Preparation and visible-light-driven photocatalytic activity of WO$_3$@TiO$_2$ core-shell nanorods

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Abstract. This study reports a visible-light-driven photocatalyst of WO$_3$@TiO$_2$ core-shell nanorods prepared by a simple hydrothermal method and followed by the sol-gel method for surface coating. The composition, morphology and the related properties were characterized by several advanced techniques, such as XRD, TEM, and UV-vis spectroscopy. The results show that the WO$_3$@TiO$_2$ core-shell nanorods are composed of the WO$_3$ nanorods with the width of ~200 nm and the TiO$_2$ shell with the thickness of 50-100 nm. The UV-vis absorption spectra show that the combination can make the adsorption range of the nanocomposites shift to long wavelength. The degradation of methylene blue (MB) was used to measure the photocatalytic activity of the catalyst under visible light irradiation. And the experimental results show that pure WO$_3$ nanorods and TiO$_2$ nanoparticles exhibit common photocatalytic performance with the degradation efficiency of 49% and 75% in 240 min and the reaction kinetic constant of 0.00267 min$^{-1}$ and 0.00554 min$^{-1}$, respectively. However, the photocatalytic performance has been greatly improved by the formation of the core-shell structure with various molar ratios of W to Ti (1:2, 1:5, and 1:7). The core-shell nanorods (1:5) exhibits the largest reaction rate constant (0.01485 min$^{-1}$), which is 5.56 times higher than that of pure WO$_3$ and 2.68 times higher than that of pure TiO$_2$, respectively. These findings may be useful for the photocatalyst for practical use.

1. Introduction

In recent years, titanium dioxide (TiO$_2$), as one of the typical photocatalytic materials, has been extensively studied due to its excellent performance in catalysis, gas sensor, and photocatalysis [1-3]. Particularly the photocatalytic property was reported by Fujishima and Honda. However, due to the wide band gap (~3.2 eV), TiO$_2$ can only be excited by ultraviolet light (less than 10% of the solar light), which highly impedes the practical applications [4-7]. The ways to improve the photocatalytic performance mainly include surface modification with noble metals or semiconductors, morphology control and elemental doping [8-9] [10-11]. Among them, surface modification has been proved to be an effective way due to its wide adjustment ability [12].

Modified metal oxide materials include tungsten oxide, iron oxide, vanadium oxide, zinc oxide, cuprous oxide, etc [13-15]. Among these semiconductors, tungsten trioxide (WO$_3$) is considered as a highly promising photocatalytic material due to the narrow bandgap (~2.8eV) [16]. For example, Hsiao et al. prepared WO$_3$·0.33H$_2$O nanoparticles by a microwave-assisted hydrothermal method. The
nano-particles show excellent photocatalytic degradation of MB under UV- and visible-light irradiation [17]. Lorret et al. reported WO$_3$-TiO$_2$ nanocomposites synthesized by a sol-gel method, in which the WO$_3$ was embedded in the surface of titanium dioxide. The nanocomposites exhibit good photocatalytic activity toward MB under visible light irradiation. In this study, the effect of the amount of WO$_3$ was systematically investigated [18]. Therefore, the WO$_3$-TiO$_2$ nanocomposites are a promising photocatalyst for practical use.

Core-shell structures, as one of the most important ways for surface modification, have obtained intensive research interests due to representing diverse functions related components integrated into one unit and widely applying in renewable energy, advanced biomedicine, and environmental protection. Considering WO$_3$ and TiO$_2$, the core-shell structure of these metal oxides (WO$_3$@TiO$_2$) can be expected for the enhanced photocatalytic activity [19]. The main reason is that the work function of tungsten oxide (about 4.5 eV) is higher than that of titanium dioxide (about 4.33 eV), which makes photogenerated electrons transferred to WO$_3$ from TiO$_2$ and lowers the electron-hole recombination effectively [20]. On the other hand, after the combination of the two nanomaterials, the Fermi level reaches equilibrium, which tunes the band gap and broadens the absorption range of the compound to the visible light range [21].

In this study, the WO$_3$@TiO$_2$ core-shell nanorods were synthesized by a hydrothermal method and a sol-gel method for the surface coating [22-23]. The composition, morphology, and related particle properties of the synthesized nanocomposites were characterized by advanced techniques such as XRD, TEM, and UV-vis spectroscopy. And the photocatalytic properties of the synthesized nanocomposites were tested by the degradation of methylene blue (MB) under visible light irradiation.

2. Experimental section

2.1 Materials.

All reagents used to prepare the nanocomposites were of analytical reagent grade. Titanium (IV) butoxide (TBT, 97%), Na$_2$WO$_4$•2H$_2$O, and HCl (36%) were purchased from Sinopharm Chemical Reagent Limited Corporation. Ultra-pure water was used in all the procedures. All the chemicals were used as received and without further purification.

2.2 Synthesis of titanium dioxide.

Tungsten oxide (WO$_3$) was prepared by hydrothermal method. Briefly, a certain amount of Na$_2$WO$_4$•2H$_2$O powder was dissolved in ultra-pure water to prepare a 0.1 mol/L aqueous solution with stirring. Then, the HCl was added into the solution to adjust the pH to 2.4. Afterward, the solution was kept at room temperature for 30 min under vigorous magnetic stirring. After that, the precursor was transferred to 20 mL Teflon-lined stainless steel autoclave for hydrothermal reaction at 180°C for 44 hours. After naturally cooled down to room temperature, the precipitates were collected by centrifugation and washed with ultra-pure water and ethanol for several times. Finally, the product was dried at 60 °C for 12 hours for further use.

2.3 Synthesis of WO$_3$@TiO$_2$ nanorods.

0.05 mL of TBT was added to 10 mL of ethylene glycol. The mixture was magnetically stirred for 8 h at room temperature and marked as solution A. Then, 10.44 mg WO$_3$ was dispersed into 150 mL acetone by sonication for 30 min, marking as solution B. 15 mL solution A was mixed with solution B under ultrasound, then it would turn into a milky white suspension. Finally, aging for several days. After centrifugation and washing with ultra-pure water for several times, the precipitate was redispersed in 10 mL ultra-pure water and heated at 100 °C for 2 hours for crystallization of TiO$_2$. Finally, the precipitate was washed with ethanol several times and dried at 60 °C for 12 hours.
2.4 Characterizations.
The composition and purity of the synthesized nanocomposites were examined using Phillips X'pert Multipurpose X-ray Diffraction System (MPD) equipped with graphite monochromatized Cu-Kα radiation (λ = 1.54 Å) in the 2θ range of 10-90°. The morphologies were observed on a JEOL 1400 microscope (TEM), operated at an accelerated voltage of 100 kV. The optical properties were obtained on a Shimadzu UV-2600 UV-vis spectrophotometer (Varian) with a 1 cm quartz cell.

2.5 Measurement of photocatalysis.
The photocatalytic performance of the as-prepared sample was investigated by the photo degradation of MB under visible light irradiation. A 300 W xenon lamp (PLS-SXE300C) equipped with AM 1.5G total reflection filters was used to obtain visible light to arouse the reaction, and the lamp was positioned about 10 cm above the liquid meniscus. 250 mL 30 ppm MB solution was transferred to the quartz reactor, then 20 mg the as-prepared photocatalyst was added to the dye solution. Before irradiation, the solution was magnetically stirred in the dark for 30 min to achieve the adsorption-desorption equilibrium. During the experiment, the suspension was continuously magnetically stirred. The circulating water was employed to cool the radiation source, and 3 ml samples were collected for every 15 min. After centrifugation, the photocatalytic degradation efficiency was examined by measuring the change in the characteristic peak of methylene blue in the supernatant by the Shimadzu UV-2600 UV-vis spectrophotometer. The degradation efficiency of MB in each sample can be represented using the following equation:

\[ \text{Degradation efficiency} = \frac{C}{C_0} \times 100\% \]  

Where \( C_0 \) is the initial MB absorbance and \( C \) is the absorbance of the sample obtained at the different time. The reaction rate (k) can be estimated as a linear relationship between \( \ln(C_0/C) \) and time (t):

\[ kt = \ln(C_0/C) \]  

3. Results and discussion

3.1 Composition analysis.
The XRD patterns of WO₃ and WO₃@TiO₂ with different molar ratios of W/Ti are shown in Fig 1. The black line shows the XRD pattern of pure WO₃, in which the peaks centered at 2θ = 14.0°, 22.8°, 24.4°, 28.2°, 33.6°, 36.6°, 37.6°, 42.9°, 44.4°, 46.5°, 49.1°, 49.9°, 52.1°, 55.6°, 58.4°, 63.5°, 69.1°, 70.7°, 72.7°, 77.7°, 80.3° and 84.8° can be indexed to (100), (001), (110), (200), (111), (201), (210), (300), (211), (002), (301), (220), (310), (221), (400), (401), (321), (222), (411), (402), (420), and (421). The other three lines represent WO₃@TiO₂ with different molar ratios of W/Ti (1:2, 1:5, and 1:7). Compared to the XRD pattern of pure WO₃, a peak at 25.7° assigned to (101) plane of TiO₂ can be observed from the patterns. It is to note that the intensity of TiO₂ (101) peak increases gradually with the proportion of TiO₂. No other peaks related to impurities are observed, which indicates the high purity of the products.
3.2 Transmission electron microscopic analysis.

Fig 2. shows the TEM images of the WO$_3$ nanorods and the WO$_3$@TiO$_2$ core-shell nanostructures. Fig. 2 (a) shows an individual WO$_3$ nanorod with the diameter of ~200 nm and the length of several micrometers. Figs 2 b-d show the TEM images of WO$_3$@TiO$_2$ nanostructures with different molar ratios of Ti to W. The high contrast part represents WO$_3$, while light contrast corresponds to TiO$_2$. It can be seen that the TiO$_2$ shell is successfully coated on the surface of WO$_3$ nanorods. And when the molar ratio of W/Ti is 1:2, the thickness of TiO$_2$ is around 50 nm. A thicker TiO$_2$ shell (~100 nm) can be observed with the ratio increase to 1:5. It is noted that the thickness of TiO$_2$ shell no longer increases when the ratio reaches 1:7, but some TiO$_2$ nanospheres appear. This may be the reason why the photocatalytic activity decreases when the molar ratio of W/Ti is 1:7.

Figure 2. TEM images of WO$_3$ (a) and WO$_3$@TiO$_2$ core-shell nanostructure with various molar ratio of W/Ti (b) 1:2, (c) 1:5, (d) 1:7.
3.3 **Optical property.**

![Figure 3. UV-vis spectra of WO₃, TiO₂, and WO₃@TiO₂ core-shell nanocomposites.](image)

The optical properties of WO₃, TiO₂, and WO₃@TiO₂ nanocomposites were characterized by the UV-vis absorbance spectra with the range of wavelength from 250 to 800 nm, as shown in Fig 3, the absorption peak of WO₃ nanorods is centered at 316 nm, and TiO₂ nanoparticles is centered at 319 nm, which is in agreement with the previous study [19]. Compared with the pure WO₃ and TiO₂, a small red-shift (from 316 nm to 320 nm for 1:2, 316 nm to 407 nm for 1:5 and 316 nm to 354 nm for 1:7) of various molar ratios of WO₃@TiO₂ core-shell nanocomposites can be seen in the results. Namely, as the Ti content increases, the red-shift of the maximum adsorption become larger first, then lower. When the molar ratio of W/Ti increases to 1:5, the adsorption peak reaches the highest: 407 nm [24].

3.4 **Photocatalytic activity.**

To evaluate the photocatalytic activity of the as-prepared catalysts, the photo-degradation of MB by various photocatalysts was investigated under visible light irradiation. Before irradiation, the solution was magnetically stirred in the dark for 30 min to achieve the adsorption-desorption equilibrium. Fig 4. (a) shows the degradation rate of MB by different photocatalysts under visible light irradiation. The photocatalytic activities of different WO₃@TiO₂ core-shell nanocomposites are better than those of pure WO₃ and TiO₂. And the catalyst with W/Ti ratio of 1:5 shows the best photocatalytic performance (100% of MB in 240 min). Conversely, only 49% and 75% of the degradation rate can be obtained from WO₃ and TiO₂ in the same period, respectively. Fig 4. (b) shows the reaction rate constant of WO₃, TiO₂, and WO₃@TiO₂ under visible light irradiation. Compared with pure WO₃ and TiO₂, WO₃@TiO₂ core-shell nanostructures show larger rate constant (0.00969 min⁻¹ for 1:2, 0.01485 min⁻¹ for 1:5 and 0.00952 min⁻¹ for 1:7). It can be seen that the WO₃@TiO₂ with the ratio of 1:5 shows the largest reaction rate constant, which is 5.56 times higher than that of pure WO₃ and 2.68 times higher than that of pure TiO₂, respectively.

The mechanism of the semiconductor photocatalysis is: electrons can be excited by irradiation from the valence band to the conduction band, and holes are generated on the valent band of TiO₂. The holes react with water to form hydroxyl radicals with high oxidation activity, which can degrade the organic contaminants in water [17-18]. When the WO₃@TiO₂ core-shell nanocomposites formed, the mechanism is slightly different. After the formation of the core-shell structures, the Fermi levels of the two materials reach equilibrium. Thus, the band gap can be bent since the work function of tungsten oxide is higher than that of titanium dioxide. Under visible light, the photo-generated electrons generated in TiO₂ can be transferred to the conduction band of WO₃. More electrons and holes can be
formed in this process and the pathway of electrons is increased which can effectively prevent electron-hole recombination, and further improve the photocatalytic performance.

4. Conclusions
In this study, WO$_3$@TiO$_2$ core-shell nanocomposites are synthesized by a simple hydrothermal method and the sol-gel method for surface coating. The structure can reduce the possibility of the recombination of electron-hole pairs. Therefore, compared with pure WO$_3$ and TiO$_2$, WO$_3$@TiO$_2$ core-shell nanorods exhibit high photocatalytic performance toward the degradation of MB under visible light. The photocatalytic performance has been greatly enhanced by the formation of the core-shell structure with various molar ratios of W to Ti (1:2, 1:5, and 1:7). The core-shell nanocomposites (1:5) exhibits the largest reaction rate constant (0.01485 min$^{-1}$), almost 5.56 times higher than that of pure WO$_3$ (0.00267 min$^{-1}$) and 2.68 times higher than that of pure TiO$_2$ (0.00267 min$^{-1}$), respectively. Besides, the mechanism of the semiconductor photocatalysis is introduced also. It is believed that these findings on WO$_3$@TiO$_2$ core-shell nanorods will be applied widely in environmental remediation.

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