CdS nanoparticles decorated anatase TiO₂ nanotubes with enhanced visible light photocatalytic activity

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ABSTRACT

One-dimensional nanotubes are promising nanostructured materials for environmental applications. In this study, CdS nanoparticles decorated anatase TiO₂ nanotubes were fabricated using an alkaline hydrothermal combined surface precipitation method. The structure and properties of the prepared samples were characterized by XRD, TEM, UV–vis/DRS, N₂ adsorption–desorption and XPS. It was found that the as-synthesized CdS/TNTs consisted of anatase TiO₂ nanotubes and cubic phase CdS. CdS nanoparticles were highly dispersed on the tube walls of TNTs. In comparison with P25 and TNTs, CdS/TNTs exhibited strong visible light absorption at about 550 nm. Compared to P25, TNTs, CdS nanoparticles and CdS/TiO₂, CdS/TNTs exhibited obviously enhanced visible light ($\lambda > 420$ nm) photocatalytic activity in the decomposition of Rh B and MO. This could be attributed to the synergic effects of some factors, such as the excellent crystallinity, electronic band structure, strong absorption in the visible light region, high specific surface area and large pore size. Based on the results of the study, the mechanism of photocatalysis on CdS/TNTs under visible light is also discussed.

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1. Introduction

One-dimensional (1D) nanostructured TiO₂ such as nanotubes, nanowires and nanoribbons, have attracted much attention due to their unique structural and electronic properties. So far, they have been extensively used in a lot of fields, such as solar cells, lithium batteries, photodetectors, light waveguides, gas sensing, photocatalysis [1–10], and particularly used as photocatalysts in the degradation of organic pollutants in environment [11]. Among 1D TiO₂ nanostructures, TiO₂ nanotubes (TNTs) possess high specific surface area and nanotubular morphology, the nanotubular features of TiO₂ provide a large amount of channels for enhanced electron transfer, which is important during photocatalytic oxidation of organic compounds. It has been reported that anatase TiO₂ nanotubes showed higher photocatalytic activity for degradation of organic compound than anatase TiO₂ nanoparticles [12–17].

However, there are two obvious drawbacks for TNTs photocatalyst [18]. First, TNT is a wide band gap semiconductor which can only absorb UV light with the wavelength below 390 nm, this significantly hinders the utilization of the solar spectrum. Second, the quantum efficiency of TNT in photocatalytic reactions under UV light irradiation is very low. To improve the visible light

photocatalytic activity, many efforts have been made, such as dye sensitisation [19], doping [20–24], and coupling with low bandgap semiconductors like PbS [25], CdTe [26], CdSe [27], ZnFe₂O₄ [28], Cu₂O [29], and CdS [18,30–32]. Among the low bandgap semiconductors, CdS has attracted much attention, it can be excited by visible light to produce electrons and holes due to the narrow band gap of 2.42 eV [33]. Previous studies have shown that in the CdS/TiO₂ system, heterojunctions between TiO₂ and CdS nanoparticles are formed and the conduction band (CB) of CdS is about 0.5 eV (more negative than that of TiO₂). So no holes generated in the CB of TiO₂, and the recombination of electrons–holes pairs is inhibited in the CdS/TiO₂ system. As a result, the coupled system can enhance light-harvesting efficiency, thus improving the photocatalytic performance of the catalyst. Recently, increasing efforts have been made on coupling TNTs with semiconductors to form efficient composite photocatalysts [34]. The prepared composites show high photocatalytic activities because of the synergic effects between TNTs and the semiconductors [34]. Various methods have been used to prepare CdS nanoparticles modified TNTs, such as ion-exchange reaction [35–37], employing sulfur powder and Cd²⁺ in dimethyl sulfoxide [38], and sequential chemical bath deposition [39,40].

In this work, we fabricate CdS nanoparticles decorated anatase TiO₂ nanotubes via an alkaline hydrothermal combined surface precipitation method. CdS nanoparticles with controllable size

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were grown onto the surfaces of TNTs by reacting Na_2S with the Cd^{2+} ions absorbed on the pretreated surfaces. Under visible light irradiation, the photogenerated electrons from CdS can transfer to the conduction band of TNTs, thus facilitating the separation of photogenerated electrons and holes, which contributes to the enhanced visible light photocatalytic activity for oxidation of organic pollutants.

2. Experimental

2.1. Photocatalyst synthesis

2.1.1. Materials

The chemicals rhodamine B (Rh B), methyl orange (MO), sodium hydroxide (NaOH), cadmium nitrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), and sodium sulfide (Na_2S) were obtained from Beijing Chemical corporation (Beijing, China). Anatase titania nanosized powder (10 nm in size) was supplied from Alfa Aesar Co., Ltd. (Tianjin, China). All of the chemicals are analytic grades and used as received without further purification. Deionized water used in the synthesis was from local sources.

2.1.2. Synthesis of TNT

For the synthesis of TNTs [18], anatase titania powder (0.5 g) and an aqueous solution of NaOH (10 M, 40 mL) were mixed and kept stirring to form a homogeneous suspension, which was then transferred into a Teflon-lined autoclave and hydrothermally treated at 120 °C for 48 h in an oven. After the reaction, the precipitate was separated by filtration and washed with deionized water until the pH was neutral. In the subsequent step, the wet cakes were dispersed into 100 mL of 0.1 M HCl solution and kept under ambient conditions for 24 h, in order to promote proton exchange. The HCl treatment process was repeated for three times, each day with a fresh 0.1 M HCl solution, followed by washing with deionized water, and then dried at 30 °C under vacuum for 48 h. The as-synthesized titanate nanotubes were then calcined at 400 °C in air for 2 h to form TiO_2 nanotubes (TNTs).

2.1.3. Fabrication of CdS/TNTs nanocomposites

The obtained TNTs were added into $\text{Cd}(\text{NO}_3)_2$ aqueous solution (20 mL, containing 0.39 g $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) to allow Cd^{2+} ions to be absorbed on the surfaces of TNTs (pH = 4.0). To grow CdS nanoparticles on the TNTs, Na_2S aqueous solution (20 mL, containing 0.11 g Na_2S) was added, significantly increasing the pH of the solution from 4.0 to 10.0. The mixture was placed in a 100 mL Teflon-lined autoclave, and then kept at 120 °C for 12 h. Interaction between Cd^{2+} and free S^{2-} ions in the solution then proceeded, resulting in the continuous formation of CdS nanoparticles on the surface of TNTs. After cooling the autoclave to room temperature, the precipitate was separated by filtration and washed with deionized water until the pH was neutral. No Cd^{2+} ion (<0.01 mg/L) was detected in the filtrate indicating that almost all Cd^{2+} ions had reacted with S^{2-} and completely loaded onto the TiO_2 TNTs. Finally, the samples were dried at 30 °C under vacuum for 48 h. TNTs were also treated by the same way mentioned above without the addition of $\text{Cd}(\text{NO}_3)_2$ (S-doped TNTs). CdS/ TiO_2 was prepared using the same method except that TNTs were replaced by anatase TiO_2 .

2.1.4. Synthesis of CdS nanoparticles

The preparation process was the same as that for CdS/TNTs nanocomposites except that no TNTs was added.

2.2. Characterization methods

The crystalline structure and phase component of the synthesized samples were determined using X-ray diffraction

(Phillips PW 1050–3710 Diffractometer) with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$), operated at a tube current of 40 mA and a voltage of 45 kV. Data were collected over 2θ values from 10° to 80°, at a scan speed of 1°/min. The surface morphology and particle size were observed by transmission electron microscopy (HRTEM, JEM-2011), with an accelerating voltage of 200 kV. N_2 adsorption–desorption isotherms of the samples were conducted in a Micromeritics ASAP 2010 instruments, the samples were degassed at 180 °C for 3 h before the actual measurement, the BET specific surface area and pore size distribution of the samples were calculated from the isotherms using the BET method and Barrer–Joyner–Halenda (BJH) method. The UV–vis diffuse reflectance spectra were measured on a Perkin Elmer Lambda 750S UV/Vis spectrometer equipped with an integrating sphere assembly. The spectra were recorded at room temperature in air from 250 to 700 nm. X-ray photoelectron spectroscopy was performed using a Perkin–Elmer RBD upgraded PHI-5000C ESCA system with monochromatic Mg K α excitation and a charge neutralizer was used to investigate the surface electronic states of the samples. All the bonding energies were calibrated to the C 1s internal standard peak (284.8 eV) of surface carbon.

2.3. Photocatalytic activity measurements

The photocatalytic activity of CdS/TNTs heterostructure photocatalyst was evaluated by the photodegradation of Rh B and MO under visible light irradiation. In this work, the photocatalytic reactions were conducted in an open reactor with a cooling–water–cycle system keeping the reaction temperature constant. The light source was a 300 W xenon lamp (CHF-XQ-500 W, Beijing Changtuo Co., Ltd., wavelength range, $\lambda = 190\text{--}1100 \text{ nm}$) equipped with a 420 nm cut-off glass filter (removing the UV irradiation below 420 nm wavelength, $\lambda > 420 \text{ nm}$), and the light intensity was 50 mW/cm². Then 250 mg of CdS/TNTs were suspended in 500 mL of Rh B (20 mg/L) or MO (20 mg/L) solution. Before the photoreactions, the suspension was stirred in the dark for 120 min to achieve adsorption/desorption equilibrium. During the photoreactions, the suspension was stirred continuously. At a given time, 4 mL of the solution was taken from the reactor. For comparison, the photocatalytic activities of P25, CdS, pure TNTs, CdS/ TiO_2 and S-doped TNTs were also examined under the same conditions. The photocatalysts were separated from the solution by centrifugation, and the concentration of the remaining Rh B and MO in solution was determined by UV–vis spectrophotometer (UV-2450, Japan) at the maximum absorbance peak (554 nm for Rh B and 465 nm for MO).

3. Results and discussion

3.1. Characterization

3.1.1. XRD analysis

XRD patterns of the as-prepared TNTs, CdS NPs and CdS/TNTs were shown in Fig. 1. As can be seen in Fig. 1a, the peaks at $2\theta \approx 25.2^\circ, 29.7^\circ, 48.1^\circ, 54.1^\circ, 54.9^\circ, 62.7^\circ, 68.9^\circ, 70.1^\circ$, and 75.1° can be ascribed to the (101), (004), (200), (105), (211), (204), (116), (220), and (215) crystalline planes of the anatase phase (JCPDS No. 21-1272), indicating that the crystal phase of TNTs is anatase TiO_2 . The XRD pattern of CdS NPs (Fig. 1b) is in good agreement with the cubic phase CdS, and the peaks at $26.5^\circ, 43.9^\circ$, and 51.9° is corresponding to the (111), (220) and (311) planes of CdS (JCPDS No. 65-2887). As can be seen in Fig. 1c, besides the anatase TiO_2 , the cubic phase CdS can also be detected in CdS/TNTs, and no other impure peaks can be observed, suggesting a two-phase composition of anatase TiO_2 and CdS in CdS/TNTs heterostructures.

Fig. 1. XRD patterns of the as-prepared anatase TiO_2 nanotubes (a), CdS nanoparticles (b) and CdS/TNTs (c).

3.1.2. TEM observation

The morphologies and structures of TNTs, CdS NPs and CdS/TNTs were characterized by TEM. It is observed from Fig. 2a that, the as-synthesized TNTs exhibited uniform nanotubular 1D structure along with the length, the inner diameter of the nanotubes is 5.0–6.0 nm whereas the outer diameter is 9.0–10.0 nm. As shown in Fig. 2b, the average size of CdS NPs is ~ 5 nm. As can be seen in Fig. 2c, the nanotubular structure of TNTs were still well-maintained in CdS/TNTs, and CdS nanocrystals with a diameter of ~ 5 nm were dispersed well on the walls of TNTs. It successfully avoids the agglomeration of CdS nanoparticles and creates intimate contacts between CdS nanoparticles and TNTs. This novel structure of CdS/TNTs is regarded as a main reason for their improved photocatalytic activity, which will be discussed in the following sections.

3.1.3. BET surface area and pore structure

Fig. 3 shows the N_2 adsorption–desorption isotherms and pore size distribution of TNTs and CdS/TNTs. The N_2 adsorption/desorption isotherms exhibit a hysteresis loop at relative pressure higher than $P/P_0 = 0.4$, indicating the existence of mesopores. The adsorption isotherms for the two samples present a typical type IV isotherm with H_3 hysteresis according to the IUPAC classification [41], suggesting the existence of slit-like pores [42]. TiO_2 nanotubes are multiwalled scrolls and formed through sheet folding or wrapping mechanism, there may be some slits on the nanotubes, so it is reasonable that they show the H_3 loop. The pore size distribution showed that the average pore diameters were 5.4 and 4.2 nm for TNTs and CdS/TNTs, respectively. The surface area

for TNTs and CdS/TNTs are 343.34 and 273.62, respectively. This may be caused by CdS nanoparticles which covered TNTs surface and deposited inside the pores of TNTs.

3.1.4. UV–vis diffuse reflectance spectra

Fig. 4 shows the optical properties of P25, TNT CdS and CdS/TNTs. It was observed that P25 and TNTs exhibited photore-sponse in the UV region with a wavelength below 390 nm due to its large energy band gap (3.2 eV), which is typical of anatase titania [33]. It was noted that blank CdS showed a sharp absorption edge at around 550 nm, it is well known that CdS has a narrow energy band gap and thus shows better visible light response ability. The introduction of CdS into TNTs has a significant effect on the optical property of CdS/TNTs, they show an enhanced absorbance in the visible light region with a sharp absorption edge at around 550 nm, and they are able to be photoexcited to generate electron–hole pairs under visible light irradiation [18].

3.1.5. XPS analysis

X-ray photoelectron spectroscopy (XPS) was used to further investigate the elemental composition and surface chemical state of CdS/TNTs. As can be seen in Fig. 5a, the elemental composition on the surface of CdS/TNTs are S, C, Cd, Ti and O, which correspond to the values of the binding energy at 162.2 eV, 285.6 eV, 405.8 eV, 458.8 eV and 531.4 eV, respectively [33]. The XPS spectrum for the C 1s peak might be attributed to the adventitious carbonaceous species formed in the process of sample preparation [32]. From the XPS spectrum of Ti 2p (Fig. 5b), the binding energies of Ti 2p_{3/2} and Ti 2p_{1/2} in CdS/TNTs are 458.6 and 464.2 eV, respectively. This can be ascribed to Ti^{4+} on the surface of CdS/TNTs [33]. Fig. 5c shows the O 1s XPS spectrum of CdS/TNTs, the asymmetric peaks located at 529.7 and 531.6 eV can be seen, the binding energy at 531.6 eV was ascribed to the oxygen of surface hydroxyl groups ($-\text{OH}$), and that at 529.7 eV was assigned to the lattice oxygen of TiO_2 [33]. Fig. 5d shows the Cd 3d XPS spectra of CdS/TNTs, there are two sharp peaks at binding energies of 411.6 eV and 404.9 eV, which was assigned to the characteristic peaks of Cd 3d_{3/2} and Cd 3d_{5/2}, respectively, indicative of Cd^{2+} in CdS/TNTs [43]. Furthermore, a spin–orbit separation of 6.7 eV between Cd 3d_{3/2} and Cd 3d_{5/2} can further confirm the existence of Cd^{2+} on the surface of CdS/TNTs. Fig. 5e demonstrates the XPS spectrum of S 2p, the peaks located at 162.1 eV and 161.0 eV could be ascribed to the characteristic peaks of S 2p_{1/2} and S 2p_{3/2}, respectively, indicating that S^{2-} is the main existing form on the surface of CdS/TNTs for S element. Furthermore, 1.1 eV difference between the binding energies of S 2p_{1/2} and S 2p_{3/2} can also indicate the existence of S^{2-} in CdS/TNTs [43]. As can be seen from the XPS results, CdS and TiO_2 co-exist in CdS/TNTs nanocomposites.

Fig. 2. TEM images of TNTs (a), CdS nanoparticles (b) and CdS/TNTs nanocomposites (c).

Fig. 3. Nitrogen adsorption-desorption isotherms (a) and pore size distribution (b) of TNTs and CdS/TNTs.

Fig. 4. UV-vis absorption spectra of P25, TNTs, CdS and CdS/TNTs.

3.2. Photocatalytic activity

In this work, the photocatalytic activity of CdS/TNTs was evaluated by the decoloration of Rh B and MO solution without investigating the degradation intermediates in detail. For comparison, the photocatalytic activities of P25, TNTs, CdS and CdS/TiO₂ as well as without the photocatalyst (direct photolysis) were also tested in the same system. As depicted in Fig. 6a, the degradation of Rh B by direct photolysis was almost negligible after 120 min of visible light irradiation. Although P25, pure TNTs could not respond to visible light, Rh B can be degraded slowly under visible light irradiation in the presence of P25 and pure TNTs, and the degradation efficiencies reached 28.5% for P25 and 47.3% for TNTs, respectively, after 120 min of photoreaction, this can be attributed to the photosensitized capability of Rh B [44]. 73.6% of Rh B could be decomposed by CdS under visible light irradiation for 120 min. 82.4% of Rh B can be removed by S-doped TNTs (not shown here). As can be seen, CdS/TNTs exhibited higher photocatalytic activity than CdS/TiO₂, and the degradation efficiency of Rh B for CdS/TNTs and CdS/TiO₂ were 99.8% and 93.1% respectively after 120 min visible light irradiation. The degradation rate of CdS/TNTs for Rh B is faster than that of CdS/TiO₂, Rh B could be almost completely degraded by CdS/TNTs after 60 min visible light irradiation.

Because of its stabilization and low photosensitized property, MO solution was more difficult to be decolorized compared to Rh B. However, as can be seen in Fig. 6b, CdS/TNTs presented highest photocatalytic activity under visible light irradiation among all samples, and the decoloration efficiency of MO solution was 91.4% under visible light irradiation for 240 min. This further confirmed that CdS/TNTs exhibited excellent visible light photocatalytic activity. As can be seen, the decoloration of Rh B and MO over

the photocatalysts prepared in this work show similar trends: CdS/TNTs possess the highest photocatalytic activity under visible light irradiation among all the samples. The excellent crystallinity, the improvement of visible-light adsorption, larger surface area, the unique morphologies and nanostructures of the tubular CdS/TNTs, the intimate contact and the synergistic effect within the heterojunctions between CdS and TNTs [44], were supposed to be responsible for the highly efficient photocatalytic activity of CdS/TNTs [45].

Fig. 7 shows that in the first cycle, the degradation efficiency decreased obviously, and in the subsequent cycles, the degradation efficiency decreased slowly, this can be attributed to the agglomeration of CdS/TNTs. However, the removal efficiency after five cycles can still reach 88.5%, indicating its high durability and stability. Therefore, the recycling of CdS/TNTs is possible, CdS/TNTs should be a promising photocatalyst for treatment of organic contamination.

3.3. Photocatalytic mechanism

Fig. 8 shows the schematic diagram of the separation of photo-generated electrons–holes pairs on the interface of CdS/TNTs under visible light irradiation. Firstly, CdS is excited to yield electron–hole pairs under visible light irradiation due to its narrow energy band gap (~2.4 eV) (Eq. (1)). The electrons in the CB of CdS, are transferred to the CB of TNTs (Eq. (2)) because of the matched CB potential position and the intimate contact between CdS nanoparticles and TNTs, thus efficiently inhibiting the recombination of electron–hole pairs. Secondly, the electrons in the CB of TNTs react with molecular oxygen to generate superoxide radical ($\cdot\text{O}_2^-$) (Eq. (3)) and hydrogen peroxide (H_2O_2) (Eq. (4)) [44]. Then $\cdot\text{O}_2^-$ and H_2O_2 inter-react to form hydroxyl radical $\cdot\text{OH}$ (Eq. (5)). Thirdly, dye molecules are oxidized by these oxidants step by step (Eq. (6)). In addition, the holes themselves can directly oxidize Rh B and MO molecules (Eq. (7)), and this is considered as the dominant pathway, because it is the prerequisite step for the photocatalytic reaction that dye molecules adsorbed on the surface of CdS/TNTs. As for this study, it is thought that both indirect oxidation by hydroxyl radical and direct oxidation by holes simultaneously functioned to oxidize dye molecules.

Fig. 5. XPS spectra of CdS/TNTs. (a) The whole survey spectrum; (b) Ti 2p XPS spectrum; (c) O 1s XPS spectrum; (d) Cd 3d XPS spectrum and (e) S 2p XPS spectrum.

Fig. 6. Decoloration curves of Rh B solution (a) and MO solution (b) by the samples under visible light irradiation ($\lambda > 420$ nm).

4. Conclusions

In this study, a new type of 1D nanostructure of CdS/TNTs heterostructures were successfully fabricated via an alkaline hydrothermal method combined surface precipitation method. From the above experimental results, it was revealed that CdS/TNTs consisted of anatase TiO_2 nanotubes and cubic phase CdS,

Fig. 7. Recycling of CdS/TNTs for photodegradation of Rh B under visible light irradiation.

Fig. 8. Energy-band diagram and photocatalytic mechanism of CdS/TNTs under visible light.

CdS nanoparticles were well deposited on the tube walls. This unique structure can transfer the photogenerated electrons very efficiently, thus effectively inhibiting the recombination of photoexcited electron–hole pairs. Compared with P25 and TNTs, the absorption edge of CdS/TNTs was drastically extended to around 550 nm. CdS/TNTs exhibited highest visible light photocatalytic activity due to the increase of specific surface area for more absorbed dyes, the electronic band structure and the additional synergistic effect between CdS and TNTs.

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