Fabrication of TiO$_2$/Fe$_2$O$_3$/CdS systems: effects of Fe$_2$O$_3$ and CdS content on superior photocatalytic activity

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A heterostructured material of CdS and Fe$_2$O$_3$ nanoparticle-modified TiO$_2$ nanotube array (NTA) photoelectrode (TiO$_2$/Fe$_2$O$_3$/CdS) is reported in this work. TiO$_2$/Fe$_2$O$_3$ was prepared by annealing TiO$_2$ NTAs pre-loaded with Fe(OH)$_3$, which was uniformly clung to TiO$_2$ NTAs using sequential chemical bath deposition (S-CBD). Subsequently, CdS nanoparticles were deposited on TiO$_2$/Fe$_2$O$_3$ using the successive ion layer adsorption and reaction (SILAR) technique. Three-dimensional (3D) TiO$_2$/Fe$_2$O$_3$/CdS samples generated a photocurrent of approximately 4.92 mA cm$^{-2}$, with a photoconversion efficiency of 4.36%, which is more than 20 times higher than that of bare TiO$_2$ NTAs (0.22%) and 6 times that of TiO$_2$/Fe$_2$O$_3$ (0.71%). The photocatalytic activity was evaluated by the degradation of p-nitrophenol (PNP) under visible light (λ > 420 nm). The TiO$_2$/Fe$_2$O$_3$/CdS exhibited the best photocatalytic activity among all samples. Almost all PNP was degraded by TiO$_2$/Fe$_2$O$_3$/CdS within 120 min. The enhancement of photocatalytic activity could be attributed to the promoted photo-induced electron and hole separation and migration on the basis of photoluminescence spectra, photocurrent measurements, and open-circuit photovoltage responses. In addition, the newly synthesized TiO$_2$/Fe$_2$O$_3$/CdS can maintain high photocatalytic efficiency for five reuse cycles. Our findings provide a new idea for the low cost synthesis of high performance photocatalysts for the photodegradation of organic pollutants in aqueous solution.

1. Introduction

TiO$_2$ is very attractive due to its fascinating features such as plentiful polymorphs, good chemical and thermal stability, and excellent electronic and optical properties. TiO$_2$ nanotubes have a larger specific surface area and exchange capacity, as well as higher surface energy and extremely strong adsorption capacity compared with other TiO$_2$ nanomaterials. Furthermore, the conductive substrate of Ti is closely connected with the highly ordered porous nanotube, which accelerates the separation of photogenerated charges and inhibits their recombination, so the photoelectric efficiency is improved. However, TiO$_2$ is active only under near-ultraviolet irradiation, only around 4% of the incident solar spectrum energy, due to its wide band gap energy of 3.0–3.2 eV.$^{15}$

Numerous attempts were made to extend the light absorption of TiO$_2$ to the visible light range, which accounts for around 48% of the incident solar energy.$^6$ Fe$_2$O$_3$ is considered to be one of the best co-catalyst candidates due to its appropriate band gap ($E_g$ ~ 2.2 eV) for solar light harvesting, good photochemical stability, earth abundance, nontoxicity and low cost.$^7$ For example, Kuang et al.$^7$ reported the fabrication, characterization and photoelectrochemical properties of Fe$_2$O$_3$ modified TiO$_2$ nanotube arrays. Moniz et al.$^8$ demonstrated that the decoration of Fe$_2$O$_3$ nanoclusters on TiO$_2$ leads to better charge separation and enhanced photocatalytic activity. Xia et al.$^9$ prepared novel Fe$_2$O$_3$@TiO$_2$ core/shell nanocomposites with improved photocatalytic activity in the visible light region. X. Lv et al.$^{10}$ designed Fe$_2$O$_3$@TiO$_2$ nanotube composite anodes for lithium-ion batteries. Sun et al.$^{11}$ demonstrated the effect of surface Fe$_2$O$_3$ clusters on the photocatalytic activity of TiO$_2$ for phenol degradation in water. Yao et al.$^{12}$ proved that Fe$_2$O$_3$ nanothorns sensitized two-dimensional TiO$_2$ nanosheets with highly efficient solar energy conversion. Cao et al.$^{13}$ synthesized Fe$_2$O$_3$–B$_2$TiO$_5$ superstructures with highly promoted photocatalytic activity and recyclability.

Previous studies have shown that co-sensitizing TiO$_2$ with different nanocrystals such as CdS/ZnIn$_2$S$_4$, CdTe/Mn–CdS, CdS–Mn/MoS$_2$/CdTe$_3$, CdS/CuInS$_2$/Au, Mn–CdS/MoS$_2$, and CdS-based photocatalysts$^{16–18}$ can extend the light absorption to the infrared range, and more importantly align the energy bands of the semiconductor. In summary, combining TiO$_2$ with Fe$_2$O$_3$ and CdS semiconductors could largely improve the photocatalytic activity of the co-sensitized electrode, as the energy
levels of Fe₂O₃ (bandgap ~2.2 eV), CdS (~2.4 eV), and TiO₂ (3.0–3.2 eV) are well suitable to one another, which benefits the separation of e⁻–h⁺ pairs.

Herein, we fabricated TiO₂/Fe₂O₃/CdS ternary heterostructures using a facile S-CBD method coupled with SILAR (Fig. 1). So far, to our knowledge, Ruiyang Yin et al. demonstrated a CdS/a-Fe₂O₃/TiO₂ nanorod array for efficient photocatalytic (PEC) water oxidation that exhibits an improved photocurrent density of 0.62 mA cm⁻², while the photocurrent density of the present work reaches 4.92 mA cm⁻² with a 20 fold photoconversion efficiency increase compared to bare TiO₂ photoanodes.

2. Experimental

2.1. Materials and methods

Titanium foil (99.8%, 0.127 mm thick) was purchased from Aldrich (Milwaukee, WI). Other reagents were of analytical grade. Double distilled water was used throughout the experiments. Titanium foil was cut into 1.0 cm x 3.5 cm strips. The strips were ultrasonically cleaned in acetone and ethanol each for 5 min, respectively. The cleaned titanium strips were anodized at a constant potential of 25 V in an electrolyte containing 0.1 M NaF and 0.5 M NaHSO₄ at room temperature for 3 h in a two electrode configuration with a platinum cathode and the Ti strip as the anode. After oxidation, the prepared TiO₂ NTAs by an anodic oxidation process were directly successively immersed in NaOH, H₂O, FeCl₃, and H₂O for 5 min each. Fe(OH)₃ was then successfully deposited onto the TiO₂ NTAs by S-CBD. The immersion cycle was repeated five times. The amount of loaded Fe(OH)₃ was controlled by varying the FeCl₃ concentration at 0.01, 0.02, 0.05, 0.08, 0.10, 0.20, and 0.30 M, respectively. The TiO₂ NTAs loaded with Fe(OH)₃ were annealed for crystallization at 550 °C for 4 h to obtain the Fe₂O₃-modified TiO₂ NTA photocatalysts. Second, the synthetic TiO₂/Fe₂O₃ was successively immersed in two different solutions for 1 min each: first in ethanol solution, 0.05 mol L⁻¹ Cd(NO₃)₂ as the cation source, and then in 0.05 mol L⁻¹ Na₂S in methanol/water (7 : 3 v/v). Following each immersion, the composite was rinsed for 2 min or longer with pure ethanol and methanol, respectively, to remove excess precursors and dried before the next dipping. The loading amount of the deposit was controlled by adjusting the number of immersion cycles; here, 1, 3, 5, 7, and 9 cycles were chosen for deposition. After washing several times with distilled water, the resulting TiO₂/Fe₂O₃/CdS heterostructure was heated under a nitrogen atmosphere at 300 °C for 2 h.

2.2. Photoelectrochemical measurements and structural characterization

The photocurrent measurements were conducted on a CHI-660C electrochemical system (Shanghai Chenhua Instrument Co. Ltd., China) using a standard three electrode cell with a working electrode, a platinum wire counter electrode, and a saturated calomel electrode (SCE) reference electrode. A solution containing 1 M KOH was used as the electrolyte. The sample (TiO₂/Fe₂O₃/CdS) was applied as the working electrode. A Xe lamp (CHF-XQ-500W, Beijing Changtuo Co. Ltd.) served as the light source. The incident light was filtered to match the AM 1.5G spectrum with an intensity of 100 mW cm⁻² as measured with a radiometer (OPHIR, Littleton, CO). Scanning electron microscopy (SEM) images were recorded on a field-emission scanning electron microscope (SEM, JSM-6700F). Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) patterns were recorded on a JEOL JEM 2100 high resolution transmission electron microscope.
microscope. An energy dispersive X-ray (EDX) spectrometer fitted to an electron microscope was used for elemental analysis. X-ray diffraction (XRD) patterns were recorded for identification of crystal structures of the samples with an X-ray diffractometer (XRD, M21X, MAC Science Ltd., Japan) employing Cu Kα radiation (\(\lambda = 1.5406 \text{ Å}\)). Light absorption properties were examined using UV-vis diffuse reflectance spectra (DRS, SHIMADZU, UV-2450) within a wavelength range of 200–800 nm. Photoluminescence (PL) spectra were recorded using a Hitachi F-4600 fluorescence spectrophotometer (Japan).

2.3. Photocatalytic degradation of PNP

The photocatalytic decomposition of PNP solution under visible light was performed to investigate the photocatalytic activities of TiO\(_2\)/Fe\(_2\)O\(_3\) and TiO\(_2\)/Fe\(_2\)O\(_3\)/CdS in comparison with those of the pure TiO\(_2\) NTAs. For the test, the incident light intensity was adjusted to 100 mW cm\(^{-2}\) through an IR cut filter (\(\lambda \geq 800 \text{ nm}\)) and a UV cut filter (\(\lambda < 400 \text{ nm}\)) from a 500 W Xe lamp. The PNP solution (0.1 L, 20 mg L\(^{-1}\)) was illuminated for 2 h under magnetic stirring. The characteristic absorption of PNP at
316 nm, analysed using a UV-vis spectrophotometer (CARY 300 Conc), was used to monitor the photocatalytic degradation. The degradation of the organic pollutant was determined following the Beer–Lambert law for the absorption band with the maximum at 316 nm for PNP. All the measurements were performed at room temperature.

2.4. Analysis of the photodegradation mechanism

Hydroxyl radicals (·OH) produced on the sample surface under AM 1.5G illumination were detected by PL analysis using terephthalic acid (TA), as the probe molecule.23,24 Experimental steps were performed in 5 × 10⁻⁴ mol L⁻¹ TA and 2 × 10⁻³ mol L⁻¹ NaOH solutions. The change of ·OH concentration during the procedure was monitored by determining the fluorescence emission intensity with an excitation wavelength of 320 nm.

3. Results and discussion

3.1. Characterization of the TiO₂/Fe₂O₃/CdS

Fig. 2 shows the SEM images of TiO₂ with/without the deposition of Fe₂O₃ and CdS. As shown in Fig. 2b and c, the surface of the TiO₂ NTAs is homogeneously covered with Fe₂O₃ and CdS nanoparticles. Fig. 2d displays the cross-sectional images of

Fig. 3 TEM (a) and HRTEM images (b), XRD patterns (c) and SAED pattern (d) of the as-synthesized CdS/Fe₂O₃/TiO₂ composites.

Fig. 4(A) Photocurrent responses in light on–off process of (a) unmodified TiO₂ nanotubes and (b–h) TiO₂/Fe₂O₃ nanotubes with increasing Fe content. (B) Short-circuit photocurrent density versus time plotted (0 V versus SCE) for TiO₂/Fe₂O₃/CdS with different cycles of CdS.
TiO$_2$/Fe$_2$O$_3$/CdS. The bare TiO$_2$ NTAs are smooth and clean (Fig. 2a). The Fe$_2$O$_3$ nanoparticles are distributed mainly on the top surface and interstices of the NTAs (Fig. 2b). After 9 cycles of CdS adsorption onto the TiO$_2$/Fe$_2$O$_3$ heterostructure, the surface of the material (Fig. 2c and e) becomes a little rougher than undecorated TiO$_2$/Fe$_2$O$_3$ (Fig. 2b), and the gap between TiO$_2$ NTAs almost disappears owing to the filling of Fe$_2$O$_3$ and CdS nanoparticles. No obvious blocking of the entrances is observed and the porosity of the structure is more beneficial for the adsorption process. Fig. 2f shows the EDS of the TiO$_2$/Fe$_2$O$_3$/CdS. EDS analysis confirms the successful attachment of the CdS and Fe$_2$O$_3$.

As depicted in the TEM image in Fig. 3a, it was observed that the TiO$_2$/Fe$_2$O$_3$/CdS product is composed of many aggregated nanocrystals. The detailed microscopic characterization of the TiO$_2$/Fe$_2$O$_3$/CdS heterostructure is performed using HRTEM images as displayed in Fig. 3b. The measured lattice spacings are consistent with the $d$-spacings of TiO$_2$ (0.297 nm, JCPDS 21-1272), CdS (0.28 nm, JCPDS 80-0019) and Fe$_2$O$_3$ (0.27 nm, JCPDS 72-469), respectively. The nanocrystalline material structure is confirmed with XRD analysis (Fig. 3c) and the SAED pattern (Fig. 3d) which further indicates the presence of TiO$_2$, Fe$_2$O$_3$ and CdS.

### 3.2. Optimization of the TiO$_2$/Fe$_2$O$_3$/CdS

Fe$_2$O$_3$ nanoparticles were firstly immobilized on TiO$_2$ NTAs by immersing the TiO$_2$ in FeCl$_3$ solution from 0.01 mol L$^{-1}$ to 0.3 mol L$^{-1}$. Fig. 4A indicates that the photocurrent response varies with Fe content, and the maximum photocurrent (1.89 mA cm$^{-2}$, curve g) is obtained on the TiO$_2$/Fe$_2$O$_3$ NTAs with 0.2 mol L$^{-1}$ Fe, which is 7.56 times that achieved on pure TiO$_2$ NTAs (0.25 mA cm$^{-2}$, curve a).

Further immobilization of CdS nanoparticles on the TiO$_2$/Fe$_2$O$_3$ NTAs resulted in a dramatic increase of the photocurrent up to 4.92 mA cm$^{-2}$ by 9 SILAR cycles (Fig. 4B, curve e). The photocurrent density increases first and then decreases (curve f) with increasing CdS loading on the electrodes. Over-loading of CdS nanoparticles beyond 9 SILAR cycles formed a significant aggregation, which is less efficient in absorption spectra as compared to un-aggregated smaller size nanocrystallites, resulting in a decrease in photocurrent.

### 3.3. Photoelectrochemical behavior evaluation

Photocurrent density–time characteristics of the samples were investigated in an electrolyte containing 0.35 mol L$^{-1}$ Na$_2$SO$_3$. Fig. 5A displays photocurrent responses of (a) TiO$_2$, (b) TiO$_2$/Fe$_2$O$_3$, (c) TiO$_2$/CdS and (d) TiO$_2$/Fe$_2$O$_3$/CdS; (B) time-dependent photocurrent response of (a) unmodified TiO$_2$ and (b) TiO$_2$/Fe$_2$O$_3$/CdS.

![Fig. 5](image-url)
and 0.24 mol L\(^{-1}\) Na\(_2\)S to examine the photoelectrochemical properties. The TiO\(_2\)/Fe\(_2\)O\(_3\)/CdS NTAs show the best performances with a photocurrent density of 4.92 mA cm\(^{-2}\) (curve d) which is much higher than those of the pure TiO\(_2\) (0.25 mA cm\(^{-2}\), curve a), TiO\(_2\)/Fe\(_2\)O\(_3\) (1.89 mA cm\(^{-2}\), curve b) and TiO\(_2\)/CdS (3.02 mA cm\(^{-2}\), curve c) (see Fig. 5A). Fig. 5B shows the time-dependent photocurrent responses of the TiO\(_2\)/Fe\(_2\)O\(_3\)/CdS and unmodified TiO\(_2\) NTAs under illumination with 100 mW cm\(^{-2}\) visible light. Both show a high stability, and the photocurrent decreases by 1.04% within 1 h.

The photoelectric performance of the TiO\(_2\)/Fe\(_2\)O\(_3\)/CdS is further investigated by the photocurrent–applied potential (\(J–V\)) relationship. As illustrated in Fig. 6A, the photocurrent response increases significantly on the TiO\(_2\)/Fe\(_2\)O\(_3\)/CdS, even at a potential of 0 V. The open circuit potential, \(V_{oc}\), which corresponds to the difference between the apparent Fermi levels of the working electrode and the reference electrode, is around 1.00 V for the TiO\(_2\)/Fe\(_2\)O\(_3\)/CdS, which is greater than that obtained with TiO\(_2\)/Fe\(_2\)O\(_3\) and TiO\(_2\)/CdS (\(V_{oc} \approx 0.88\) V) and pure TiO\(_2\) NTAs (\(V_{oc} \approx 0.72\) V), demonstrating a shift in the Fermi level to a more negative potential in the TiO\(_2\)/Fe\(_2\)O\(_3\)/CdS composite system, which can improve the photogenerated electron–hole separation and suppress the recombination of photogenerated charge carriers.\(^{28}\) Fig. 6B displays the corresponding photoconversion efficiency calculated using eqn (1):\(^{26}\)

\[
\eta (\%) = J_p [E_{rev}^{\text{app}} - |E_{app}|] \times 100 / J_0
\]

where \(J_p\) is the photocurrent density (mA cm\(^{-2}\)), \(J_p E_{rev}^{\text{app}}\) is the total power output, \(J_p|E_{app}|\) is the power input, and \(J_0\) is the power density of incident light (100 mW cm\(^{-2}\)). \(E_{rev}^{\text{app}}\) equals 1.23 V, which is the standard potential for the water splitting reaction. The applied potential is \(E_{app} = E_{\text{meas}} - E_{\text{aoc}}\), where \(E_{\text{meas}}\) is the electrode potential (vs. SCE) of the working electrode and \(E_{\text{aoc}}\) is the electrode potential (vs. SCE) of the same working electrode under open-circuit conditions. As expected, the TiO\(_2\)/Fe\(_2\)O\(_3\)/CdS photoelectrode achieves the highest efficiency of 4.36% at −0.68 V vs. SCE which is about 20 times the efficiency of pure TiO\(_2\) (0.22%) as shown in Fig. 6B.

The open-circuit voltage-decay measurements were conducted by monitoring the \(V_{oc}\) transient during relaxation from an illuminated quasi-equilibrium state to the dark equilibrium.
When the AM 1.5G illumination on the TiO2/Fe2O3/CdS photoelectrode at open circuit is interrupted, the excess electrons are removed due to recombination with holes trapped in the composite and dissolved oxygen in the electrolyte. The photo-voltage decay rate directly relates to the electron lifetime by expression (2):

$$\tau_e = \frac{-k_B T}{e} \left( \frac{dV_{oc}}{dt} \right)^{-1}$$

where $k_B T$ is the thermal energy, $e$ is the positive elementary charge, and $dV_{oc}/dt$ is the derivative of the open-circuit voltage transient. Fig. 7B is the plot of the response time obtained by applying eqn (2) to the data in Fig. 7A. At the same $V_{oc}$ value, the response time of the photoelectrodes follows an order of TiO2/Fe2O3/CdS > TiO2/Fe2O3 > TiO2 NTAs. Based on the above analyses, the TiO2/Fe2O3/CdS NTA photoelectrode exhibits superior recombination characteristics, with the longer lifetimes indicating enhanced separation of the photogenerated charges in the structure.

The optical properties of the samples were characterized using the UV-vis diffuse reflectance spectra and PL spectra. Fig. 8A shows that the absorption in the visible range was significantly enhanced with the stepwise modifications of Fe2O3 and CdS nanoparticles (curves b and d). Fig. 8B displays a decrease in PL intensity. The photoluminescence is the result of the recombination of photogenerated electron–hole pairs, and consequently a longer lifetime of photogenerated carriers, which implies higher photoelectric conversion efficiency. The TiO2/Fe2O3/CdS NTAs achieve the highest photoelectric conversion efficiency (Fig. 6B), which is consistent with their highest absorbance in visible light.

3.4. Photocatalytic performance and mechanism of the TiO2/Fe2O3/CdS

Photocatalytic degradation of PNP solution under visible light was performed to investigate the photocatalytic activities of TiO2 NTAs (Fig. 9A), TiO2/Fe2O3 (Fig. 9B) and TiO2/Fe2O3/CdS (Fig. 9C). The change in PNP concentration during the degradation process was characterized following the Beer–Lambert law by its characteristic absorption at 316 nm. After 120 min of illumination, the photocatalytic degradation of PNP on TiO2/Fe2O3/CdS shows the maximum efficiency; 100% removal is achieved (Fig. 9C), while only 17% and 57.8% removals are achieved on pure TiO2 NTAs and TiO2/Fe2O3 under identical conditions. The removal efficiency is calculated using formula (3):

$$\text{Removal efficiency} = \left( \frac{C_0 - C}{C_0} \right) \times 100\%$$

where $C$ is the PNP concentration obtained after various intervals of time and $C_0$ is the initial concentration. As shown in Fig. 9D, the TiO2/Fe2O3/CdS photoelectrode shows the highest
activity. Based on previous reports and the results mentioned above, we hypothesize the following photocatalytic degradation mechanism as illustrated in Fig. 10 with the following equations:

$$\text{TiO}_2 \rightarrow \text{TiO}_2(h^+ + e^-)$$; \hspace{1em} \text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_2\text{O}_3(h^+ + e^-)$$; CDs \rightarrow CDs(h^+ + e^-). \hspace{1em} \text{(4)}

$$\text{TiO}_2(h^+ + e^-) + \text{Fe}_2\text{O}_3(h^+ + e^-) + \text{CdS}(h^+ + e^-) \rightarrow \text{TiO}_2 + \text{CdS}(h_{\text{total}}^+) + \text{Fe}_2\text{O}_3(e_{\text{total}}^-) \hspace{1em} \text{(5)}$$

$$\text{Fe}_2\text{O}_3(e_{\text{total}}^-) + \text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + \cdot\text{O}_2^- \hspace{1em} \text{(6)}$$

$$\text{H}^+ + \cdot\text{O}_2^- \rightarrow \cdot\text{OH} \hspace{1em} \text{(7)}$$

$$\cdot\text{O}_2\text{H} + \cdot\text{O}_2\text{H} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \hspace{1em} \text{(8)}$$

$$\text{H}_2\text{O}_2 + \text{H}^+ + e^- \rightarrow \cdot\text{OH} + \text{H}_2\text{O} \hspace{1em} \text{(9)}$$

$$\text{CdS}(h_{\text{total}}^+) + \text{H}_2\text{O} \rightarrow \text{CdS} + \cdot\text{OH} + \text{H}^+ \hspace{1em} \text{(10)}$$

$$\cdot\text{OH} + \text{organic pollutants} \rightarrow \text{degradation products} \hspace{1em} \text{(11)}$$

Electron–hole pairs are produced in the Fe$_2$O$_3$, CdS and TiO$_2$ (eqn (4)) under illumination. The band gap of TiO$_2$ (3.2 eV), CdS (2.4 eV) and Fe$_2$O$_3$ (2.2 eV) reduces progressively with the CB and VB increasing progressively to form a stepwise heterostructure that can absorb visible light. The potentials of the conduction band (CB) and valence band (VB) edges of TiO$_2$, CdS and Fe$_2$O$_3$ were determined using the following formulas:

$$E_{\text{VB}} = X - E_0 + 0.5E_g \hspace{1em} \text{(12)}$$

$$E_{\text{CB}} = E_{\text{VB}} - E_g \hspace{1em} \text{(13)}$$

where $E_{\text{VB}}$ and $E_{\text{CB}}$ are the VB and CB edge potentials and $X$ is the electronegativity of the semiconductor; the $X$ values for TiO$_2$, Fe$_2$O$_3$ and CdS are 5.81 eV, 4.78 eV and 5.18 eV, respectively. $E_0$ is a constant, about 4.5 eV. According to the formulas, the VB and CB values of CdS are calculated to be 1.45 and $-0.89$ eV, those of TiO$_2$ are 2.90 and $-0.30$ eV, and those of Fe$_2$O$_3$ are determined to be 2.54 and $-0.35$ eV, respectively.\cite{35} Photo-excited electrons in the CB of CdS transfer to Fe$_2$O$_3$, and then migrate to TiO$_2$. On the contrary, the holes in the VB of TiO$_2$ are transferred to the VB of Fe$_2$O$_3$ and CdS stage by stage and eventually accumulate on the surface of CdS (eqn (5)).\cite{35}–\cite{39} The separated electrons and the holes are captured by dissolved oxygen molecules and H$_2$O species respectively to form hydroxyl radicals (·OH) (eqn (6)–(10)), a strong oxidizing agent to decompose organic pollutants (eqn (11)).\cite{24,40}

The PL technique was employed to help understand the degradation mechanism.\cite{41} TA and ·OH formed on the photolimited electrode surface under UV-vis irradiation readily react to produce a highly fluorescent product, 2-hydroxyterephthalic acid.\cite{42} When the TiO$_2$/Fe$_2$O$_3$/CdS serves as the photoelectrode, the PL intensity increases gradually with the increasing irradiation time, indicating that ·OH was produced indeed during the photocatalytic process (depicted in Fig. 11A). Fig. 11B shows the PL obtained after 20 min of irradiation for different photoelectrodes, and the TiO$_2$/Fe$_2$O$_3$/CdS (curve c) shows the best photocatalytic performance.

![Fig. 10](image1.png) Schematic mechanism of the possible photogenerated charge separation and transport in the TiO$_2$/Fe$_2$O$_3$/CdS heterostructure.

![Fig. 11](image2.png) (A) PL spectra measured during illumination of TiO$_2$/Fe$_2$O$_3$/CdS and different photoelectrodes (B): (a) TiO$_2$, (b) TiO$_2$/Fe$_2$O$_3$ and (c) TiO$_2$/Fe$_2$O$_3$/CdS.
4. Conclusions

A TiO\textsubscript{2}/Fe\textsubscript{2}O\textsubscript{3}/CdS heterostructure was prepared for the first time via annealing amorphous TiO\textsubscript{2} NTAs which were pre-loaded with Fe(OH)\textsubscript{3} by S-CBD and SILAR processes. The modification of TiO\textsubscript{2} NTAs with Fe\textsubscript{2}O\textsubscript{3} and CdS results in a negative shift of the zero-current potential from ~0.72, ~0.88 to ~1.0 V, and a significant increase in photocurrent. The optimal sample demonstrates a solar spectrum photconversion efficiency of approximately 4.36% and an excellent photocatalytic activity for the removal of PNP. A photodegradation mechanism was proposed on the basis of the matched energy band of TiO\textsubscript{2}/Fe\textsubscript{2}O\textsubscript{3}/CdS favoring the charge transfer and suppressing the photo-induced carrier recombination, leading to the enhanced photocatalytic activity. We believe that it is promising towards the low cost synthesis of high performance photocatalysts for the photodegradation of organic pollutants in aqueous solution.

Conflicts of interest

The authors declare no competing financial interest.

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