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Positive effects of phosphotungstic acid on the in-situ solid-state polymerization and visible light photocatalytic activity of polyimide-based photocatalyst

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ABSTRACT

A series of $H_3PW_{12}O_{40}$ (HPW)-containing polyimide (PI) hybrid composites (TPI) are prepared through in-situ solid-state polymerization using HPW, melem and pyromellitic dianhydride as precursors. The effect of HPW on the morphology, porosity, chemical structure, and optical and visible-light photocatalytic degradation efficiency of TPI composites are systematically investigated by various characteristic methods. By comparing the structure, property and photocatalytic activity of the TPI composites and the HPW-PI composites (prepared by the impregnation method), it indicates that HPW can promote the formation of C—N bond in the five-membered imide rings between amines and anhydrides during the in-situ solid-state condensation process. Subsequently, the visible-light ($\lambda > 400$ nm) photocatalytic degradation efficiency of imidacloprid on TPI composites is also enhanced compared with the pristine PI because of the enhancement of the in-situ solid-state condensation reaction, photogenerated electron-hole separation efficiency and visible-light utilization efficiency after the introduction of HPW. The visible-light photocatalytic degradation rate constant k of 15% TPI composites prepared at 300 °C and 5% TPI composites prepared at 325 °C are about 10.33 and 2.42 times of the corresponding pristine PI, respectively. Compared with commercial P25, the photocatalytic degradation efficiency of 15% TPI-300 and 5% TPI-325 are about 4.58 and 5.13 times of P25 under visible light irradiation.

1. Introduction

The photocatalytic degradation of organic pollutants in water, such as pesticide, dye, surfactant and pharmaceuticals [1–3], is the focus of environmental science. In the development of heterogeneous photocatalysts for water pollution remediation, the traditional inorganic semiconductor photocatalysts, like TiO_2 and ZnO [4–6], have been extensively investigated. However, their practical application will be limited by the weak visible light photocatalytic activity for their wide bandgap and weak visible light responsiveness. In recent years, the conjugated polymer-based photocatalysts has won widespread attention for their excellent photocatalytic activity, low cost and abundant sources [7]. The graphitic carbon nitride (g-C_3N_4) as an outstanding representative of conjugated polymer-based photocatalyst has been widely used in photocatalytic water splitting, degradation of organic pollutants and reduction of CO_2 for its suitable band structure and excellent visible light response [8–10]. Originally, polyimide (PI), as a special conjugated polymer engineering material, is widely used in the field of microelectronics, separation membranes and nanomaterials [11,12]. Reportedly, a polyimide prepared using melamine (MA) and pyromellitic dianhydride (PMDA) can show excellent visible light response for its suitable band structure [13]. Even so, the photocatalytic degradation efficiency of PI is still low for the inherent transfer property and the persistent recombination of photogenerated carriers of polymer and its negative valence band (VB) potential compared to TiO_2, ZnO, WO_3 and so on [14].

To improve the photocatalytic efficiency of PI, a series of strategies, including co-catalysts [14–17], heteroatoms doping [18,19], heterojunctions [19–25], are used to promote the separation of photogenerated electrons (e^-) and holes (h^+) or the positive shift of the valence band position. In detail, (i) for the co-catalysts represented by Pt and MoS_2 [14–17], they can be considered as electronic pools to suppress photogenerated carriers recombination [26]. (ii) The introduction of element S into the structural unit of PI, the conduction band (CB) and VB potential of PI will be significantly positive shifted [18,19]. (iii) The construction of heterojunctions in the form of hybrid composites is a worthwhile way to improve the photocatalytic oxidation capacity of photocatalysts [27]. As far as we know, catalysts that have been used to form heterojunctions with PI include tungsten oxide [19,20], $Zn_{0.25}Cd_{0.75}S$ [21], MoO_3 [22,23], ZnO [24] and g-C_3N_4 [25].

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This construction of such heterojunctions can suppress the photogenerated carriers recombination, and also enhance the visible-light utilization efficiency or the photocatalytic oxidation ability of PI on account of that their band structure are suitable for that of PI. However, phosphotungstic acid ($H_3PW_{12}O_{40}$, HPW) is an excellent homogeneous photocatalyst, also is an electronic acceptor or mediator for its excellent capability to accept or donate electrons with a well-defined Keggin structure [28,29]. Hence, the introduction of HPW into PI may suppress the photogenerated carriers recombination. Besides, due to the strong acidity and oxidation of phosphotungstic acid, it can catalyze many organic synthesis reactions, including esterification, oxidation and C—N bond formation [30–32]. The PI photocatalyst involved in this research is synthesized by imidization of amines and anhydrides [14]. Therefore, when HPW-containing PI hybrid composites (TPI) are prepared by in-situ solid-state polymerization using HPW with amines and anhydrides, HPW may promote the imidization of amines and anhydrides [32]. Given those assumption, it would be significant to investigate the incorporation of HPW and PI, and the effect of HPW on the synthesis and photocatalytic degradation efficiency of TPI composites.

Herein, a series of TPI composites are prepared through in-situ solid-state polymerization using HPW, MA and PMDA as precursors in this work. Due to the PI with different polymerization temperature will have different polymerization degree [16], so we study the effect of HPW on the in-situ solid-state polymerization by comparing the characterization results of TPI, HPW-PI and pristine PI with different polymerization temperature. Besides, the effect of HPW content on the morphology, adsorption capacity, chemical structure and optical properties of TPI composites are investigated by systematic characterization. The effect of HPW on the visible-light photocatalytic degradation efficiency of TPI composites are also systematically investigated. The possible photocatalytic mechanism are also proposed. The prepared TPI composites are expected to exhibit higher visible-light photocatalytic activity than pristine PI, because HPW can promote the formation of C—N bond between amines and anhydrides and can accept electrons.

2. Experimental

2.1. Chemicals and reagents

Melamine, pyromellitic dianhydride, phosphotungstic acid hydrate and ethyl acetate were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Imidacloprid (98%) was provided by The Institute of Plant Protection, Chinese Academy of Agricultural Sciences. Deionized water was used in photocatalytic degradation of imidacloprid. All chemicals were analytical reagents and used without further purification.

2.2. Synthesis of melem

10 g of MA was put into a 40 mL porcelain crucible with a cover. Then, the crucible was calcined to 425 °C from room temperature in a muffle furnace with a heating rate of 10 °C min^{-1} under ambient pressure in air. Keeping the temperature at 425 °C for 4 h, the melem was obtained after grinding, washing with deionized water and absolute ethyl alcohol and drying at 80 °C for 10 h in an air-circulating oven.

2.3. Synthesis of TPI composites

The TPI composites were prepared through an in-situ solid-state polymerization process in air. In a typical process, 2.182 g melem were dispersed in 20 mL ethyl acetate containing 0.230 g HPW under magnetic stirring to form a slurry. After stirring for 30 min, the slurry was treatment for 1 h in an ultrasonic bath and maintained the temperature at about 23 °C. Furthermore, 2.181 g PMDA were added into the slurry after continuing stirring 30 min. Then, the solvent was evaporated, and the residues was dried at 80 °C for 10 h to obtain the TPI precursor. Moreover, the precursor of TPI was heated at 325 °C for 4 h with a rate of 10 °C min^{-1}. Finally, the resulting pale yellow solid powder was denoted as 5% TPI-325. According to this method, a series of x% TPI-y composites (x and y represent the HPW content in the precursor mixture and polymerization temperature, respectively) were prepared with different HPW content and polymerization conditions. Besides, the HPW content determined by ICP-MS in 15% TPI-300 and 5% TPI-325 composites are 14.22% and 4.87%, respectively. However, the pristine PI was also synthesized by the same method without adding HPW.

2.4. Synthesis of HPW-PI composites

The synthesis of HPW-PI composites was carried out by the impregnation method [33]. Typically, 0.105 g HPW was dissolved in deionized water, and then 2.000 g PI-325 was added into the HPW aqueous solution with stirring at ambient temperature for 12 h. Afterward, the water was evaporated at 80 °C, and the residues was dried continuously in the oven at 80 °C for 10 h to obtain the 5% HPW-PI-325 composites. Also, the 15% HPW-PI-300 composites was obtained using the same method.

2.5. Characterization

The crystalline structure of the pristine PI and TPI composites were confirmed by X-ray diffractometer (XRD, Bruker D8 ADVANCE diffractometer, Bruker AXS Company, Germany) using Cu-K_α radiation. The molecular structural information of the samples were analyzed by Fourier transform infrared spectroscopy (FT-IR, PerkinElmer Spectrum 100 FT-IR Spectrometer, PerkinElmer Optoelectronics, America) using KBr pellet support with the wavenumber range of 400–4000 cm^{-1}. The morphologies and microstructures of TPI composites were examined with scanning electron microscope (SEM, Hitachi S-4800 electron microscope, Hitachi, Ltd., Japan) and transmission electron microscope (TEM, Tecnai G2 F20 electron microscope, FEI company, America) with a carbon-coated copper grid as the sample holder. The BET (Brunauer, Emmett and Teller) specific surface area was determined by N_2 adsorption–desorption isothermals (ASAP 2020, Micromeritics Instrument Corp, America). Meanwhile, the surface composition elements of the samples were detected with energy-dispersive X-ray spectra (EDS, HORIBA EX-350 spectrometer, Horiba, Ltd., Japan) equipped on the SEM. Furthermore, the accurate content of W in the TPI composites were analyzed by the inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500ce system, Agilent Technologies Inc., America). Also, the chemical state and valance band of the samples were obtained by X-ray photoelectron spectra (XPS, Thermo Scientific Escalab 250Xi X-ray photoelectron spectrometer, Thermo Fisher Scientific, America). The spectrum response range of the samples were measured by UV–vis diffuse reflectance spectra (UV–vis DRS, Specord 200 spectrophotometer, Analytikjena, Germany) using $BaSO_4$ as the reference. Moreover, The PL spectra were recorded on a FluoroMax-4 Spectrofluorometer (Horiba Jobin Yvon Inc., America) with an excitation wavelength of 325 nm.

2.6. Photocatalytic activity test

The photocatalytic activity of the pristine PI and TPI composites were evaluated by the degradation of imidacloprid under visible light ($\lambda > 400$ nm) irradiation [28,34]. Imidacloprid is a pervasive commercial neonicotinoid insecticide, and it has a negative impact on non-target species including humans [35]. Now, imidacloprid can be detected in surface and ground water for its water solubility (510 mg L^{-1}, 20 °C) and mobility [2]. The light source was a PLS-SXE300UV Xe lamp (15 A, 225 W). 1 mL samples was taken out from 50 mL imidacloprid aqueous solution at the specified time, and the imidacloprid concentration was detected after removal of the photocatalyst with a