 6.0 cm², pH: natural, temperature: ca. 20 °C, magnetic stirring rate: 0 rpm and pulse time: 100 s) and fluorescence spectra (supporting electrolyte: 30 ml of 3 mM terephthalic acid, UV-Vis intensity: 350 W xenon lamp, effective electrode area: 6.0 cm², pH: 11.0, temperature: ca. 20 °C, magnetic stirring rate: 500 rpm and reaction time: 20 min).
- Fig. 4** Photocatalytic degradation efficiency and absolute removal quantity of RhB (a and b), Atrazine (c and d) and textile wastewater (e and f) by different photocatalysts. Photocatalytic degradation conditions: solution (30 ml artificial or real wastewater), concentration (5 mg L⁻¹ for RhB and Atrazine, 80 mg L⁻¹ TOC for real wastewater), UV-Vis intensity (350 W xenon lamp), effective electrode area (6 cm²), pH (natural), temperature (ca. 20 °C), magnetic stirring rate (500 rpm) and reaction time (2, 3 or 6 h).
- Fig. 5** Cyclic degradation of lowly-concentrated Atrazine on the ZnO/CdS/TiO₂ and the CdS/TiO₂ with and without sacrificial reagents (0.1 M Na₂S + 0.01 M Na₂SO₃) (a) and the cumulative concentrations of released Cd²⁺ (b) and SO₄²⁻ oxidized from S²⁻ (c) during five cyclic usages. Photocatalytic degradation conditions: solution (30 ml artificial wastewater), concentration (5 mg L⁻¹ Atrazine), UV-Vis intensity (350 W xenon lamp), effective electrode area (6 cm²), pH (natural), temperature (ca. 20 °C), magnetic stirring rate (500 rpm) and reaction time (3 h).
- Fig. 6** DRS evolution of CdS/TiO₂ (a) and ZnO/CdS/TiO₂ (b) before and after two or five cyclic usages. Photocatalytic degradation conditions: solution (30 ml artificial wastewater), concentration (5 mg L⁻¹ Atrazine), UV-Vis intensity (350 W xenon lamp), effective electrode area (6 cm²), pH (natural), temperature (ca. 20 °C), magnetic stirring rate (500 rpm) and reaction time (3 h).
- Fig. 7** Working principles of the ZnO/CdS/TiO₂ hybrid under solar light irradiation.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7