In situ synthesis and visible-light photocatalytic application of CdTeSe@TiO₂ nanotube composites with high electron transfer rate

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Abstract

High quality ternary-alloyed CdTeSe quantum dots (QDs) have been synthesized via a simple one-pot approach in aqueous phase. CdTeSe QDs show an average size of 3.0 nm with good crystallinity, excellent monodispersity and relatively narrow size distribution. TiO₂ nanotubes (TNTs) were prepared by hydrothermal method with larger specific surface area (364.2 m²·g⁻¹), and CdTeSe@TNTs were synthesized by in situ process. The absorption edge of CdTeSe@TNTs is red shifted significantly toward 697 nm. After sensitized with CdTeSe, the photoluminescence (PL) emission of CdTeSe@TNTs is significantly quenched, and the fluorescence lifetime of the composites is drastically decayed from 105.82 ns to 0.13 ns with a high photoinduced electron transfer rate ($k_{\text{et}} = 7.98 \times 10^9 \text{ s}^{-1}$) because of their high matchable lattice constant. In addition, under visible-light irradiation, the photocatalytic efficiency of rhodamine B (RhB) with CdTeSe@TNTs reaches 90% for 80 min. And the photocatalytic reaction rate constant for CdTeSe@TNTs is 0.0272 min⁻¹, which is 5.4 and 3.4 times larger than that of pure TNTs and CdTeSe QDs, respectively. It is due to the broad visible absorption of CdTeSe@TNTs and the faster photoinduced electron transfer from CdTeSe QDs to TNTs.

Keywords:

TiO₂ nanotubes; CdTeSe quantum dots; Electron transfer; Visible-light; Photocatalysts

1. Introduction

TiO₂ have many advantages, such as low cost, high photoelectric conversion activity, powerful oxidation capacity, good stability and containing no toxic elements, so are utilized as sensor, photocatalysis, photoelectrochemical devices, etc. [1,2] It is a regrettable thing that pure TiO₂ only work under UV light irradiation. However, only 5 % of solar spectrum locates in the UV range, while the solar spectrum has broad range of wavelengths, spanning from 250 to 2500 nm [3]. Hence, TiO₂ is urged to be modified to expand its photo-response to the visible region for photocatalysis in several ways, including doping with cations/anions [4-6], coupling with dyes [7,8], sensitized by noble metal [9,10], or quantum dots (QDs) [11,12]. Compared to organic dyes, QDs have wide absorption range and are higher reliability and stability. The QDs-sensitized TiO₂ can tailor optical absorption over the whole visible-light region more than possible for dyes-sensitized TiO₂ [13]. Therefore, the QD-sensitization technique will be an innovative technology that could play an important role in developing efficient and cost-effective semiconductor photocatalyst. The most efforts are focused on II–VI materials, chiefly CdSe and CdTe QDs. The photoelectric conversion efficiency of CdSe QDs is only 3.6% when the photoanode is photoelectrochemically etched, comparatively, CdTeSe alloys could reach up to 8% [14]. Moreover, optical properties of ternary quantum dots are found to be different from those of simpler binary or core/shell nanocrystals [15]. Apparently, CdTeSe is a more promising photocatalyst than CdSe and CdTe because of its better photoelectric properties and stability. And CdTeSe can efficiently emit light in NIR wavelength window and be potentially applied in biomedical imaging and detecting field [16].

It is well known that the photocatalytic properties of QDs sensitized TiO₂ composites depend

heavily upon not only QDs but supporting materials [17]. TiO₂ nanotubes (TNTs) have larger specific surface area compared to the other morphologies of TiO₂, but their high photocatalytic efficiency just works in the UV region. The photocatalysts based on TNTs modified CdTeSe by ternary QDs are expected to show a excellent photocatalytic performance, ascribing to their prominent photogenerated charge transfer and separation properties and stability. However, there are few reports about the synthesis of CdTeSe@TNTs nanocomposites and their photocatalysis under visible-light.

This work firstly reports that the nanocomposites of ternary alloy CdTeSe QDs and TNTs were prepared with a simple in situ growth process and used as visible-light photocatalysts to degrade RhB. In this work, the obtained CdTeSe ternary alloy QDs are with high-quality and water-soluble and capped with 3-mercaptopropionic acid (3-MPA), where the mercapto group is conjugated with the Cd²⁺ ion on the surface of CdTeSe QDs. The ionized carboxylate group has improved the hydrophilicity of CdTeSe QDs, and also promoted CdTeSe QDs directly attach to TNTs. So, the CdTeSe@TNTs nanocomposites can be easily prepared by in situ growth process. On the other hand, TNTs are hydrophilic after conversion to anatase [18], which also ensure enough QDs deposited on TNTs. Therefore, the electron transfer rate constant between CdTeSe and TNTs is high with $7.98 \times 10^9 \text{ s}^{-1}$, which is helpful to the photodegradation of RhB. And the as-prepared CdTeSe@TNTs nanocomposites display an efficient under visible-light irradiation. Moreover, the photodegradation mechanism is studied in detail.

2. Materials and methods

2.1. Materials

Tellurium powder (Te, 99.999%) was purchased from Alfa Aesar W (Alfa Aesar China, Beijing, China). Selenium powder (Se, 99.95%) was obtained from Shanghai Meixing Chemical Company (Shanghai, China). 3-Mercaptopropionic acid (3-MPA, > 99%) and rhodamine B (95% QY) were obtained from Sigma-Aldrich (Sigma-Aldrich Shanghai Trading Co. Ltd, Shanghai, china). Cadmium acetate ($\text{Cd}(\text{CH}_3\text{COO})_2$, 99%) and NaBH_4 (96%) were obtained from Sinopharm Chemical Reagent Company (Shanghai, China). All other chemicals were of analytical grade.

2.2. Synthesis of CdTeSe QDs and CdTeSe@TNTs

The synthesis of CdTeSe alloy nanocrystals was based on the synthesis of CdTe previously [19]. All reactions were conducted under nitrogen atmosphere. Typically, 53.3 mg of $\text{Cd}(\text{CH}_3\text{COO})_2$ and 100 mL of 3-MPA solution (0.5 mM, pH 10~11) were deaerated with nitrogen bubbled in a 250 mL three-neck round-bottom flask for 60 min. Then, the solution was heated to 100 °C. A selenium stock solution (0.3 M, NaHSe) was prepared by dissolving 0.0487g of Se and 0.1256g of NaBH_4 in 2.0 mL of deionized water and stirring in ambient temperatures and anaerobic environment to achieve complete dissolution. Similarly, a tellurium stock solution (0.3 M, NaHTe) was prepared by adding 0.778g of Te and 0.1256g of NaBH_4 into 2.0 mL of deionized water and hitting to 40-60 °C until all tellurium had dissolved. To prepare nanocrystals of CdTeSe, a solution composed of 41.6 μL of Se stock solution and 41.6 μL of Se stock solution was swiftly injected into the flask. The temperature was then cooled to 30 °C, and the nanocrystals were allowed to grow until the desired size had been achieved. Once synthesized, the nanocrystals were isolated by precipitation with a mixture of acetone and ethanol, then centrifuged, and the resulting nanocrystal pellets were resuspended in deionized water.

TNTs were prepared according to the classical hydrothermal method. Simply, 0.8g of the P25

powder (Degussa P25, Germany) was mixed with 80 mL of 10 M NaOH solution, followed by thermal treatment of the mixture at 140 °C in a Teflon-lined autoclave for 24 h. After the treatment, the filtered sample was then neutralized by mixing with 200mL of 0.1 M HCl solution for 5 h until pH = 7. The powder was dried at 60°C and calcined at 300 °C for 30 min.

The in situ synthesis process of CdTeSe@TNTs is as Scheme 1 shown. The as-prepared TNTs were immersed in 3-MPA solution and stirring for 1 h under nitrogen atmosphere. Then Cd(CH₃COO)₂ solution was added and stirring for 0.5 h, following Se and Te stock solutions were added as the ratio of 1:1, condensation reflux for 0.5 h. The resulting TNTs, linked with CdTeSe, were washed with deionized water and dried in air. After modification with CdTeSe QDs, TNTs were annealed at 300 °C in nitrogen gas for 30 min to improve the CdTeSe@TNTs interface and to vaporize the linking molecules.

2.3. Characterization

Photoluminescence (PL) spectra were taken on a Cary Eclipse (Varian, USA) at room temperature. Fluorescence emission decay measurements were performed on an FLS 920 Steady state lifetime fluorescence spectrometer (Edinburgh Instruments, Edinburg, UK). Surface morphologies of the samples across the entire substrate were characterized by field-emission scanning electron microscopy (FE-SEM, Hitachi S4800, Japan). High-resolution transmission electron microscopy (HRTEM) images and energy-dispersive X-ray elemental (EDX) were taken on a Tecnai G2 F20 S-TWIN, 200kV, FEI, USA. TEM samples were prepared by placing a drop of nanocrystals diluted in ethanol to an optical density <0.1 onto an ultrathin carbon-on-Formvar TEM grid (Ted Pella, Inc.), wicking away any excess solvent. X-ray diffraction (XRD) patterns were obtained using a Scintag X1 automated powder X-ray diffractometer (Thermo, USA).

UV-vis absorption and diffuse reflectance spectra were measured on a Perkin-Elmer Lambda 900 spectrophotometer. Specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method using Autosorb-1 (Quantachrome Instruments, USA). The photoelectric properties of the samples were performed on an electrochemical workstation (CHI 660D, CH Instrument Company, China) with a conventional three-electrode system. A platinum wire was acted as counter electrode, a saturated Ag/AgCl electrode was used as reference electrode, and the working electrode was TNTs or CdTeSe@TNTs/ITO electrode. It was created as follow: TNTs or CdTeSe@TNTs were dispersed in a mixture of deionized water and ethanol with a volume ratio of 1:2, then the obtained suspensions were spread on ITO substrate (active surface area of 1.0 cm²). The ITO electrode was dried in air, and then annealed at 300 °C for 20 min. The electrolyte solution was 0.1 M Na₂SO₄ solution. Electron spin resonance signals of radicals trapped by 5,5-Dimethyl-pyrroline-oxide (DMPO) were recorded at ambient temperature on a Bruker A300 spectrometer.

2.4. Measurements of photocatalytic degradation of RhB

The photocatalytic degradation of RhB was performed under visible region irradiation using a xenon lamp with a UV glass filter (Optima Inc., China), which transmits light at a wavelength $\lambda > 390$ nm. 5 mg of the CdTeSe@TNTs was suspended in an aqueous solution (50 mL) containing 5 μ M RhB by stirring for 30 min. Then at a definite time interval, 4 mL samples were withdrawn for analysis using a UV-vis spectrophotometer (PE Lambda 900). The degradation efficiency was defined as $\eta = (1 - c/c_0) \times 100\%$, where c and c_0 were the equilibrium concentration of RhB after and before visible-light irradiation. And the concentration of RhB was linear proportion to absorption (A), thus $c/c_0 = A/A_0$.

3. Results and discussion

3.1 Morphology and structure of CdTeSe QDs and CdTeSe@TNTs

As shown in Fig. 1, the XRD patterns of CdTeSe@TNTs (curve b) contain the characteristic diffraction peaks of TNTs (curve a) but with not obvious CdTeSe QDs diffraction peaks (curve c) which is attributed to the smaller nanosize of CdTeSe QDs. It shows obviously diminished and widening diffraction peaks compared to pattern of TNT (curve a), illustrating that CdTeSe QDs had successfully attached to TNTs. In the present study, the anatase phase is the desirable phase compared to other TiO₂ phases (rutile and brookite) because it exhibits the highest photocatalytic activity [20]. In our case, anatase is the major phase.

From HRTEM images (Fig. 2a), it shows that CdTeSe QDs have a highly crystalline, axiolitic structure. The average diameter of CdTeSe QDs is around 3 nm with good monodispersity and relatively narrow size distribution. By examining several isolated particles under high magnification, the average lattice fringe of CdTeSe QDs is estimated to be 3.55 Å corresponding to the (111) planes of cubic CdTeSe (Fig. 2b).

Here, open-ended TNTs were synthesized using the hydrothermal process. SEM image (inset of Fig. 2c) clearly displays the nanotubes with a long and tubular shape morphology. TEM image of the TNTs (Fig. 2c) shows that the multiwall TNTs have about 4.5 nm inner diameters and 8 nm outer, while the lengths of TNTs are several micrometers. And the specific surface area of TNTs reach 364.2 m²·g⁻¹. From Fig.1, it could be found that CdTeSe QDs have a close lattice constant compared with (101) plane of anatase TNTs (3.55 Å for CdTeSe and 3.51 Å for TNTs). SEM (inset of Fig. 2d) and TEM images (Fig. 2d and e) all indicate that CdTeSe QDs have covered the surface of TNTs. The interplanar spacing (inset of Fig. 2e) with weak difference are assigned to

(111) plane of CdTeSe QDs (3.55Å) and (101) plane of anatase TNTs (3.51 Å), respectively, indicating better lattice matching between CdTeSe QDs and anatase TNTs and in favor of the transition of photoexcited charge between ternary QDs and TNTs as shown below. In this model, the electron transfer rate between QDs and TNTs is expected to vary exponentially with the tunneling distance [21], the length between QDs and TNTs is short due to the lattice matching at the interface between QDs and TNTs. EDX analysis of CdTeSe@TNTs demonstrates the presence of Ti, O, Cd, Se, and Te elements as shown in Fig. 3d, further confirming formation of CdTeSe@TNTs without excess impurities. And CdTeSe@TNTs also have a larger specific surface area, 267.3 m²·g⁻¹.

3.2. Optical property of CdTeSe@TNTs

Fig.3 illustrates UV-vis diffuse reflection absorption spectra obtained from TNTs before and after the deposition of CdTeSe QDs. The CdTeSe QDs are with an absorption edge at 687 nm. The spectrum obtained from the plain TNTs (Fig. 3) demonstrates that the absorption of TNTs mainly locates in the ultraviolet light with a wavelength below 400 nm. After the deposition of CdTeSe QDs, the absorption edge of CdTeSe@TNTs is shifted significantly toward 697nm. Specially, it is noticed that not only the spectrum of CdTeSe@TNTs exhibits a simple superposition of the spectrum of pure CdTeSe QDs and TNTs, but its the absorption edge presents about 10nm red shift compared to that of pure CdTeSe QDs. The bathochromic shift for CdTeSe@TNTs can be explained by the type II electronic structures of the core-shell heterojunctions [22], which enable an interface transition coupling a hole state in the shell (CdTeSe QDs) with an electron state in the TNTs core.

Fig. 4a shows PL emission spectra obtained from CdTeSe QDs before and after being

deposited into TNTs. As shown in Fig. 4a, ternary QDs exhibit a characteristic emission peak at 566 nm with a FWHM about 23.3 nm. The FWHM of PL spectra could indirectly reflect the size distribution of the prepared QDs. The smaller FWHM indicates that the size distribution of the ternary QDs is narrow [16], which is demonstrated with HRTEM results (Fig. 2a). After CdTeSe QDs were deposited onto TiO₂ nanotubes, the hybrid nanostructures display a weak emission peak, illustrating that the emission is significantly quenched. The quenching behavior confirms that most of the photoexcited electrons from CdTeSe QDs have transferred to TNTs, significantly improving the transiting performance of the photoexcited charges induced by QDs. The rate of charge recombination and transfer process influences the PL emission (Eq. (1)) and quenching (Eq. (2)) of CdTeSe QDs.

The fluorescence emission decay of CdTeSe@TNTs is show in Fig. 4b. Compared to plain CdTeSe QDs, CdTeSe@TNTs are observed with significant decrease lifetime. In particular, the fast component, which contributes nearly 95% of the decay, implies a major decrease in lifetime from 105.82 ns in CdTeSe QDs to 0.13 ns in the CdTeSe@TNTs system. In addition, we calculated the apparent electron transfer rate constants (k_{et}) for the charge injection process by comparing the lifetimes of CdTeSe QDs (τ_0) and CdTeSe@ TNTs system (τ) using Eq. (3) [23].

$$k_{et} = 1/\tau - 1/\tau_0 \quad (3)$$

the apparent electron transfer rate constants was estimated to $7.98 \times 10^9 \text{ s}^{-1}$, far greater than previous investigation ($4 \pm 1 \times 10^6 \text{ s}^{-1}$) [24], indicating the major fraction of the charge injection event occurs on an ultrafast time scale. It is due to the crystallite match between TNTs and

CdTeSe QDs as shown above. The mechanism for electron transfer in the case of CdTeSe QDs located on TNTs involves tunneling through the QD-metal oxide junction (Scheme 2).

3.3. Photoelectrochemical response of CdTeSe@TNTs

To further investigate photoelectrochemical properties, the amperometric $I-t$ curves were measured upon the transient photocurrent responses with visible light (Fig. 5a), and the applied voltage was 0.25 V vs. Ag/AgCl bias. The results exhibit that the photocurrent of CdTeSe@TNTs electrode is about 0.10 mA, however, TNTs show a very weak photocurrent with 0.0042 mA because of their big band gaps. It demonstrates that CdTeSe QDs can extend the light absorbing of the composite.

Electrochemical impedance spectroscopy (EIS) was used to measure the current response to the application of an ac voltage as a function of the frequency and characterizing electrochemical interfacial reactions. Fig. 5b shows the Nyquist plots of CdTeSe@TNTs and TNTs under dark conditions. The diameter of the arc radius on the Nyquist plots of CdTeSe@TNTs is larger than that of pure TNTs due to the charge transfer resistance (R_{ct}) between CdTeSe QDs and TNTs.

3.4. Photocatalytic activity and mechanism of CdTeSe@TNTs

We expect that the photocatalytic capability could be improved by the excellent electron transfer rate. The experimental photocatalytic characteristics measured from the different samples are presented in Fig. 6. The photocatalytic activity of the samples was evaluated by photodegradation of RhB aqueous solution under visible-light irradiation by 80 min. TiO_2 nanoparticles (TiO_2 NPs, P25) almost have no photocatalytic property, and their degradation efficiency is near the self-photodegradation. The pure TNTs samples show a faintly stronger

visible-light photocatalytic activity (as shown in Fig. 6a), which is due to presence of chemisorbed RhB as a photosensitizer and the higher specific surface area of TNTs ($364.2\text{m}^2\cdot\text{g}^{-1}$). The photocatalytic efficiency of CdTeSe QDs@TNTs is much higher than that of pure TNTs and TiO_2 NPs. The photocatalytic degradation efficiency is increased from 9% for TiO_2 NPs, 35% for the plain TNTs, 48% for CdTeSe QDs to 90% for CdTeSe@TNTs (Fig. 6a) in 80min, respectively. This photocatalytic efficiency of RhB for CdTeSe@TNTs is also higher than CdSe/ TiO_2 nanorods [25] and CdTe/ TiO_2 [26], demonstrating the advantage of the ternary QDs.

The linear relationship of the natural logarithm of the ratio between the initial concentration of RhB and its concentration at different times ($\ln c/c_0$) versus the corresponding irradiation time is shown in Fig. 6b. The results indicate that the photodegradation of RhB under visible-light illumination follow first order kinetic model as Eq. (4).

$$-\ln c/c_0 = kt \quad (4)$$

where k is the photocatalytic reaction rate constant. Kinetic parameters for the photodegradation of RhB are presented in Table 1. The photocatalytic reaction rate constant for CdTeSe@TNTs is 0.0272 min^{-1} , which is 5.4 and 3.4 times larger than that of pure TNTs and CdTeSe QDs, respectively. According to the UV-vis spectra (Fig. 3), the incorporation of CdTeSe QDs into TNTs extends the absorption spectrum of the plain TNTs significantly into the visible region. When illuminated, CdTeSe QDs effectively absorbs visible-lights (with absorption edge centers at 697 nm), and excite electrons and holes pairs. Since the conduction band edge of CdTeSe QDs is above that of the TNTs [27], local band bending occurs at the CdTeSe@TNTs interface, which results in a local electric field pushing the photogenerated electrons toward the conduction band of TNTs (Scheme 2). The photoinduced electrons transfer from CdTeSe QDs to TNTs conduction

band, and the injected electrons are scavenged by adsorbed oxygen molecules to yield superoxide radical anions $\bullet\text{O}_2^-$. The radical anions can combine with H^+ to generate $\bullet\text{OOH}$, then $\bullet\text{OOH}$ radicals and the trapped electrons combine to produce H_2O_2 , finally resulting $\bullet\text{OH}$ radicals. Photodegradation of RhB can subsequently take place through $\bullet\text{OH}$ radicals attack the RhB molecules.

Electron spin resonance (ESR) is a highly sensitive spectroscopic technique for examining radical species. DMPO spin-trapping ESR spectra of CdTeSe@TNTs were carried out to further confirm the role of radicals, and the results are shown in Fig. 7. No ESR signals are observed during the entire reaction in the dark (curve a and c). Under the light illuminated, four characteristic peaks of the $\text{DMPO}\cdot\bullet\text{O}_2^-$ are detected in methanol solutions (curve b) [28], and a quartet of signals with relative intensities of 1:2:2:1 attribute to $\text{DMPO}\cdot\bullet\text{OH}$ are captured in aqueous solution (curve d). The results suggest that $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ are formed in the photocatalytic reaction, which demonstrates the photocatalytic mechanism for CdTeSe@TNTs.

On the basis of the above discussion, it is concluded that CdTeSe QDs on the surface of TiO_2 nanotubes serve as electron sources (Eq. (1)) for degradation of RhB and TNTs act as a media for the electrons transfer (Eq. (2)). Under visible-light irradiation, CdTeSe QDs can provide photoinduced electron via surface plasmon resonance, then the photoinduced electron transfer to TNTs and arrive on the surface to form $\bullet\text{OH}$ radicals. Moreover, high match of the lattice constant between CdTeSe QDs and TiO_2 is beneficial to accelerating photogenerated electron transfer process. Consequentially, it is reasonable that the CdTeSe@TNTs exhibit the higher visible-light photocatalytic activity in our system.

The photocatalytic experiments were carried out at different initial concentration of RhB

with CdTeSe@TNTs. As shown in Fig. 8a, the photocatalytic degradation efficiency decreases with the increase of the initial concentration of RhB. This could be ascribed to the limit of the active oxygen species when the initial concentration of RhB is increased [26]. The photocatalytic degradation efficiency can still reach 73% at 20 μ M initial dye concentration. Moreover, it is found in Fig. 8b that the catalysts of CdTeSe@TNTs are stable and the decrease of photocatalytic efficiency is negligible after reusing for three times.

4. Conclusions

In this work, CdTeSe@TNTs composites were in situ synthesized as photocatalysts. The UV-vis diffuse reflection absorption spectra shows that the absorption edge of CdTeSe@TNTs is red shifted significantly toward 697 nm, which red shift 10 nm compared to pure CdTeSe QDs. It is due to the type II electronic structures of the core-shell heterojunctions. The photocatalytic degradation efficiency is only 9% for the TiO₂ NPs, 35% for the plain TNTs, 48% for CdTeSe QDs, and up to 90% for the CdTeSe@TNTs. And the photocatalytic reaction rate constant for CdTeSe@TNTs is 0.0272 min⁻¹, which is 5.4 and 3.4 times larger than that of pure TNTs and CdTeSe QDs, respectively. The quenching PL spectra of CdTeSe@TNTs confirm that most of the photoexcited electrons from CdTeSe QDs have transferred to the TNTs. The higher photocatalytic degradation efficiency can attribute to the apparent rate constants for the charge injection process of CdTeSe@TNTs with $k_{et} = 7.98 \times 10^9$ s⁻¹ because of their high matchable lattice constant. The results confirm that ternary CdTeSe QDs can be used as effective sensitizers, and the CdTeSe@TNTs system is potentially applied in visible-light photocatalysis. Additionally, the novel CdTeSe@TNTs composites are hoped to be applied for solar cells, photoelectrochemical

biosensors, and other devices.

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Table 1. Kinetic parameters for the photodegradation of RhB under visible-light.

Table 1.

Samples	Without catalyst	TiO ₂ NPs	TNTs	CdTeSe QDs	CdTeSe@TNTs
R^2	0.9806	0.9617	0.9682	0.9912	0.9847
k (min ⁻¹)	0.0012	0.0012	0.005	0.008	0.0272
$t_{1/2}$ (min)	577.6	577.6	138.6	86.6	25.5

Figure Captions

Fig. 1. XRD patterns of (a) TNTs, (b) CdTeSe@TNTs and (c) CdTeSe QDs.

Fig. 2. HRTEM images for the as-prepared (a, b) CdTeSe QDs, (c) TNTs, (d,e) CdTeSe@TNTs and (f) EDX spectra of CdTeSe@TNTs. The insets of (c) and (d) are SEM images of TNTs and CdTeSe @TNTs, respectively.

Fig. 3. UV-vis diffuse reflection absorption spectra of TNTs, CdTeSe QDs and CdTeSe@TNTs.

Fig. 4. (a) PL emission spectra and (b) fluorescence lifetime obtained from CdTeSe QDs and CdTeSe@TNTs excited by 400 nm.

Fig. 5. (a) Amperometric $I-t$ curves and (b) electrochemical impedance spectroscopy for TNTs and CdTeSe@TNTs.

Fig. 6. (a) Photodegradation efficiency of RhB and (b) the kinetics of RhB photodegradation with different photocatalysts or without photocatalyst.

Fig. 7. DMPO spin-trapping ESR spectra of CdTeSe@TNTs in (a, b) methanol solutions and (c, d) aqueous solutions, respectively.

Fig. 8. (a) Effect of initial RhB concentration on photocatalytic degradation, and (b) three consecutive cycles of photocatalytic degradation of RhB.

Scheme 1. Model proposed for the formation of CdTeSe@TNTs nanocomposites.

Scheme 2. Schematic photocatalytic mechanism of CdTeSe@TNTs nanocomposites.

Fig.1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.

Scheme 1.

Scheme 2.