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Perfect inhibition of CdS photocorrosion by graphene sheltering engineering on TiO$_2$ nanotube array for highly stable photocatalytic activity

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ABSTRACT

An artful graphene sheltering engineering onto TiO$_2$ nanotube array for perfect inhibition of CdS photocorrosion (RGO/CdS–TiO$_2$ NT) has been developed by one-step electrodeposition method. The CdS photocorrosion driven by both holes and radicals has been systematically investigated and identified. The RGO layer provides a perfect protection to CdS through (i) blocking the attack of active species especially •OH radicals and (ii) offering a closed electron-rich microenvironment where the stored electrons RGO(e$^-$) not only reduce intermediate species S•$^-$ to S$_2^{2-}$ but also compensate the valence band of CdS for its loss of electrons to alleviate CdS photocorrosion from oxidation by holes. The photocatalyst exhibits extremely high stability. RGO/CdS–TiO$_2$ NT shows high visible-light photocatalytic activity for the degradations of organic dye methylene blue (MB), industrial chemical p-nitrophenol (PNP) and herbicide 2,4–dichlorophenoxyacetic acid (2,4–D). This work provides a new insight into the protection of photosensitive semiconductors from photocorrosion.
1. Introduction

As a visible-light-driven photocatalyst, cadmium sulfide (CdS) has been extensively investigated. However, the core problem is still related to its photocorrosion. It greatly obstructs its practical application due to loss of activity and cadmium leakage pollution. Therefore, many efforts have been done to restrain the photochemical instability of CdS by introducing sacrificial reagents [1], coupling CdS with wide-bandgap semiconductor [2,3] or oxidation co-catalyst [4], and constructing a core-shell heterostructure [5,6]. Commonly, people have charged the photocorrosion to the factor that the sulfide ion is highly prone to oxidation by photogenerated holes [7]. In fact, other active species, especially hydroxyl radicals (•OH), may be also involved in the oxidation of sulfur [8]. However, these factors are neglected in the theoretical analysis. These active species are strong enough to oxidize sulfide ion and the exposure of CdS to these active species is still fatal [9]. It is therefore absolutely vital to develop suitable interface engineering methods to satisfy the inhibition of CdS photocorrosion from the oxidation by both photogenerated holes and active radicals. Constructing a shield between CdS and active radicals seems a feasible way to inhibiting the photocorrosion from the attack of active radicals. However, the shield may not only reduce the inherent optical absorption of CdS but also block the transfer
of photogenerated charges to the interface between photocatalyst and reaction medium. Therefore, developing a suitable sheltering engineering between CdS and shield is very challenging.

We demonstrate herein one-step co-electrodeposition of CdS nanoparticles and reduced graphene oxide (RGO) film onto TiO$_2$ nanotube array (RGO/CdS–TiO$_2$ NT) where CdS nanoparticles are well blanketed with a thin layer of RGO film (Scheme 1). Although graphene has been used in anti-photocorrosion of photosensitive semiconductors, the synthetical affection of active species including radicals on photocorrosion are neglected [10-12]. The factors on photocorrosion of CdS have been herein systematically investigated and CdS photocorrosion driven by both h$^+$ and •OH radicals has been identified. The RGO sheltering engineering effectively inhibits the photocorrosion from hole and active radical-induced oxidation. The photocatalytic performance of RGO/CdS–TiO$_2$ NT is evaluated by the photocatalytic degradation of typical organic pollutants.

2. Experimental

2.1. Materials

Titanium foil (99.8%, 250 μm thickness) was purchased from Aldrich (Milwaukee, WI), graphite powder about 50 μm was purchased from Shanghai
Carbon Co., Ltd., and other reagents are of analytical grade and used as received. Deionized water was used for preparation of all aqueous solutions.

2.2. Fabrication of RGO/CdS–TiO$_2$ NT

The TiO$_2$ NT was prepared by the method of anode oxidation. Typically, prior to anodization, titanium foils were ultrasonically cleaned in acetone and ethanol, respectively. The anodizing cell was a two-electrode system using platinum as the counter electrode. The cleaned foil was anodized at 15 V in an electrolyte containing 0.1 M NaF and 0.5 M NaHSO$_4$ at room temperature for 3 h. The efficient electrode area is 4 cm $\times$ 1 cm. The as-anodized TiO$_2$ NT was sintered in oxygen atmosphere at 500ºC for 3 h with heating and cooling rates of 2ºC·min$^{-1}$ to obtain photoactive anatase phase. Reduced graphene oxide (RGO) and CdS were co-deposited onto TiO$_2$ NT by cyclic voltammetric electrodeposition. Typically, the as-prepared graphite oxide from a modified Hummers method was ultrasonically exfoliated in 0.1 M citrate buffer solution of pH 4.0 for 3 h to form a homogeneous electrolyte A (graphene oxide, GO). CdCl$_2$ and Na$_2$S$_2$O$_3$ were dissolved in a 0.1 M citrate buffer solution of pH 4.0 to form electrolyte B. The precursor electrolyte was prepared by mixing A and electrolyte B with a concentration of 0.3 mg·mL$^{-1}$, 0.06 M and 0.1 M for GO, CdCl$_2$ and Na$_2$S$_2$O$_3$, respectively. The cyclic voltammetric reduction was performed in the
precursor electrolyte, using a three-electrode configuration with the annealed TiO$_2$ NT/Ti sheet as the working electrode, a Pt foil as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode on a CHI 660D electrochemical workstation (Chenhua, Shanghai, China). The scan was from −1.5 to 0.6 V with a rate of 25 mV·s$^{-1}$. After deposition, the working electrode was washed with deionized water, getting RGO/CdS–TiO$_2$ NT hybrid. As a control, RGO–TiO$_2$ NT was prepared by only using electrolyte A (0.3 mg·mL$^{-1}$ GO) with a scan rate of 50 mV s$^{-1}$ from −1.5 to 1 V and CdS–TiO$_2$ NT was prepared by using electrolyte B (0.06 M CdCl$_2$ and 0.1 M Na$_2$S$_2$O$_3$) with a scan rate of 25 mV s$^{-1}$ from −1.5 to 0.6 V. The loading of graphene or CdS was controlled by the number of potential cycles.

2.3. Structure characterization

The morphologies of the hybrids were characterized by a field emission scanning electron microscope (FESEM, Hitachi S−4800, Japan) and a transmission electron microscope (TEM, JEOL JEM-2100F, Japan). Energy dispersive X–ray (EDX) spectrometer fitted to the electron microscope was applied for elemental analysis. The crystal phases of the hybrids were determined by an X–ray diffractometer with Cu–K$_\alpha$ radiation (XRD, M21X, MAC Science Ltd., Japan). The binding energies of S, Cd and C of the composites were determined by X-ray photoelectron spectroscopy

2.4. Property measurement

The UV–vis diffuse reflectance spectra (DRS) were recorded with a UV–visible spectrophotometer (Cary 300, USA) equipped with an integrating sphere with the radius of 150 mm. The photocurrents were recorded on the CHI 660D electrochemical workstation by using a three–electrode configuration with bare TiO₂ NT or the modified TiO₂ NT/Ti sheet as the working electrode, Pt foil as the counter electrode and an SCE as the reference electrode in 0.5 M Na₂SO₄ solution. A 500 W xenon arc lamp with a 420 nm optical filter (CHF–XQ–500W, Beijing Changtuo Co., Ltd.) served as visible light source with the photon flux of 100 mW·cm⁻² measured by NOVA Oriel 70260 with a thermodetector. The temperature-programmed oxidation (TPO) experiments were carried out on AutoChem II 2920 (Micromeritics, USA) at a ramping rate of 10 K/min in mixed helium and oxygen flow.

2.5. Evaluation of photocatalytic performance

Three typical organic pollutants were chosen in terms of quantities used and potential environmental impacts: Organic dye methylene blue (MB), industrial chemical p-nitrophenol (PNP) and herbicide 2,4–dichlorophenoxyacetic acid (2,4–D).
The photocatalytic degradation experiments were carried out under stirring in a quartz beaker containing 50 mL 10 mg·L⁻¹ MB, PNP or 2,4-D. The photocatalyst samples with a total active area of 8.0 cm² were vertically placed in the quartz beaker. A 500 W xenon arc lamp with a UV-cutoff filter ≥ 420 nm and the photon flux of 100 mW·cm⁻² (CHF–XQ–500W, Beijing Changtuo Co. Ltd., China) served as a visible light source. Before irradiation, the system was maintained in the dark for 0.5 h to reach complete adsorption–desorption equilibrium, so that the decreased concentration of pollutants with irradiation time can fully reflect the photocatalytic activities of the catalysts. The real-time concentration of pollutants was determined by UV–vis spectrophotometry at the characteristic absorbance of 664 nm for MB, 317 nm for PNP or 227 nm for 2,4-D in a spectrophotometer (Cary 300, Varian, USA). The accurate concentrations of pollutants were determined by high–performance liquid chromatography (HPLC, Agilent 1100HPLC, USA).

2.6. Photocorrosion test

The photocorrosion on CdS–TiO₂ NT and RGO/CdS–TiO₂ NT under visible light irradiation was evaluated by the amount of Cd leakage which was determined by an inductively coupled plasma emission spectroscopy (ICP, 5300DV, PerkinElmer, USA). Additionally, the structures and morphologies of CdS–TiO₂ NT and
RGO/CdS–TiO₂ NT during photocorrosion test were determined by FESEM. In order to investigate the effect of active species on photocorrosion, herein, iBuOH was used to eliminate •OH radicals, EDTA-2Na was used to remove h⁺, and N₂ was injected to clear out oxygen. The •OH radicals produced on CdS–TiO₂ NT and RGO/CdS–TiO₂ NT under visible-light irradiation were measured by the fluorescence method using terephthalic acid (TA) as a probe molecule (•OH + TA → TAOH). The fluorescence signals of TAOH were measured on a fluorescence spectrophotometer (Hitachi F-7000, Japan). The photoluminescence (PL) intensity of TAOH at 425 nm excited by 315 nm light was measured every 10 minutes.

3. Results and discussion

3.1. Characterization

Fig. 1 shows the SEM images of bare TiO₂ NT, CdS–TiO₂ NT, RGO–TiO₂ NT, and RGO/CdS(x)–TiO₂ NT, where x is the number of deposition cycle. Bare TiO₂ NT possesses a uniform tubular structure in pore size of 90 nm (Fig. 1a). The size of CdS nanoparticles in CdS–TiO₂ NT is about 50 nm (Fig. 1b). The RGO film layer forms in RGO–TiO₂ NT (Fig. 1c). The amount of CdS nanoparticles in RGO/CdS–TiO₂ NT increases with increasing deposition cycle but the size of CdS nanoparticles keep 30-50 nm (Fig. 1d-f). The RGO layer also becomes thicker with increasing potential
cycle. It is worthwhile to note that the CdS nanoparticles are compactly covered with RGO film layer. The vertical view of TEM image of RGO/CdS(5)–TiO2 NT clearly displays the spherical morphology of CdS nanoparticles in size of 30-50 nm (Fig. 1g). The energy dispersive X-ray (EDX) spectroscopy analysis (Fig. 1h) exhibits the characteristic peaks of C, O, S, Ti and Cd with the atom contents of 2.53% C, 0.2% Cd and 0.19% S. The nearly 1:1 molar ratio of Cd to S indicates the existence of CdS. Based on the photocurrent measurement of RGO/CdS(x)–TiO2 NT (x= 5, 7, 10), RGO/CdS(5)–TiO2 NT shows the highest photocurrent density (Fig. 2). This could be explained by the facts: 1) the shadowing effect of the thicker RGO layer probably reduces the transmission of light to semiconductor, resulting in less photogenerated electrons; 2) the aggregation of more CdS nanoparticles is unfavorable for the transfer and separation of photoinduced carriers [13, 14]. Unless otherwise specified, RGO/CdS–TiO2 NT only represents RGO/CdS(5)–TiO2 NT.

XRD characterization is an effective method to determine the crystal phase of materials. The XRD patterns in Fig. 3A reveal that all the samples display diffraction peaks indicative of anatase TiO2 (JCPDS 21-1272) and wurtzite CdS (JCPDS 41-1049). Compared with other crystal phases, these crystal phases have been found to favor higher photocatalytic activity [15]. However, there is no characteristic peak of
C in the XRD pattern of RGO/CdS–TiO$_2$ NT, probably due to the amorphous state of graphene or its low crystal content resulting in low diffraction intensity [16].

Temperature-programmed oxidation (TPO) measurement can evaluate the chemical stability of materials. Fig. 3B shows the TPO curves of CdS, CdS–TiO$_2$ NT and RGO/CdS–TiO$_2$ NT. It displays that the oxidation of S$^{2-}$ in CdS–TiO$_2$ NT occurs at 845K slightly higher than that in pure CdS (834K). In contrast, RGO/CdS–TiO$_2$ NT exhibits a higher oxidation temperature around 906K. The high oxidation temperature for RGO/CdS–TiO$_2$ NT reveals a strong interaction between CdS and RGO, inhibiting the oxidation of CdS.

The results of XPS spectra are shown in Fig. 4. Compared with the binding energies (BEs) of both S 2p and Cd 3d in pure CdS, those in CdS-TiO$_2$ NT increase slightly while those in RGO/CdS–TiO$_2$ NT increase significantly (Fig. 4B and C). The shift of binding energies in RGO/CdS–TiO$_2$ NT can be attributed to the strong interactions between CdS nanoparticles and RGO sheets [17,18]. The results are well consistent with the results of TPO analysis (Fig. 3B). The XPS spectrum of C 1s reveals that the peaks of C-O at 286.5 eV and C=O at 288.6 eV in GO (graphene oxide) nearly disappear after electrodeposition of GO onto TiO$_2$ NT (Fig. 4D), implying that the oxygen-containing functional groups in GO have been reduced.
during electrochemical deposition process, resulting in RGO (reduce graphene oxide) [19]. When simultaneously depositing CdS and RGO onto TiO$_2$ NT, the peak at 288.6 eV increases again due to the formation of S-C bond resulting in higher binding energy of C 1s [20] which further confirms the strong interaction between RGO and CdS.

3.2. Photoelectrochemical property

The UV-vis diffuse reflectance spectroscopy (DRS) is commonly employed to characterize the absorption property of the materials. Among the samples, RGO/CdS–TiO$_2$ NT exhibits the strongest visible–light absorption attributed to the combined action of CdS and RGO (Fig. 5A). Obviously, the coating of transparent RGO layer does not impede the inherent optical absorption of CdS. The boosted absorption of light for RGO/CdS–TiO$_2$ NT in the visible light region can enhance the photoexcitation efficiency which is approved by photocurrent response where RGO/CdS–TiO$_2$ NT displays the highest photocurrent density (Fig. 5B). The high photocurrent density of RGO/CdS–TiO$_2$ NT should attribute to the fact that graphene has a strong ability in capturing and transporting photogenerated electrons from semiconductor [21]. The intimate contact between RGO and CdS is also crucial for the charge transport from CdS to RGO. It is worthwhile to note that under irradiation,
the photocurrent of CdS–TiO₂ NT gradually decreases while that of RGO/CdS–TiO₂ NT shows a stable trend. This strongly indicates that the RGO shield would highly strengthens the resistance to CdS photocorrosion.

3.3. Photocatalytic performance

Cadmium sulfide, one of the most technologically important semiconductor materials, has applications in a wide range of fields including photovoltaics [17], optoelectronics [18], chemical sensors [22], and photocatalysis [23]. As one of its application fields, the photocatalytic performances of the photocatalysts are evaluated for the degradation of organic dye methylene blue (MB), industrial chemical p-nitrophenol (PNP) and herbicide 2,4–dichlorophenoxyacetic acid (2,4–D). For the selected pollutants, conventional wastewater treatment methods are gradually becoming inadequate to meet the requirements of a higher environmental quality [24].

Adsorptivity of catalysts towards pollutant molecules is a crucial factor required for efficient degradation. For convenient viewing of color change, MB was chosen as model pollutant for the adsorption experiment. All graphene modified TiO₂ NT hybrids, including RGO–TiO₂ NT and RGO/CdS–TiO₂ NT show higher adsorption amount of MB than bare TiO₂ NT and CdS–TiO₂ NT (Fig. 6A), due to the high
specific surface area of graphene nanosheets and their good affinity toward organic molecules through hydrophobic or specific $\pi$--$\pi$ interactions [25].

The visible light photocatalytic degradation efficiencies of MB over the hybrids are shown in Fig. 6B. Obviously, MB is very stable in the absence of a photocatalyst (direct photolysis). After 100–min irradiation, CdS–TiO$_2$ NT and RGO/CdS–TiO$_2$ NT show 83% and nearly 100% decomposition efficiency of MB, respectively. In contrast, the photocatalysts without CdS (bare TiO$_2$ NT and RGO–TiO$_2$ NT) exhibit low decomposition efficiency of MB due to their poor absorption in visible light region. The degradation efficiencies of MB over the photocatalysts with RGO are higher than those over the photocatalysts without RGO (RGO–TiO$_2$ NT vs bare TiO$_2$ NT and RGO/CdS–TiO$_2$ NT vs CdS–TiO$_2$ NT), which is presumably benefited from the high charge separation (Fig. 5B) and adsorption capacity of RGO (Fig. 6A). Undoubtedly, the highest photocatalytic degradation efficiency of MB over RGO/CdS–TiO$_2$ NT should be attributed to the synergetic effect between RGO and CdS.

Kinetic constant can clearly reflect the decomposition rate of pollutants over photocatalysts. High decomposition rate is very significant for practical applications. The decomposition kinetics of MB under visible light irradiation follows essentially a first order kinetics, with classical equation $\ln(C/C_0) = k \cdot t$, where $k$ is pseudo–first rate
kinetic constant and \( t \) is time (Fig. 6C). It demonstrates that under visible light irradiation the MB photodegradation rate over RGO/CdS–TiO\(_2\) NT (\( k = 0.03968 \text{ min}^{-1} \)) is about 165, 104, and 1.7 times that over bare TiO\(_2\) NT (\( k = 0.00024 \text{ min}^{-1} \)), RGO–TiO\(_2\) NT (\( k = 0.00038 \text{ min}^{-1} \)), and CdS–TiO\(_2\) NT (\( k = 0.02279 \text{ min}^{-1} \)), respectively. The results clearly show that RGO/CdS–TiO\(_2\) NT is a highly effective visible light photocatalyst.

Good longevity is very important for practical application of photocatalysts. CdS has been widely used as photoelectric material while its poor stability blocks its further application. Herein, the longevities of the photocatalysts are investigated by recycling the photocatalysts for MB photocatalytic degradation under visible-light irradiation. As shown in Fig. 6D, CdS–TiO\(_2\) NT almost completely loses photocatalytic activity after 2000-min visible-light irradiation, which should be mainly caused by serious photocorrosion of CdS. On the contrary, after even 3600-min visible-light irradiation, there is only an insignificant loss in the photocatalytic activity of RGO/CdS–TiO\(_2\) NT, which might be partly caused by loss of CdS during each round of collection and rinsing. The excellent recycling performance and longevity of RGO/CdS–TiO\(_2\) NT makes it a qualified candidate in practical applications.
In order to furthermore evaluate the photocatalytic property of RGO/CdS–TiO$_2$ NT photocatalyst, the photocatalytic degradations of PNP and 2,4-D over RGO/CdS–TiO$_2$ NT under visible-light irradiation are investigated (Fig. 7). After 0.5 h immersion in the dark to reach complete adsorption–desorption equilibrium, about 10% PNP or 2,4-D are adsorbed onto RGO/CdS–TiO$_2$ NT. Although PNP and 2,4-D are intractable due to their highly chemical stability, the photocatalytic decomposition efficiencies of them over RGO/CdS–TiO$_2$ NT still achieve nearly 100% after 140-min visible light irradiation.

3.4. Photocatalytic mechanisms

The photocatalytic mechanism of RGO/CdS–TiO$_2$ NT is shown as Scheme 2. Under visible light irradiation, the electrons of CdS are excited from the valence band (VB) to the conduction band (CB). The CB electrons of CdS can transfer to the CB of TiO$_2$ and then to RGO. Meanwhile, the CB electrons of CdS can directly transfer to RGO. Thus, the exciton recombination is highly suppressed in the ternary RGO/CdS–TiO$_2$ NT photocatalyst. During the photocatalysis process, the accumulated electrons in RGO will react with surface adsorbed oxygen molecules or dissolved oxygen in water to form O$_2$•$^-$ superoxide ion radical. The O$_2$•$^-$ superoxide ion radicals can directly attack organics or combine with protons (H$^+$) to generate
oxidative H$_2$O$_2$ and hydroxyl radicals (•OH). One the other hand, the holes may react with OH$^-$ ions (or H$_2$O) to form •OH free radicals. The thus produced strongly oxidative •OH radicals along with the generated holes will attack organic pollutant molecules.

3.5. Photocorrosion tests

For photocorrosion tests, tBuOH was used to eliminate •OH radicals, EDTA-2Na was used to remove h$^+$, and N$_2$ was injected to clear out oxygen which could capture photogenerated electrons to form •OH radicals. The hydroxyl radicals (•OH) produced from CdS–TiO$_2$ NT and RGO/CdS–TiO$_2$ NT under visible-light irradiation were measured by the fluorescence method using terephthalic acid (TA) as a probe molecule (•OH + TA → TAOH) [26]. In the absence of any scavengers, the PL intensities of TAOH at 425 nm on both CdS–TiO$_2$ NT and RGO/CdS–TiO$_2$ NT steadily increase with prolonging irradiation time, revealing that more and more •OH radicals produce with increasing irradiation time (Fig. 8).

The results of photocorrosion tests on CdS–TiO$_2$ NT and RGO/CdS–TiO$_2$ NT under visible light irradiation are shown in Fig. 9. After 2000-min visible light irradiation in the presence of EDTA-2Na and N$_2$ without formation of h$^+$ and •OH radicals, both CdS–TiO$_2$ NT and RGO/CdS–TiO$_2$ NT keep intact structures and
morphologies (Fig. 9a1 and b1), accompanying with no leaching of Cd\(^{2+}\) (Fig. 9 c1). After 2000-min irradiation in the presence of only EDTA-2Na used to remove h\(^+\), the photocorrosion of CdS–TiO\(_2\) NT occurs, where the CdS particles become smaller and even disappear with significant leaching of Cd\(^{2+}\) (Fig. 9a2 and c2). In contrast, the CdS in RGO/CdS–TiO\(_2\) NT is still stable with undetectable leaching of Cd\(^{2+}\) (Fig. 9b2 and c2). Undoubtedly, the S\(^{2-}\) in CdS–TiO\(_2\) NT is highly prone to oxidation by photogenerated •OH radicals while the S\(^{2-}\) in RGO/CdS–TiO\(_2\) NT survives due to the safeguard of RGO shield. After 2000-min irradiation in the presence of only tBuOH used to remove •OH radicals, the photocorrosion of CdS–TiO\(_2\) NT also occurs with obvious leaching of Cd\(^{2+}\) due to the oxidation of h\(^+\) (Fig. 9a3 and c3) while RGO/CdS–TiO\(_2\) NT maintains intact structure and morphology with negligible leaching of Cd\(^{2+}\) (Fig. 9b3 and c3). Thus it can be seen that the RGO shield can effectively restrain the h\(^+\)-induced photocorrosion of CdS in RGO/CdS–TiO\(_2\) NT. After 2000-min irradiation in the absence of scavengers and N\(_2\), the photocorrosion significantly occurs on CdS–TiO\(_2\) NT leaving tiny particles with serious leaching of Cd\(^{2+}\) (Fig. 9a4 and c4) due to the double attack from h\(^+\) and •OH radicals while the CdS nanoparticles in RGO/CdS–TiO\(_2\) NT are still tightly sheltered by RGO blanket with undetectable Cd\(^{2+}\) leakage (Fig. 9b4 and c4).
The results clearly present that both h+ and •OH radicals but not only h+ are responsible for photocorrosion of CdS and the RGO shield effectively inhibits the photocorrosion of CdS in RGO/CdS–TiO2 NT. The photocorrosion inhibition mechanism is schematically illustrated as Scheme 3. The RGO layer not only significantly inhibits the photocorrosion of CdS from oxidation by active species especially •OH radicals through blocking the contact between these active species and CdS nanoparticles, but also provides a closed electron-rich microenvironment where the stored electrons RGO(e−) can react with intermediate species S•− to regenerate S2− [27]. Furthermore, the dissolution of CdS sheltered in a closed RGO blanket can be effectively restrained whereas the unbridled diffusion of S2− into solution accelerates the dissolution of CdS in CdS–TiO2 NT. In terms of the ambipolar charge transport [28] and heterogeneous electron transfer in graphene [29,30], the stored electrons RGO(e−) serve as electron donors which can compensate the valence band of CdS for its loss of electrons, effectively alleviating the photocorrosion of CdS from oxidation by holes.

4. Conclusions

Perfect inhibition of CdS photocorrosion has been successfully achieved by RGO sheltering engineering built from one-step electrodeposition. The photocorrosion of
CdS by the oxidation of both h+ and •OH radicals has been identified. The synergistic effect among CdS, RGO and TiO2 NT guarantees excellent photocatalytic activity and photochemical stability of RGO/CdS–TiO2 NT photocatalyst. The present result is therefore very encouraging and is expected to be a new strategy to enhance the photochemical stability of photosensitive semiconductors. Better understanding such high photochemical stability would give further hints for the design and assembly of more efficient photocatalytic systems.

Acknowledgments

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References


Captions and legends for Figures and Schemes

Fig. 1. SEM images of: (a) bare TiO$_2$ NT, (b) CdS–TiO$_2$ NT, (c) RGO–TiO$_2$ NT, (d) RGO/CdS$_{5}$–TiO$_2$ NT, (e) RGO/CdS$_{7}$–TiO$_2$ NT, and (f) RGO/CdS$_{10}$–TiO$_2$ NT. (g) TEM image of RGO/CdS$_{5}$–TiO$_2$ NT and (h) EDX of RGO/CdS$_{5}$–TiO$_2$ NT.

Fig. 2. Photocurrent responses of RGO/CdS–TiO$_2$ NT photocatalysts from different deposition cycles under UV-vis irradiation.

Fig. 3. XRD pattern of bare TiO$_2$ NT, CdS–TiO$_2$ NT and RGO/CdS–TiO$_2$ NT (A) and TPO profiles of CdS (1), CdS–TiO$_2$ NT (2), and RGO/CdS–TiO$_2$ NT (3) (B).

Fig. 4. Full XPS spectra (A); high resolution XPS spectra of S 2p (B) and Cd 3d (C): pure CdS (a), CdS–TiO$_2$ NT (b) and RGO/CdS–TiO$_2$ NT (c); high resolution XPS spectrum of C 1s (D): GO (a), RGO–TiO$_2$ NT (b) and RGO/CdS–TiO$_2$ NT (c).

Fig. 5. Diffuse reflectance UV-vis spectra of the photocatalysts under UV-vis irradiation (A) and their photocurrent responses (B).

Fig. 6. Adsorption of MB over different photocatalysts (The initial concentration of MB is 1 mg.L$^{-1}$) (A), photocatalytic degradation of MB over different photocatalysts under visible light irradiation (B), corresponding variation of ln(C$_0$/C) with MB degradation time (C), and photocatalytic stability of the photocatalysts on MB photocatalytic removal under visible-light irradiation (D).
**Fig. 7.** Photocatalytic degradation of PNP (A) or 2,4-D (B) over RGO/CdS–TiO$_2$ NT under visible light irradiation and the inset curves are the corresponding UV-vis absorbance variation of PNP or 2,4-D with degradation time.

**Fig. 8.** Time-dependent fluorescence emission of TAOH formed by the reaction of TA with •OH radicals generated by the photocatalysts under visible-light irradiation.

**Fig. 9.** SEM images of CdS–TiO$_2$ NT (a1-4) and RGO/CdS–TiO$_2$ NT (b1-4) after 2000-min visible light irradiation: in the presence of EDTA-2Na and N$_2$ (a1 and b1), in the presence of only EDTA-2Na (a2 and b2), in the presence of only $t$BuOH (a3 and b3), and in the absence of scavenger and N$_2$ (a4 and b4). The corresponding curves of irradiation time-dependent Cd concentration in solution on CdS–TiO$_2$ NT (Black line) and RGO/CdS–TiO$_2$ NT (Red line) (c1-c4).

**Scheme 1.** Scheme of RGO/CdS–TiO$_2$ NT structure.

**Scheme 2.** Photocatalytic mechanism of RGO/CdS–TiO$_2$ NT.

**Scheme 3.** Schematic diagram of photocorrosion inhibition mechanism.
Fig. 1
Fig. 2

![Graph showing photocurrent density versus time for different samples. The x-axis represents time in seconds (0 to 250), and the y-axis represents photocurrent density in mA cm$^{-2}$. The graph compares the performance of RGO/CdS(5)-TiO$_2$ NT, RGO/CdS(7)-TiO$_2$ NT, RGO/CdS(10)-TiO$_2$ NT, and bare TiO$_2$ NT. Light on and light off periods are indicated for each sample. The legend shows the different sample types.](image-url)
Fig. 3

(A) anatase TiO$_2$ W: wurtzite CdS T: Ti substrate RGO/CdS-TiO$_2$ NT

(B) 906 K 845 K 834 K

TCD Signal / a. u. 700 800 900 1000 1100 T / K

2-Theta (degree) 25 30 35 40 45 50 55 60 65 70 75
Fig. 4

(A) Cd 3d
(B) S 2p
(C) C 1s
(D) Cd 3d

Intensity / a.u.
Binding Energy / eV

Intensity / a.u.
Binding Energy / eV
Fig. 5

(A) Absorbance / a.u.

Wavelength / nm

(B) J / mA cm$^{-2}$

$t / s$

on

off
Fig. 6

(A) Remaining MB (mgL⁻¹) vs. Catalyst

(B) Absorption

(C) ln(\(c_0/c\)) vs. t / min

(D) MB removal efficiency (%) vs. t / min
Fig. 7

(A) Absorbance (a.u.)

(B) Absorbance (a.u.)
Fig. 8

(a) TAOH on CdS-TiO$_2$ NT

(b) TAOH on RGO/CdS-TiO$_2$ NT
Fig. 9
Scheme 1

Scheme 2

Scheme 3