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Full Length Article

In-situ synthesis of WO_3 nanoplates anchored on g-C_3N_4 Z-scheme photocatalysts for significantly enhanced photocatalytic activity

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ABSTRACT

The Z-scheme photocatalysts of WO_3/g-C_3N_4 composites with WO_3 nanoplates anchored on the surface of g-C_3N_4 were synthesized by *in-situ* acidic precipitation and following calcination procedure. The resultant photocatalysts were characterized by various analytical techniques. This face-to-face intimate contact between g-C_3N_4 and plate-like WO_3 not only increases the interfacial contact areas, but also facilitates the transfer and separation of photogenerated charge carriers. The photocatalytic activities of degradation Rhodamine (RhB) solution over WO_3/g-C_3N_4 composites were evaluated under visible light irradiation. The enhanced photocatalytic activity of WO_3/g-C_3N_4 composite could be attributed to the formation of the Z-scheme heterojunction system based on the active species trapping and hydroxyl radicals photoluminescence (PL) detection experiments. Furthermore, electrochemical impedance spectroscopy (EIS) and transient photocurrent measurements confirm the more efficient separation and transfer of photogenerated charge carriers on the WO_3/g-C_3N_4 composite than that of pure WO_3 or g-C_3N_4. This work would provide new insights into the design and preparation of face-to-face contact heterojunction photocatalysts for organic contaminant removal.

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1. Introduction

Semiconductor-based photocatalysis possesses a huge potential to solve the increasing energy demand crisis and severe environmental contamination problems under the solar light irradiation [1–4]. The efficient separation of photogenerated electron-hole pairs and inhibition recombination on the surface of photocatalysts is regarded as the critical issue to improve the photocatalytic activity. Unfortunately, single semiconductor photocatalyst alone is very difficult to achieve the effective separation of charge carriers due to the strong Coulombic force [3]. To promote the separation efficiency of photoexcited electrons and holes, construction of heterojunction composites has been extensively investigated for recent two decades [5–18]. However, the conventional type II heterojunction photocatalysts with a staggered band gap will lead to unfavorable losses of redox ability for photogenerated electrons and holes, which is hoped to be avoided [3]. More recently, the Z-scheme photocatalysts have been developed through rational integration of two narrow band gap semiconductors with the plants-inspired band structure arrangement, which not only enhances the charge separation efficiency, but also maximizes the redox abilities of the constituent photocatalysts [3]. Therefore, engineering the novel Z-scheme photocatalysts is becoming the urgent task to significantly enhance the photocatalytic activities of semiconductors.

Graphitic carbon nitride (g-C_3N_4), as a visible-light response (band gap about 2.7 eV), low-cost, non-metal and highly chemical stability photocatalyst, has recently received considerable attention. Due to its relatively negative conduction band (CB) edge position (about -1.2 eV vs. NHE), g-C_3N_4 usually has a good reduction capability of photoelectrons in the photocatalytic reaction. To further improve the photocatalytic activity of g-C_3N_4, design and preparation of g-C_3N_4 based Z-scheme photocatalysts is much desirable. Inspired by the above consideration, a lots of Z-scheme photocatalysts by integrating g-C_3N_4 with other semiconductors have been reported in the past five years, such as SnS_2/g-C_3N_4, TiO_2/g-C_3N_4, ZnO/g-C_3N_4, $BiVO_4$/Ag/g-C_3N_4, Ag_2CrO_4/g-C_3N_4, Bi_2MoO_6/g-C_3N_4, WO_3/g-C_3N_4 and so on [19–34]. The results show that the obtained Z-scheme photocatalytic systems could remarkably enhance the photocatalytic performance compared with single g-C_3N_4. Among these Z-scheme photocatalysts, WO_3/g-C_3N_4 systems have attracted more attention because WO_3 not only has a small band gap (about 2.7 eV) but also has relatively high valence band (VB) position (about 3.4 eV vs. NHE), which causes holes generated on the VB of WO_3 possess the excellent oxidation ability

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[35–40]. Moreover, the short distance between the VB position of g-C_3N_4 (about 1.5 eV vs. NHE) and the CB position of WO_3 (about 0.7 eV vs. NHE) is favorable for the transfer of photogenerated electrons from CB of WO_3 to the VB of g-C_3N_4 to form the fascinating Z-scheme photocatalytic system [30]. Although there are some reports on WO_3/g-C_3N_4 Z-scheme systems very recently, preparation of this heterojunction photocatalysts through a facile and low-cost method is still a challenge.

Herein, WO_3 nanoplates were directly deposited on the surface of g-C_3N_4 by *in-situ* acidic precipitation and the following calcination procedure. The photocatalytic activities for degradation of RhB under visible light irradiation over the WO_3/g-C_3N_4 composites with different WO_3 contents were comparatively investigated. The possible mechanism for the enhanced photocatalytic activity was proposed based on the obtained experimental results.

2. Experimental

2.1. Material preparation

g-C_3N_4 was synthesized by direct calcining of 10 g melamine at 550 °C for 3 h in an alumina crucible with a cover. The resultant yellow powders were collected for use without further treatment.

WO_3/g-C_3N_4 heterojunction composites were prepared as follows: an appropriate amount of as-fabricated g-C_3N_4 was added into 50 mL deionized water and sonicated for 30 min to ensure g-C_3N_4 disperse well. 0.79 g $Na_2WO_4 \cdot 2H_2O$ were dissolved into the above suspension solution under vigorous stirring at 80 °C. And then, 15 mL 10 mol/L hydrochloric acid was slowly dropped into the above mixture. After stirring for 5 min, the mixed solution was aged at 80 °C for 24 h. The resultant powders were collected and washed with ethanol and deionized water for several times, dried in air at 60 °C for 8 h. The collected precipitate was then calcined at 400 °C for 2 h in air with a heating rate of 5 °C/min. The WO_3/g-C_3N_4 composites with different WO_3 weight ratios were obtained by changing the addition amount of g-C_3N_4 as aforesaid procedure. The actual contents of WO_3 in the composites were determined by thermogravimetric (TG) measurement. For comparison, pure WO_3 was prepared at the same conditions without adding g-C_3N_4 powders at the beginning. Single g-C_3N_4 was second calcined at 400 °C for 2 h as reference.

2.2. Material characterization

The crystal phases of photocatalysts were analyzed by powder X-ray diffraction (XRD, Shimadzu XRD-7000 diffractometer) using Cu Kα irradiation at 40 kV and 30 mA. The morphology and elemental mapping distributions were measured on a JSM-7100F field emission scanning electronic microscope (FESEM). Microstructure analysis was performed by a JEOL JEM 2100F high-resolution transmission electronic microscope (HRTEM). TG analysis was carried out using Hitachi STA 7300 from 50 °C to 800 °C in an air flow with a heating rate of 10 °C/min. The X-ray photoelectron spectroscopy (XPS) was implemented on a VG Multilab 2000 with Al Kα source operating at 300 W. The ultraviolet–visible diffuse reflectance absorption spectra (UV-DRS) were recorded by a Purkinje General TU-1901 spectrophotometer using $BaSO_4$ as a reference. The fourier transform infrared spectra (FTIR) of samples were measured on a Thermo Nicolet Avatar 360 spectrometer using conventional KBr pellets. The Brunauer-Emmett-Teller (BET) specific surface areas of samples were determined by a Micromeritics ASAP 2020 nitrogen adsorption apparatus. The PL spectra were detected at room temperature on a PerkinElmer LS55 fluorescence spectrometer with the excitation wavelength of 320 nm.

2.3. Photocatalytic activity measurement

The photocatalytic activities of the WO_3/g-C_3N_4 heterojunction composites were evaluated by degradation of RhB aqueous solution under visible light irradiation on a photo-reactive equipment BL-GHX-IV (Shanghai Bilang Instrument Co. Ltd, China). In each experiment, 50 mg of photocatalysts were added into 50 mL of RhB solution with the initial concentration of 1.0×10^{-5} mol/L. A 300 W long-arc xenon lamp was used as the light source equipped 420 nm cutoff filters. Prior to turn on the light, the suspensions were stirred in the dark for 30 min to ensure the establishment of an adsorption-desorption equilibrium. At given irradiation time intervals, about 4 mL of the suspensions were collected and then the slurry samples including the photocatalysts and RhB solution were centrifuged (10000 rpm, 8 min) to remove the photocatalysts. The TU-1810 spectrometer was performed to analyze the concentration changes of RhB solution with the wavelength of 554 nm.

2.4. Photoelectrochemical measurement

EIS and transient photocurrent tests were conducted on an electrochemical system (CHI 760D, Shanghai Chenhua Instruments, China) with a three-electrode cell. The working electrodes were prepared on the indium tin oxide (ITO) glass. 10 mg of the photocatalyst was mixed with ethanol (1 mL) and Nafion aqueous solution (1 mL, 5 wt%) by sonication. The mixture (0.1 mL) was then dropped on ITO glass with an effective working area of 1 cm^2. After evaporation of ethanol in air, the photocatalyst was attached to the ITO glass surface. A platinum plate and Ag/AgCl electrode were used as the counter and reference electrodes, respectively. 0.1 mol/L Na_2SO_4 solution was used as the electrolyte. EIS measurements were carried out in darkness at 0.5 V with the amplitude of 5 mV under open circuit potential conditions. The frequency range was kept within 1 Hz to 100 kHz. A 300 W Xe lamp with a 420 nm cut-off filter acted as the light source in the transient photocurrent tests.

2.5. Active species trapping measurement

To determine the active species in the photocatalytic process, triethanolamine (TEOA), isopropanol (IPA) and *p*-benzoquinone (BQ) were respectively added into photocatalytic reactive solutions as the scavengers of holes (h^+), hydroxyl radicals ($\cdot OH$), and superoxide radicals ($\cdot O_2^-$) to investigate the effects of active species on the photocatalytic degrading RhB. The method was similar to the former photocatalytic activity test except for adding scavengers in the solution. The concentrations of TEOA, IPA, and BQ were 10 mmol/L, 10 mmol/L and 1 mmol/L, respectively.

3. Results and discussion

3.1. Photocatalyst characterization

TG analysis measurement was performed in air to determine the contents of WO_3 in the WO_3/g-C_3N_4 composites. As shown in Fig. 1, the WO_3 is relatively stable under heating in air from 50 °C to 800 °C and exhibits almost no weight loss. The pure g-C_3N_4 starts obvious weight loss at about 450 °C and decomposes totally approximately at 750 °C. The content of WO_3 in the composites can be calculated from the remaining weight after heating the samples at above 750 °C. For the four WO_3/g-C_3N_4 composites, the WO_3 contents in the composites are determined to be 11.6, 18.6, 33.4 and 49.3 wt%, respectively. It can be found that the g-C_3N_4 phase in the composites becomes more unstable with the increase of

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