



Full Length Article

Self-assembly of tungstophosphoric acid/acidified carbon nitride hybrids with enhanced visible-light-driven photocatalytic activity for the degradation of imidacloprid and acetamiprid

Yanhong Sun, Pengcheng Meng, Xia Liu*

College of Science, China Agricultural University, Beijing 100193, China

ARTICLE INFO

Keywords:

Visible light photocatalytic degradation
 Acidification graphitic carbon nitride
 Tungstophosphoric acid
 Imidacloprid
 Acetamiprid

ABSTRACT

In this paper, a novel efficient hybrid photocatalyst consisting of tungstophosphoric acid (HPW) and acidified carbon nitride (ACN) was successfully prepared. HPW and ACN interact through hydrogen bonding interactions to improve the photocatalytic activity of the HPW/ACN composite by means of enhanced photogenerated hole-electron separation efficiency. Graphitic carbon nitride was treated with a mixture of concentrated nitric acid and sulfuric acid to obtain porous ACN. The composite photocatalyst was then prepared by self-assembly of acidified carbon nitride and HPW under acidic conditions. The characterization results of HPW/ACN indicated the successful introduction of HPW and the effective interaction between HPW and ACN. Based on photocatalytic degradation experiments, it was concluded that HPW could act as the photogenerated electron trapping agent, providing adsorption sites as well as photocatalytic redox reaction sites. Moreover, the HPW/ACN showed excellent performance in the degradation of imidacloprid and acetamiprid under visible light irradiation ($\lambda > 400$ nm). The results of photocatalytic degradation revealed that the degradation rate constant of HPW/ACN (0.0058 min^{-1}) was 16 times higher than that of ACN ($3.55 \times 10^{-4} \text{ min}^{-1}$) in the photocatalytic degradation of imidacloprid and that the photocatalytic degradation rate constant of HPW/ACN (0.0017 min^{-1}) was 30 times higher than that of ACN ($5.64 \times 10^{-5} \text{ min}^{-1}$) in degrading acetamiprid.

1. Introduction

Graphite carbon nitride (CN), as a metal-free polymeric photocatalyst, has attracted tremendous attention for its visible light response, low cost, nontoxicity, thermal and chemical stabilization [1–3]. CN has been widely used in photocatalytic hydrogen production and degradation of organic pollutants [4–6]. Although CN with a layered structure is responsive to visible light, the photocatalytic activity of bulk CN is insufficient due to its high recombination rate of photogenerated electrons and holes, low superficial area, and few active sites or adsorption sites [7]. To improve the photochemical properties, much effort has been made in recent years [8–10]. In particular, acid treatment is an excellent method for the synthesis of porous polymeric carbon nitrides without the extra step of removing the hard template silica structures. Furthermore, acidified carbon nitride (ACN) has altered electronic band gaps, higher ionic conductivity and improved water dispersion compared to that of carbon nitride [11,12]. For example, protonation of CN with concentrated hydrochloric acid can increase the specific surface area from 8 to $30 \text{ m}^2/\text{g}$ and change the zeta potential from negative to positive without chemically decomposing

carbon nitrides [13]. Additionally, some oxygen-containing functional groups such as carboxyl and hydroxyl may be present in the porous structure under appropriate acidification conditions. These functional groups can provide more adsorption sites and active sites to facilitate the formation of hydrogen bonds or electrostatic interactions with other polar substances to achieve post-functionalization [14]. Incomplete destruction of carbon nitride molecules and introduction of oxygen-containing functional groups requires a mixture of concentrated nitric acid and sulfuric acid with appropriate acidity and oxidation [15]. When CN is treated with a mixture of concentrated sulfuric acid and concentrated nitric acid, the exfoliation of CN can occur due to the intercalation of H_2SO_4 in the interlayer space of CN and the intense heat release during the subsequent dilution process [16]. Simultaneously, concentrated nitric acid, with its strong oxidizing ability, can introduce oxygen-functional groups into ACN. In this way, a porous, less lamellar and oxygen-containing functionalized ACN can be obtained. This effect cannot be achieved by using either of the strong acids alone. It is worth noting that the reaction temperature must be controlled during treatment with mixed acid. Once the temperature is too high, the ACN will gel, which is not conducive to the combination of tungstophosphoric

* Corresponding author at: College of science, China Agricultural University, Yuanmingyuan West Road No. 2, Haidian District, Beijing 100193, China.
 E-mail address: liuxiacau@163.com (X. Liu).

acid (HPW) and ACN in the following sequence [17].

Polyoxometallate (POM) is characterized as metal-oxygen clusters of tungsten and has many interesting properties such as multielectron transfer [18], thermal stability, low toxicity and the ability to serve as an electron and oxygen relay [19]. POMs have a strong ability to accept or donate electrons and act as electron pools in the transfer of electrons in photocatalytic systems [20]. Hence, HPW can be used for storing electrons, capturing photogenerated electrons and facilitating photogenerated charge separation for the composite catalyst [21]. Regardless of the fact that HPW has excellent catalytic activity, it is commonly used in homogeneous catalytic reactions for its polar solubility [22]. Compounding HPW and other semiconductors with high surface area is also a useful method for improving photocatalytic performance in heterogeneous reactions [23–25]. How to combine polyanion clusters with target components is, however, a difficult problem, especially for polymer semiconductors. Fortunately, HPW can interact with other proton donors through hydrogen bonding, which can be utilized to prepare self-assembled materials [26]. Gang Yan et al. prepared a series of Keggin-type polyoxoanion modified g-C₃N₄ composites by electrostatic and hydrogen bonding interactions, and the composites exhibit enhanced photocatalytic activity in the process of methyl orange degradation and hydrogen production under visible light irradiation [27]. Therefore, it is feasible to construct a HPW/g-C₃N₄ composite photocatalyst with effective interaction and enhanced photocatalytic capacity through hydrogen bonding between carbon nitride nanosheets and HPW [28]. When the g-C₃N₄ is treated by a mixture of concentrated nitric acid and sulfuric acid, the number of surface hydroxyl and carboxyl groups is greatly increased. These oxygen-containing functional groups can form hydrogen bonds with HPW under mild conditions to enhance the support of HPW on the carrier. Simultaneously, the HPW on ACN provides new adsorption sites [29]. Previous studies have proven that impregnation of HPW can reduce the specific surface area of the materials. The Keggin HPW can, however, improve the adsorption capacity of the catalyst to imidacloprid [30]. Correspondingly, increased adsorption sites promote the efficiency of the material to photocatalytically degrade the substrate. In summary, an ideal method would be to combine HPW with ACN through hydrogen bonding to improve the photocatalytic activity of the composite photocatalyst.

In this paper, HPW/ACN was prepared by implanting HPW into carbon nitride via hydrogen bonds between oxygen-containing functional groups formed on carbon nitride and terminal-oxygen of HPW. The advantages of this method were as follows: (1) the specific surface area of g-C₃N₄ was increased by acidification treatment, and oxygen-containing functional groups were introduced as new adsorption and active sites to facilitate post-functionalization; (2) the combination of HPW and ACN led to the separation of photogenerated electrons and holes, thereby improving the photocatalytic activity of the composite material; and (3) HPW supported on ACN also provided new adsorption sites to enhance the catalytic performance of the materials. Furthermore, if HPW is activated under the irradiation containing ultraviolet light, it will play a synergistic catalytic role with the ACN and further improve the photocatalytic activity of the composite material.

Imidacloprid and acetamiprid, as neonicotinoid insecticides, are very commonly used in agricultural production and are detected in the environment due to their water solubility. In particular, the degradation mode of imidacloprid in the natural environment is mainly photolysis and hydrolysis [31]. These two compounds were thus chosen to act as organic pollutants to test the photocatalytic activity of the as-prepared HPW/ACN photocatalysts under visible light irradiation.

2. Experimental

2.1. Chemicals and materials

Melamine (99%) and tungstophosphoric acid hydrate were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Sulfuric

acid (98%, H₂SO₄), nitric acid (65–68%, HNO₃) and hydrogen chloride aqueous solution (36–38%, HCl) were purchased from Tianjin Damao Chemical Reagent Factory (China). Deionized water used during the experimental process was prepared with an ultra-pure purification system. All the chemicals were of an analytically pure grade and were used without further purification.

2.2. Preparation of ACN

Bulk g-C₃N₄ was synthesized based on the thermal polycondensation of melamine as reported previously [32]. Typically, 10 g of melamine was put into an alumina crucible with a cover and heated in a muffle furnace from room temperature to 550 °C with a heating rate of 2 °C Min⁻¹. After calcination at 550 °C for 4 h, the product was cooled to room temperature, ground into a powder and collected for the subsequent procedure.

The ACN was achieved using the method mentioned in reference [33]. One gram of bulk g-C₃N₄ was put into a flask, and then, 20 mL of H₂SO₄ and 20 mL of HNO₃ were added. The suspension was magnetically stirred at 35 °C for 2 h and poured into 1 L of deionized water. After stirring fully, the mixture was vacuum filtered and washed with deionized water until the filtrate pH was neutral. The residue was dried at 60 °C under vacuum for 24 h, and the ACN was obtained as a pure white powder.

2.3. Preparation of HPW/ACN

ACN (150 mg) was dispersed in 10 mL of water and sonicated for 20 min. Meanwhile, 0.5 g of HPW was dissolved in 5 mL of water in a flask, followed by dropwise addition of 1 mL of HCl with magnetic stirring. Then, the ACN dispersion was slowly injected into the HPW solution at 80 °C and reacted for 1 h with magnetic stirring. The aqueous suspension was filtered immediately, and the residue was washed with abundant deionized water until the filtrate was neutral. Finally, the solid was dried at 60 °C under vacuum for 24 h. An off-white powder was obtained and denoted HPW/ACN. The scheme of synthetic methods is shown in Fig. 1.

2.4. Characterization methods

The morphology of photocatalysts was examined by field emission scanning electron microscopy (FESEM, QUANTA250, FEI Corporation, USA) and transmission electron microscopy (TEM, Tecnai G220) with an accelerating voltage of 200 kV. Energy dispersive X-ray spectroscopy (EDS) and element mapping of materials were investigated by FESEM measurements. The crystal structure of the samples was determined by X-ray powder diffraction (XRD, D8 ADVANCE, Bruker Corporation, Germany) with Cu K α radiation in the range of $2\theta = 5\text{--}90^\circ$. The molecular structural and composites information was obtained from Fourier transform infrared spectroscopy (FTIR, AVATAR 370FTIR, Thermo Nicolet, USA) and X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI, Thermo Fisher, USA) with a monochromatic X-ray source of Al K α ($h\nu = 1486.6\text{ eV}$). The binding energy was calibrated by the C1s adventitious carbon peak at 284.8 eV. The optical properties were recorded on a UV–visible diffuse reflectance spectrophotometer (UV–Vis DRS, Hitachi U-4100, Japan) equipped with an integrating sphere using BaSO₄ as the reference. The photoluminescence spectra (PL, FLS 980, UK) were obtained on a fluorescence spectrometer, with excitation at 420 nm. The generation of $\cdot\text{OH}$ radical during the photocatalytic process was monitored by electron spin resonance spectrometry (ESR, JES FA200, Japan).

2.5. Photocatalytic experiments

The photocatalytic degradation of imidacloprid and acetamiprid was carried out in a CEL-LAB500 series multidigit photochemical

Download English Version:

<https://daneshyari.com/en/article/7833072>

Download Persian Version:

<https://daneshyari.com/article/7833072>

[Daneshyari.com](https://daneshyari.com)