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Unprecedented enhancement in visible-light-driven photoactivity of modified graphitic C_3N_4 by coupling with H_2WO_4

Qianqian Liu [a], Jing Ding [a], Yuanyuan Chai [a], Junqi Zhao [b], Shibiao Cheng [b], Baoning Zong [b], Wei-Lin Dai [a,*]

[a] *Department of Chemistry and Shanghai Key Laboratory of Molecular Catalysis and Innovative material, Fudan University, Shanghai 200433, PR China*
[b] *State Key Laboratory of Catalytic Materials and Reaction Engineering, Research Institute of Petroleum Processing, China Petroleum and Chemical Corporation, Beijing 100083, PR China*

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ABSTRACT

The modified graphitic carbon nitride (g-C_3N_4) nanosheets by coupling with H_2WO_4 are fabricated via an easy, mild and environmental-friendly impregnation method for the first time. Compared with bare g-C_3N_4 and H_2WO_4, the H_2WO_4/g-C_3N_4 composite shows significant enhancement in the visible-light-driven photoactivity toward the degradation of Rhodamine B (RhB). It is found that 10 wt.% H_2WO_4/g-C_3N_4 exhibits the best photocatalytic performance, with around 20 times higher activity than that of pure g-C_3N_4 nanosheets. The remarkably increased performance is mainly attributed to the existing synergistic interaction between H_2WO_4 and g-C_3N_4. The strong interaction could reduce the photoinduced electron–hole recombination and further improve the photocatalytic activity. Additionally, $^{\bullet}O_2^-$ is the dominating reactive species for the degradation of RhB, which has been confirmed by the radical scavengers tests. The synthesized photocatalysts present super stability even after nine successive runs. Considering the low-cost, easy preparation process and ultra-high activity, the H_2WO_4/g-C_3N_4 photocatalyst can be served as a promising candidate for environment cleaning and waste water treatment.

Introduction

Photocatalysis, based on its application in environment cleaning, waste water treatment, and water photo-splitting, has been a research focus in the field of environment science [1–3]. To date, nanostructured semiconductor materials (such as TiO_2, ZnO, ZnS, CdS, WO_3, graphitic carbon nitride (g-C_3N_4), etc.), which demonstrate as active photocatalysts, have exhibited great potential for photodegradation of organic pollutants under visible light [4,5]. Graphitic C_3N_4, a novel stable metal-free polymeric semiconductor photocatalyst, is a good candidate in this regard due to its high efficiency, low cost and a band gap of 2.7 eV which can absorb visible light up to 460 nm [6–8]. However, the photocatalytic efficiency of pure g-C_3N_4 is limited by the disadvantages of rapid photogenerated electron–hole (e^-–h^+) pair recombination and low visible-light utilization efficiency [9–11]. Hence, it is urgently needed to explore new and simple methods to enhance the mineralization ability of g-C_3N_4.

Currently, many strategies have been attempted to improve the visible-light-driven photocatalytic activity of g-C_3N_4, including the integration of heteroatoms within the g-C_3N_4 structure [12], preparation of nanostructured g-C_3N_4 [13,14], coupling g-C_3N_4 with other materials to form hybrids [15]. Among them, modified g-C_3N_4 by coupling with other materials, one of the most effective ways to separate photoinduced electron–hole pairs and enhance photocatalytic performance, has attracted great research interests for a long time [16,17], such as ZnO/C_3N_4 [18], TiO_2/C_3N_4 [19], Ag_3PO_4/C_3N_4 [20] and MoS_2/C_3N_4 [21], etc. In these systems, two components with matching band potentials are coupled into a heterojunction photocatalyst which can greatly improve the lifetime of charge carriers, promote quantum efficiency and suppress the recombination of the electron–hole pairs [22,23].

To the best of our knowledge, WO_3 is regarded as a promising photoactive material due to its narrow band gap (2.4–2.8 eV), nontoxicity and stable physicochemical properties [24]. Thus, considerable attention has been paid to WO_3/C_3N_4 heterojunction photocatalyst recently. However, the photocatalytic efficiency of WO_3/C_3N_4 composites still needs to be improved. It is known that H_2WO_4 is a hydrated form of WO_3. Several recent reports describe H_2WO_4 with other materials to form heterojunctions composites,

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* Corresponding author. Tel.: +86 5566 4678; fax: +86 5566 5572.
E-mail address: wldai@fudan.edu.cn (W.-L. Dai).

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resulting in the enhancement of photocatalytic performance. Wang et al. developed a plasmonic Z-scheme visible-light-driven $H_2WO_4 \cdot H_2O/Ag/AgCl$ photocatalyst with good photocatalytic activity [25]. Cao et al. fabricated WO_3/H_2WO_4 photocatalyst through a thermo-decomposition method to improve the visible light response [26]. These intriguing findings drive us to explore H_2WO_4-based new materials to form composite photocatalysts. Herein, we firstly report a facile and cheap way to fabricate modified g-C_3N_4 by coupling with H_2WO_4, whose photocatalytic efficiency is dramatically higher than pure H_2WO_4 and g-C_3N_4. This result will provide new insights in the preparation of highly efficient photocatalysts.

In this work, H_2WO_4 modified g-C_3N_4 with different proportions were synthesized via a simple and low-cost impregnation method. The photocatalysts were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), UV–vis diffuse reflectance spectroscopy (DRS) and N_2-adsorption–desorption isotherms (BET). The photocatalytic activity was evaluated by degradation of Rhodamine B (RhB) under visible light irradiation ($\lambda > 420$ nm), and further extended to degrade representative model organic pollutants including methyl orange (MO) and methylene blue (MB). Moreover, the stability of the synthesized photocatalysts was also explored through successive recycling test. A possible photocatalytic mechanism for the degradation of RhB over H_2WO_4/g-C_3N_4 composites under visible-light was proposed.

Experimental

Materials

Melamine ($C_3H_6N_6$, CP grade, MW = 126.12 g mol^{-1}) and tungstic acid (H_2WO_4, AR grade, MW = 249.86 g mol^{-1}) were supplied by Sinopharm Chemical Reagent Co., Ltd. All chemicals were used without further purification. Deionized water was used throughout the whole study.

Catalyst preparation

Preparation of g-C_3N_4

Pure g-C_3N_4 was prepared via directly calcining melamine in air muffle furnace. A certain amount of melamine was put into an alumina crucible with a cover. The crucible was heated to 550 °C from room temperature at a heating rate of 5 °C min^{-1}. Keeping the temperature at 550 °C for 3 h, the yellow products were obtained after natural cooling to room temperature.

Preparation of H_2WO_4/g-C_3N_4 hybrid materials

H_2WO_4/g-C_3N_4 composites were prepared via a simple impregnation method. Typically, certain amount of H_2WO_4 (0.14, 0.30, 0.47, and 0.67 g) was completely dissolved into aqueous H_2O_2 (0.038 mol, 44%) under stirring. After the solution was pellucid, 2.69 g of g-C_3N_4 was added. The mixture was kept stirring at 90 °C for 5 h. Afterwards, the composite photocatalysts were obtained by drying at 100 °C for 24 h in an oven.

Characterization of the catalysts

TEM images were obtained on a JOEL JEM 2010 transmission electron microscope. The samples were supported on carbon-coated copper grids for the experiment. XRD patterns were obtained on a Bruker D8 advance spectrometer with Cu $K\alpha$ radiation ($\lambda = 0.154$ nm), operated at 40 mA and 40 kV, respectively. The FT-IR spectra were carried out on a Nicolet Avatar-360 FT-IR spectrometer. The Laser Raman experiments were performed with a Jobin Yvon Dilor Labram I Raman spectrometer equipped with a holographic notch filter, CCD detector, and He–Ne laser radiating at 632.8 nm. XPS was performed using a PerkinElmer PHI 5000C ESCA system equipped with a dual X-ray source, of which the Mg $K\alpha$ (1253.6 eV) anode and a hemispherical energy analyzer was used. The background pressure during data acquisition was maintained at $<10^{-6}$ Pa. Measurements were performed at a pass energy of 93.90 eV. All binding energies were calibrated using contaminant carbon (C 1s = 284.6 eV). Photoluminescence (PL) spectra were carried out on a JASCO FP-6500 type fluorescence spectrophotometer. The photocurrents were measured on an electrochemical system (CHI 660 D, China). Ultraviolet visible (UV–vis) DRS spectra were carried out using a SHIMADZU UV-2450 instrument with a collection speed of 40 nm min^{-1} using $BaSO_4$ as the reference.

Evaluation of photocatalytic activity

Activity experiments were carried out in a beaker placed under the lamp bracket, containing reaction solution of RhB, MO or MB which were chosen as the degrading pollutions. A 50 mg of catalyst powder was dispersed in RhB, MO or MB aqueous solution (100 mL, 10 mg L^{-1}). The wavelength of visible light was controlled by a 300 W Xenon lamp (CEL-HXF) equipped with wavelength cut off filters for $\lambda \leq 420$ nm. In the experiments, the solution was stirred in dark for 30 min to achieve the adsorption/desorption equilibrium. After turning on the lamp, 5 mL of solution was sampled at certain time intervals and centrifuged at 13,000 rpm for 10 min to remove the particles. The upper clear liquid was analyzed by recording the characteristic absorption peak of RhB at 520 nm to calculate the concentration of the compounds according to the work curve previously drawn.

Results and discussion

Characterization

Crystalline structure

The XRD patterns of pure g-C_3N_4, H_2WO_4, and H_2WO_4/g-C_3N_4 composite photocatalysts with different ratios are shown in Fig. 1. The characteristic diffraction peaks of H_2WO_4 match well with the standard card of orthorhombic phase (JCPDS 43-0679) with lattice constants of $a = 5.238$ Å, $b = 10.704$ Å, $c = 5.120$ Å. For the pure g-C_3N_4 (Fig. 1f), two basic diffraction peaks at around 27.4° and 12.8°

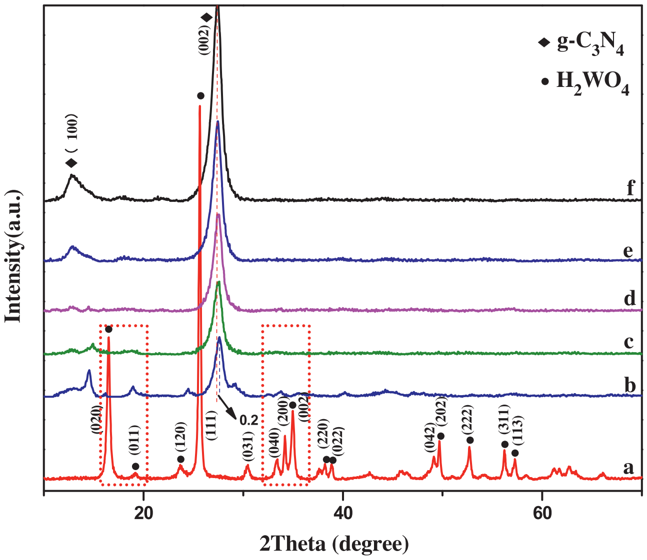

Fig. 1. XRD patterns of (a) H_2WO_4, (b) 20% H_2WO_4/C_3N_4, (C) 15% H_2WO_4/C_3N_4, (d) 10% H_2WO_4/C_3N_4, (e) 5% H_2WO_4/C_3N_4, and (f) C_3N_4.