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Article

Fabrication of highly dispersed platinum-deposited porous g-C₃N₄ by a simple *in situ* photoreduction strategy and their excellent visible light photocatalytic activity toward aqueous 4-fluorophenol degradation

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ARTICLE INFO

Article history:

Received 17 September 2016

Accepted 6 November 2016

Published 5 January 2017

Keywords:

Photocatalysis

Porous graphitic carbon nitride

Photoreduction

Platinum deposition

4-Fluorophenol

ABSTRACT

A series of highly dispersed platinum-deposited porous g-C₃N₄ (Pt/pg-C₃N₄) were successfully fabricated by a simple *in situ* photoreduction strategy using chloroplatinic acid and porous g-C₃N₄ as precursors. Porous g-C₃N₄ was fabricated by a pretreatment strategy using melamine as a raw material. The morphology, porosity, phase, chemical structure, and optical and electronic properties of as-prepared Pt/pg-C₃N₄ were characterized. The photocatalytic activity of as-prepared Pt/pg-C₃N₄ was preliminarily evaluated by the degradation of aqueous azo dyes methyl orange under visible light irradiation. The as-prepared Pt/pg-C₃N₄ were further applied to the degradation and mineralization of aqueous 4-fluorophenol. The recyclability of Pt/pg-C₃N₄ was evaluated under four consecutive photocatalytic runs.

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1. Introduction

The highly efficient degradation of aqueous organic pollutants by photocatalytic oxidation under visible light irradiation is of great significance to sustainable development [1–6]. However, as a new type of aqueous organic pollutants, organic fluorine compounds are difficult to degrade using conventional visible light photocatalysts because of the large bond energy of C–F [7–9]. Therefore, the development of photocatalysts with high visible light photocatalytic activity is a key for the successful degradation of aqueous organic fluorine compounds under visible light irradiation.

As a metal-free semiconductor photocatalyst, graphitic carbon nitride (g-C₃N₄) has been widely used for the removal of aqueous organic pollutants because of its advantages such as visible light response, environmentally friendly, and low cost [10–12]. However, its bulk layered structure severely limits the visible light photocatalytic activity of g-C₃N₄. On the one hand, this structure is not conducive to the surface migration of photogenerated electron. On the other hand, it increases the mass transfer resistance during photocatalytic reaction.

Morphology control synthesis is an effective strategy to enhance the visible light photocatalytic activity of g-C₃N₄. For example, Zhang et al. [13] fabricated single-layered g-C₃N₄

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This work was supported by the National Natural Science Foundation of China (51568049, 51208248, 51468043, 21366024), the National Science Fund for Excellent Young Scholars (51422807), the Natural Science Foundation of Jiangxi Province, China (20161BAB206118, 20114BAB213015), and the Natural Science Foundation of Jiangxi Provincial Department of Education, China (GJJ14515, GJJ12456).

DOI: 10.1016/S1872-2067(16)62589-5 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 38, No. 1, January 2017

quantum dots by an alternative treatment strategy using bulk layered g-C₃N₄ as a precursor. Sun et al. [14] developed a highly stable hollow carbon nitride nanosphere with controlled shell thicknesses using nanostructured silica as a template. Our previous work has shown that constructing tubular nanostructure can effectively improve the photocatalytic activity of bulk layered g-C₃N₄ [15–18].

Noble metal deposition by *in situ* photoreduction is an effective, environmentally friendly, and low-cost strategy to improve the visible light photocatalytic activity of g-C₃N₄ [19–21]. On the one hand, the deposited noble metals on the surface of g-C₃N₄ can effectively capture the photogenerated electrons, thereby decreasing the recombination probability of electron-hole (e⁻-h⁺) pairs. On the other hand, it is different from chemical and hydrothermal reduction techniques, because there is neither addition of reducing agent nor consumption of thermal energy during photoreduction. Therefore, *in situ* photoreduction is an environmentally friendly and low-cost strategy for noble metal deposition.

To develop a reusable photocatalyst with excellent visible light photocatalytic activity to achieve highly efficient degradation and mineralization of aqueous organic fluorine compounds under visible light irradiation, a series of highly dispersed platinum-deposited porous g-C₃N₄ (Pt/pg-C₃N₄) were successfully fabricated by a simple *in situ* photoreduction strategy using chloroplatinic acid and porous g-C₃N₄ as precursors. Compared with conventional platinum-deposited g-C₃N₄ (Pt/g-C₃N₄) materials [22–24], Pt nanoparticles can be highly dispersed on the inner and outer surfaces of porous g-C₃N₄ because of the exposed internal and external geometrical surfaces of porous g-C₃N₄ precursor. Therefore, the electron capture effect of Pt nanoparticles is significantly enhanced. In addition, the *in situ* photoreduction can effectively inhibit the self-aggregation of Pt nanoparticles compared with other reduction strategies.

The photocatalytic activity of as-prepared Pt/pg-C₃N₄ was preliminarily evaluated by the degradation of aqueous azo dyes methyl orange (MO) under visible light irradiation. The as-prepared Pt/pg-C₃N₄ was applied to the degradation and mineralization of aqueous 4-fluorophenol (4-FP). As an organic intermediate, 4-FP has been widely used in many areas such as pharmaceutical engineering, fungicide in herbicide synthesis, and the manufacture of special liquid crystal materials [25–27]. The discharged 4-FP residues in water have drawn attention because they have significant biological effects as enzyme inhibitors and can accumulate in the body through food chains [28–30]. Since 1976, 4-FP has been listed as a priority pollutant by the U.S. Environmental Protection Agency [31]. However, the studies of photocatalytic degradation of aqueous 4-FP under visible light condition have not yet been reported because of its stable chemical structure.

2. Experimental

2.1. Chemicals and reagents

Melamine (CP grade) and H₂PtCl₆·6H₂O (GR grade) were purchased from Sinopharm Chemical Reagent Co. Ltd. Hydro-

chloric acid (HCl, analytical reagent grade) and ethylene glycol (EG, AR grade) were purchased from Xilong Chemical Co. Ltd. MO (AR grade) was purchased from Shanghai Fine Chemical Technology Co. Ltd. 4-FP (99%) was purchased from Aladdin Chemistry Co. Ltd. All chemicals were used without further purification. Double distilled water was used in the catalyst preparation and catalytic tests.

2.2. Fabrication of porous g-C₃N₄ and highly dispersed platinum-deposited porous g-C₃N₄

In a typical synthesis of porous g-C₃N₄, 3 g of melamine was placed into a 100-mL beaker, and 10 mL HCl, 10 mL EG, and 3 mL water were added. After stirring the white viscous suspension for 1 h at room temperature, the HCl/EG-pretreated melamine precursor was obtained by washing, centrifugation, and drying. The HCl/EG-pretreated melamine precursor was transferred into a 10-mL alumina crucible with a cover. The crucible was heated to 250 °C from room temperature in a muffle furnace at a heating rate of 5 °C/min, and then heated to 550 °C at a heating rate of 10 °C/min. After keeping the temperature at 550 °C for 2 h, a yellow porous g-C₃N₄ sample was obtained after cooling and denoted as pg-C₃N₄. For comparison, g-C₃N₄ was also prepared by the conventional high temperature polycondensation method using melamine as a precursor.

A series of highly dispersed platinum-deposited porous g-C₃N₄ was fabricated by *in situ* photoreduction using H₂PtCl₆·6H₂O and pg-C₃N₄ as precursors. First, 1 g of H₂PtCl₆·6H₂O was dissolved into 50 mL H₂O to obtain a 2 × 10⁴ mg/L H₂PtCl₆·6H₂O aqueous solution, and 0.6 g of pg-C₃N₄ was uniformly dispersed into 100 mL H₂O using a 500-W ultrasonic crusher for 10 min to obtain a pg-C₃N₄/H₂O suspension. H₂PtCl₆·6H₂O aqueous solution (0.8, 1.6, 2.4, or 3.2 mL) was added dropwise into the above pg-C₃N₄/H₂O suspension. After λ > 420 nm visible light irradiation for 4 h, the final products were obtained by washing and drying, and they were denoted as Pt(x%)/pg-C₃N₄, where x% represents the theoretical mass percentage of Pt element in the products. For comparison, Pt(3%)/g-C₃N₄ was also prepared by the same method but using g-C₃N₄ as a support.

2.3. Characterization

High resolution transmission electron microscopy (HRTEM) was recorded on a JEM-2100F at an accelerating voltage of 200 kV. The chemical compositions of the samples were determined by energy-dispersive X-ray spectroscopy (EDX) equipped on the microscope. Nitrogen gas porosimetry measurements were performed on a Quantachrome NOVA 2000e surface area and porosity analyzer after the samples were outgassed under a vacuum at 70 °C for 20 min and 150 °C for 6 h. X-ray diffraction (XRD) patterns were obtained using a D8ADVANCE diffractometer via Cu-K_α radiation. Fourier transform infrared (FTIR) spectra were recorded on a Bruker VERTEX 70 FTIR apparatus. X-ray photoelectron spectroscopy (XPS) was performed using an Axis Ultra DLD instrument with a monochromated Al-K_α source at a residual gas pressure of

less than 10^{-8} Pa. All the binding energies were referenced to the C 1s peak at 285 eV of the surface adventitious carbon. Ultraviolet–visible diffuse reflectance spectroscopy (UV-vis/DRS) was conducted using a Lambda 750S UV/VIS/NIR spectrometer. Photoluminescence (PL) measurements were carried out on a Hitachi F-7000 fluorescence spectrophotometer.

2.4. Photocurrent measurements

Photocurrent measurements used a conventional three-electrode setup connected to an electrochemical station (CHI 630E, Shanghai Chenhua, China). In this electrochemical system, the prepared catalyst/Ti sheet was used as the working electrode; a Pt wire was used as the counter electrode, and an Ag/AgCl electrode (saturated KCl) was used as the reference electrode. The electrolyte was 0.01 mol/L Na_2SO_4 aqueous solution (100 mL). A 300-W Xe lamp served as a light source. The measurements were carried out at a constant potential of +1.0 V to the working electrode.

2.5. Photocatalytic tests

A PLS-SXE300 Xe lamp (300-W, Beijing PerfectLight Co. Ltd., China) was the light source, and the output wavelength was $\lambda > 320$ nm. The visible light irradiation was obtained by removing the UV irradiation from the lamp using a 420-nm cut filter, which can control the output wavelength $\lambda > 420$ nm. 100 mg of solid photocatalyst and 100 mL of organic pollutant (MO or 4-FP) aqueous solution were poured into a 300-mL

self-designed quartz reactor. The initial concentration of MO or 4-FP is 10 mg/L. The suspension was ultrasonicated for 10 min and stirred in the dark until adsorption–desorption equilibrium. Subsequently, the light source was switched on, and stirring was continued. The temperature of the suspension was maintained at 35 ± 2 °C by circulation of water through an external cooling jacket. At specific intervals of irradiation, fixed amounts of the reaction solution were extracted, centrifuged, and filtered. Changes in the MO concentrations were analyzed using an UNICO UV-2000 spectrophotometer at $\lambda = 464$. Changes in the 4-FP concentrations were analyzed using an Agilent 1100 series high-performance liquid chromatography: C_{18} column, UV detector ($\lambda = 277$ nm), and acetonitrile/water (70/30 v/v) was used as a mobile phase at a flow rate of 1.0 mL/min. Changes in total organic carbon in the reaction system were monitored using a Shimadzu TOC-L CSH total organic carbon analysis system.

3. Results and discussion

3.1. Characterization

3.1.1. Morphology and textural property

The morphologies of $\text{g-C}_3\text{N}_4$, $\text{Pt}(3\%)/\text{g-C}_3\text{N}_4$, $\text{pg-C}_3\text{N}_4$, and $\text{Pt}(3\%)/\text{pg-C}_3\text{N}_4$ were observed by TEM (Fig. 1). As shown in Fig. 1(a), $\text{g-C}_3\text{N}_4$ exhibits a bulk layered graphite-like structure, which originates from the polycondensation of melamine under high temperature. Fig. 1(b) and (c) show that highly dispersed Pt nanoparticles were homogeneously deposited on the

Fig. 1. TEM images of $\text{g-C}_3\text{N}_4$ (a), $\text{Pt}(3\%)/\text{g-C}_3\text{N}_4$ (b, c), $\text{pg-C}_3\text{N}_4$ (d), and $\text{Pt}(3\%)/\text{pg-C}_3\text{N}_4$ (e, f); HRTEM (g) and EDX spectrum (h) of $\text{Pt}(3\%)/\text{pg-C}_3\text{N}_4$.

surface of g-C₃N₄ after *in situ* photoreduction reaction. This result indicates that the interaction between H₂PtCl₆·6H₂O precursor and –NH₂ groups on the surface of g-C₃N₄ effectively inhibits the self-aggregation of Pt nanoparticles during photoreduction reaction. As shown in Fig. 1(d), pg-C₃N₄ with three-dimensional pore geometry was successfully fabricated using HCl and EG to pretreat melamine as a precursor. This result indicates that HCl and EG will change the condensation mode of melamine precursor, inducing the formation of porous microstructure, i.e., some melamine molecules were protected by HCl and EG through acid–base and hydrogen bonding interactions. Therefore, the protected melamine cannot react with the other melamine molecules, resulting in the termination of melamine thermal condensation. The porous microstructure was fabricated in the terminal region of melamine thermal condensation (Scheme 1). From Fig. 1(e) and (f), highly dis-

persed Pt nanoparticles homogeneously were deposited on the inner and outer surfaces of porous g-C₃N₄ after the *in situ* photoreduction reaction. This result indicates that construction of three-dimensional porous microstructure is beneficial to the Pt nanoparticles deposition because of the increased contact area. A representative Pt nanoparticle shown in Fig. 1(g) indicates that the average diameter of Pt nanoparticles is about 2 nm. EDX result shows that only C, N, and Pt elements were present in the Pt(3%)/pg-C₃N₄ sample (Fig. 1(h)).

The textural property of g-C₃N₄, Pt(3%)/g-C₃N₄, pg-C₃N₄, and Pt(3%)/pg-C₃N₄ was characterized by nitrogen gas porosity measurement (Fig. 2). As shown in Fig. 2(a), the type II isotherms of g-C₃N₄ and Pt(3%)/g-C₃N₄ correspond to their non-porous structural characteristic. The type IV isotherms with H3-type hysteresis loops for the pg-C₃N₄ and Pt(3%)/pg-C₃N₄ correspond to their porous microstructure. The Brunau-

Scheme 1. The designed route for fabrication of Pt/pg-C₃N₄ and the separation and transportation of photoinduced charge carriers in the Pt/pg-C₃N₄ system under visible-light irradiation.

Fig. 2. Nitrogen gas sorption isotherms (a) and pore-size distribution curves (b) of g-C₃N₄, Pt(3%)/g-C₃N₄, pg-C₃N₄, and Pt(3%)/pg-C₃N₄.

er-Emmett-Teller (BET) surface areas of pg-C₃N₄ and Pt(3%)/pg-C₃N₄ are larger than those of g-C₃N₄ and Pt(3%)/g-C₃N₄ because the porous microstructure has more exposed geometrical surfaces compared with the bulk layered structure. As shown in Fig. 2(b), the Barrett-Joyner-Halenda (BJH) pore size distribution curves reveal that all of the tested materials exhibit a weak narrow peak in the range of 3–5 nm, which can be attributed to the released NH₃ molecules that act as soft-templates during melamine polycondensation. Compared with g-C₃N₄ and Pt(3%)/g-C₃N₄, the stronger broad pore size distribution peaks of pg-C₃N₄ and Pt(3%)/pg-C₃N₄ in the range of 5–120 nm can be attributed to the porous microstructure.

3.1.2. Compositional and structural information

The phase structures of g-C₃N₄, pg-C₃N₄, and Pt(x%)/pg-C₃N₄ were characterized by XRD analysis (Fig. 3). The results reveal that g-C₃N₄ exhibits a typical (002) interlayer stacking peak at 27.5°, which corresponds to an interlayer distance of $d = 0.33$ nm, whereas the (100) peak at 12.9° represents in-plane structural packing motif with a period of 0.675 nm. Compared with g-C₃N₄, the weaker diffraction intensity of (002) peak for the pg-C₃N₄ and Pt(x%)/pg-C₃N₄ can be attributed to the reduced amount of layered structure because of the porous microstructure. In addition, the diffractions related to Pt nanoparticles were not observed, implying a highly homogeneous dispersion of Pt nanoparticles throughout the pg-C₃N₄ support.

The FTIR spectra of g-C₃N₄, pg-C₃N₄, and Pt(x%)/pg-C₃N₄ are shown in Fig. 4. For all the tested materials, the sharp peak at 813.5 cm⁻¹ is the typical bending vibration of s-triazine units. A series of peaks in the range of 1100–1700 cm⁻¹ are attributed to the stretching modes of C–N and C=N in the CN heterocycles. The broad absorption peaks located in the range of 2900–3400 cm⁻¹ originate from the stretching vibration modes of primary (–NH₂) and secondary (–NH) amines. The FTIR spectra of pg-C₃N₄ and Pt(x%)/pg-C₃N₄ are similar to that of g-C₃N₄, indi-

Fig. 3. XRD patterns of g-C₃N₄, pg-C₃N₄, Pt(1%)/pg-C₃N₄, Pt(2%)/pg-C₃N₄, Pt(3%)/pg-C₃N₄, and Pt(4%)/pg-C₃N₄.

Fig. 4. FTIR spectra of g-C₃N₄, pg-C₃N₄, Pt(1%)/pg-C₃N₄, Pt(2%)/pg-C₃N₄, Pt(3%)/pg-C₃N₄, and Pt(4%)/pg-C₃N₄.

cating that pg-C₃N₄ and Pt(x%)/pg-C₃N₄ have the same chemical structure as g-C₃N₄ after the formation of porous microstructure and deposition of Pt nanoparticles. However, pg-C₃N₄ and Pt(x%)/pg-C₃N₄ demonstrated a stronger FTIR mode compared with g-C₃N₄ because their more exposed surface functional groups.

The surface composition and chemical state of the constituent elements of g-C₃N₄, pg-C₃N₄, and Pt(3%)/pg-C₃N₄ in the C 1s, N 1s, and Pt 4f binding energy regions were characterized by a high-resolution XPS probe technique (Fig. 5). As shown in Fig. 5(a), the peak of g-C₃N₄ in C 1s binding energy regions centered at 285.0 eV is typically assigned to C–C and/or C=C, which originates from the reference carbon on the surface. The peak centered at 288.2 eV originates from *sp*² C atoms bonded to N in an aromatic ring (N=C–(N)₂), whereas the peak centered at 289.1 eV is assigned to *sp*² C atoms in the aromatic ring attached to the primary and secondary amines (N=C(N)–NH₂, N=C(N)–NH). Compared with g-C₃N₄, the XPS peaks of *sp*² C atoms for the pg-C₃N₄ strengthen and shift to a higher binding energy because the porous microstructure increases the number of exposed surface functional groups and the original electronic environment of *sp*² C atoms is perturbed by the increase of surface –NH₂ and –NH groups. Compared with pg-C₃N₄, the large shift of *sp*² C XPS peaks for the Pt(3%)/pg-C₃N₄ can be attributed to the electron-withdrawing effect of Pt nanoparticles that increases the binding energy of *sp*² C atoms. The high-resolution XPS results of N 1s binding energy regions support the high-resolution XPS analysis of C 1s binding energy regions described above (Fig. 5(b)). For the g-C₃N₄, the peak centered at 398.8 eV is assigned to *sp*²-hybridized aromatic nitrogen atoms bonded to carbon atoms (C=N–C). The peak centered at 400.2 eV is related to either tertiary nitrogen groups ((C)₃–N) linking structural motifs (C₆N₇) or amino groups carrying hydrogen ((C)₂–NH, C–NH₂) in connection with structural defects and incomplete condensation. The peak at 401.1 eV corresponds to nitrogen atoms bonded to three carbon atoms in the aromatic cycles (N–(C)₃). A weak peak at

Fig. 5. High-resolution XPS spectra of g-C₃N₄, pg-C₃N₄, and Pt(3%)/pg-C₃N₄ in the C 1s (a), N 1s (b), and Pt 4f (c) binding energy regions.

404.3 eV is attributed to charging effects or positive charge localization in heterocycles. For the pg-C₃N₄, the XPS peaks of N 1s binding energy regions strengthen and shift to a higher binding energy compared with that of g-C₃N₄ because of the increased number of exposed surface functional groups and the changes in original electronic environment of nitrogen atoms. For the Pt(3%)/pg-C₃N₄, the XPS peaks of N 1s binding energy regions greatly shift to a higher binding energy compared with that of pg-C₃N₄ can also be attributed to the electron-withdrawing effect of Pt nanoparticles that increases the binding energy of N 1s atomic orbit. Fig. 5(c) presents the high-resolution XPS of Pt(3%)/pg-C₃N₄ in the Pt 4f binding energy region. The peaks at 71.0 and 74.3 eV can be attributed to the metallic Pt (Pt⁰) that originates from the reduction of Pt⁴⁺ precursor by photogenerated electrons.

3.1.3. Optical and electronic properties

The light absorption abilities of g-C₃N₄, Pt(3%)/g-C₃N₄, pg-C₃N₄, and Pt(x%)/pg-C₃N₄ were studied by UV-vis/DRS. As shown in Fig. 6, g-C₃N₄ shows a typical semiconductor absorption within the region of 200–450 nm, which is the electronic transition from the valence band populated by an N 2p orbital to the conduction band formed by a C 2p orbital. Compared

with g-C₃N₄, the enhanced light absorption ability in the region of 200–450 nm for the pg-C₃N₄ and Pt(3%)/g-C₃N₄ can be attributed to their increased electronic transition efficiency from the valence band to the conduction band, because both porous microstructure and deposited Pt nanoparticles are beneficial for multiple reflections of incident light. Therefore, compared with g-C₃N₄, more photogenerated carriers are generated for the pg-C₃N₄ and Pt(3%)/g-C₃N₄ under the same visible light excitation condition. Similarly, the light absorption ability of Pt(x%)/pg-C₃N₄ in the region of 200–450 nm gradually enhanced with increasing Pt-nanoparticle loading from 0% to 4% because of the gradually increased electronic transition efficiency from the valence band to the conduction band. Compared with g-C₃N₄, the increased light absorption abilities of pg-C₃N₄, Pt(3%)/g-C₃N₄, and Pt(x%)/pg-C₃N₄ in the region of 450–800 nm can be attributed to the decrease in reflectivity evidenced by the dark grey color of the sample.

The photocatalytic quantum efficiency was studied by PL measurements and photoelectrochemistry tests (Figs. 7 and 8). As shown in Fig. 7, g-C₃N₄ exhibits a broad fluorescence emission peak in the range of 400–600 nm with an excitation wavelength of 330 nm and an operating voltage of 400 V. This finding suggests that photoinduced e⁻-h⁺ pairs are generated and

Fig. 6. UV-vis/DRS of g-C₃N₄, Pt(3%)/g-C₃N₄, pg-C₃N₄, Pt(1%)/pg-C₃N₄, Pt(2%)/pg-C₃N₄, Pt(3%)/pg-C₃N₄, and Pt(4%)/pg-C₃N₄.

Fig. 7. PL spectra of g-C₃N₄, Pt(3%)/g-C₃N₄, pg-C₃N₄, Pt(1%)/pg-C₃N₄, Pt(2%)/pg-C₃N₄, Pt(3%)/pg-C₃N₄, and Pt(4%)/pg-C₃N₄.

Fig. 8. Photocurrent responses of g-C₃N₄ (1), Pt(3%)/g-C₃N₄ (2), pg-C₃N₄ (3), and Pt(3%)/pg-C₃N₄ (4) electrodes under Xe lamp irradiation.

recombined within the g-C₃N₄. Compared with g-C₃N₄, the decreased PL intensities of pg-C₃N₄ and Pt(3%)/g-C₃N₄ indicate that the efficient separation and transportation of photogenerated carriers are realized after the formation of porous microstructure and deposition of Pt nanoparticles. In addition, the PL intensities of Pt(*x*%)/pg-C₃N₄ gradually decrease with increasing Pt-nanoparticle loading from 0% to 3%. However, the PL intensity of Pt(4%)/pg-C₃N₄ increases, suggesting a weak photogenerated carriers transfer capability because new e[−]–h⁺ recombination centers were fabricated by the aggregation of excessive Pt nanoparticles. Sharp increases in photocurrent responses were observed in all the tested working electrodes once the pulse Xe lamp irradiation was activated, as displayed by the photocurrent–time (*I*–*t*) curves shown in Fig. 8. The generated photocurrents are reproducible and stable during four intermittent on–off irradiation cycles. The prompt increase in photocurrent response from the light-off to the light-on state was because of the quick separation and transportation of

photogenerated electrons on the surfaces of working electrodes. The photocurrent response of pg-C₃N₄ was higher than that of g-C₃N₄ and the photocurrent responses of Pt(3%)/g-C₃N₄ and Pt(3%)/pg-C₃N₄ were higher than those of g-C₃N₄ and pg-C₃N₄. The results of photoelectrochemical experiment are consistent with the PL measurements described above, indicating that the porous microstructure and deposited Pt nanoparticles can effectively slow down the recombination rate of photogenerated e[−]–h⁺ pairs.

3.2. Photocatalytic tests

3.2.1. Adsorption and photocatalytic degradation of aqueous MO and 4-FP

Photocatalytic tests were conducted in an aqueous solution containing oxygen molecules from dissolved air. Visible light irradiation was provided by a Xe lamp, and UV irradiation was eliminated using a 420-nm cut filter. The photocatalytic activities of as-prepared materials were preliminarily evaluated by the degradation of aqueous azo dyes MO. The as-prepared materials were applied to the degradation and mineralization of aqueous 4-FP. As shown in Fig. 9(a) and (b), direct photodegradation experiments indicate that changes in MO and 4-FP concentrations were negligible under visible light irradiation for 4 h, and the adsorption test result shows that the adsorption–desorption equilibrium was reached prior to Xe lamp irradiation. The photocatalytic activities of as-prepared materials showed a similar order for the MO and 4-FP degradation, i.e., Pt(3%)/pg-C₃N₄ > Pt(4%)/pg-C₃N₄ > Pt(2%)/pg-C₃N₄ > Pt(1%)/pg-C₃N₄ > pg-C₃N₄ > Pt(3%)/g-C₃N₄ > g-C₃N₄. The degradation rate of 4-FP is slower than that of MO under similar conditions because of its stable chemical structure.

The mineralization of aqueous 4-FP was evaluated by monitoring the changes in total organic carbon in the reaction system, and g-C₃N₄ and Pt(3%)/pg-C₃N₄ were selected as the representative photocatalysts. As shown in Fig. 10, the degradation of total organic carbon is negligible using g-C₃N₄ as a photo-

Fig. 9. Adsorption properties and photocatalytic activities of as-prepared materials toward aqueous MO (a) and 4-FP (b) degradation under visible-light irradiation.

Fig. 10. Evolution of TOC during the course of photocatalytic degradation of aqueous 4-FP over g-C₃N₄ and Pt(3%)/pg-C₃N₄.

catalyst under visible light irradiation for 24 h, indicating that the produced organic intermediates cannot decompose into inorganic species because of the low photocatalytic activity of g-C₃N₄. However, the total organic carbon of 4-FP is degraded totally using Pt(3%)/pg-C₃N₄ as a photocatalyst under visible

light irradiation for 24 h, indicating that the produced organic intermediates can decompose into inorganic species because of the high photocatalytic activity of Pt(3%)/pg-C₃N₄.

3.2.2. Recyclability of Pt/pg-C₃N₄ composite materials

The above 4-FP degradation reaction was repeated four times to evaluate the stability of as-prepared Pt/pg-C₃N₄ composite materials in a photocatalytic degradation system. After the first catalytic run, the catalyst was recovered by centrifugation and washed by water at room temperature. The recovered catalyst was used for the subsequent catalytic runs under the same experimental conditions. As shown in Fig. 11(a), the tested catalyst exhibited a considerably high stability and maintained a similar level of reactivity after four catalytic cycles. A gradually decreased photocatalytic activity can be attributed to the loss of photocatalyst in the recovery process. The characterization results of the used Pt(3%)/pg-C₃N₄ sample after photocatalytic reaction are shown in Fig. 11(b)–(d). The chemical structure and photoelectric properties of the used Pt(3%)/pg-C₃N₄ remain intact after the photocatalytic reaction.

3.2.3. Discussion of the photocatalytic test results

The excellent photocatalytic activity of as-prepared

Fig. 11. Recycling experiments of photocatalytic degradation of aqueous 4-FP over Pt(3%)/pg-C₃N₄ (a); FTIR spectra (b), UV-vis/DRS (c), and PL spectra (d) of the used Pt(3%)/pg-C₃N₄ after photocatalytic reaction.

Pt/pg-C₃N₄ is primarily attributed to the following three reasons.

First, the fabrication of porous microstructure is of great significance to improve the photocatalytic activity of Pt/pg-C₃N₄. On the one hand, a porous microstructure can ensure that the target pollutant degradation reaction is performed throughout the catalyst and lower the mass transfer limit. On the other hand, a porous microstructure can reduce the recombination of photogenerated e⁻-h⁺ pairs by improving electron transfer capability, prolonging charge lifespan, and transferring photogenerated charges to the reactants. In addition, the photogenerated electron capture effect of Pt nanoparticles was significantly enhanced due to a good contact between Pt nanoparticles and pg-C₃N₄ support. Therefore, the photocatalytic activities of pg-C₃N₄ and Pt(3%)/pg-C₃N₄ are higher than that of g-C₃N₄ and Pt(3%)/g-C₃N₄.

Second, the highly dispersed Pt nanoparticles produced by *in situ* photoreduction significantly enhance the photocatalytic quantum efficiency because of the strong electron acceptability of Pt nanoparticles. Therefore, the photocatalytic activities of Pt/pg-C₃N₄ gradually enhance with increasing Pt-nanoparticle loading from 0% to 3%. However, the photocatalytic activity of Pt/pg-C₃N₄ declines by increasing the loading to 4% because the aggregation of excessive Pt nanoparticles constructs new e⁻-h⁺ recombination centers that lower the photocatalytic quantum efficiency of Pt/pg-C₃N₄.

Third, the increased electronic transition efficiency of Pt/pg-C₃N₄ has a positive effect on their photocatalytic activity because more photogenerated e⁻-h⁺ pairs were produced than that in pg-C₃N₄ under similar visible light irradiation conditions.

4. Conclusions

A series of highly dispersed platinum-deposited porous g-C₃N₄ (Pt/pg-C₃N₄) were successfully fabricated by a simple *in situ* photoreduction strategy using chloroplatinic acid and porous g-C₃N₄ as precursors, and porous g-C₃N₄ was fabricated by

a simple precursor pretreatment strategy using melamine as a raw material. The as-prepared Pt/pg-C₃N₄ exhibits considerably high photocatalytic activity under visible light irradiation. The high photocatalytic activity is attributed to the unique porous microstructure and highly-dispersed Pt nanoparticles. The as-prepared Pt/pg-C₃N₄ composite materials can be widely used as a visible light photocatalyst in aqueous persistent organic pollutants degradation. They may also be broadly applied in other areas, such as photocatalytic hydrogen evolution from water-splitting, decomposition of NO, and reduction of CO₂.

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Graphical Abstract

Chin. J. Catal., 2017, 38: 29–38 doi: 10.1016/S1872-2067(16)62589-5

Fabrication of highly dispersed platinum-deposited porous g-C₃N₄ by a simple *in situ* photoreduction strategy and their excellent visible light photocatalytic activity toward aqueous 4-fluorophenol degradation

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A series of highly dispersed platinum-deposited porous g-C₃N₄ (Pt/pg-C₃N₄) were successfully fabricated by a simple *in situ* photoreduction strategy and applied to the degradation and mineralization of aqueous 4-fluorophenol under visible-light irradiation.

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原位光还原法制备高分散铂沉积多孔氮化碳复合材料及其降解水中4-氟苯酚的高效可见光光催化活性

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摘要: 作为一种新型水中有有机污染物, 有机氟化物中C–F共价键的键能较大, 因而很难通过传统的可见光光催化剂降解。因此, 开发高效可见光光催化剂是实现在可见光照射下成功降解水中有有机氟化物的关键。作为一种非金属半导体光催化剂, 石墨相氮化碳(g-C₃N₄)因具有可见光响应、环境友好及低成本等优点而广泛应用于水中有有机污染物去除。然而, 体相层状结构严重限制了g-C₃N₄的可见光活性。这是由于体相层状结构不利于光生电子的表面迁移, 同时增加了光催化反应过程的传质阻力。

为了开发一种可重复使用且具有优异可见光活性的光催化剂, 进而实现在可见光照射下水中有有机氟化物的高效降解及矿化, 本文以氯铂酸和多孔氮化碳(pg-C₃N₄)为前驱体, 运用简单的原位光还原法成功制备出一系列高分散铂沉积多孔氮化碳复合材料(Pt/pg-C₃N₄), 而pg-C₃N₄则是以三聚氰胺为原料采用前驱体预处理法制备。与传统铂沉积石墨相氮化碳(Pt/g-C₃N₄)复合材料相比, 由于多孔氮化碳前驱体具有暴露的几何内外表面, 铂纳米粒子可高度分散于其上。因此, 铂纳米粒子的电子捕获效应显著增强。另外, 与其他传统还原法相比, 原位光还原技术还可有效抑制铂纳米粒子的自凝聚。

我们对制备的Pt/pg-C₃N₄复合材料的形貌、孔隙率、相结构、化学组成及光电性质进行了详细表征。结果显示, 与传统Pt/g-C₃N₄复合材料相比, 由于多孔微观结构的构建以及高度分散铂纳米粒子的沉积, 制备的Pt/pg-C₃N₄复合材料的BET比表面积显著增大, 光吸收能力明显增强, 光催化量子效率显著提高。在可见光条件下, 初步评价了该复合材料光催化降解水中偶氮染料甲基橙的活性, 然后将其进一步应用于水中4-氟苯酚的降解及矿化。结果表明, 由于多孔微观结构的构建以及高度分散铂纳米粒子的沉积, 所制备Pt/pg-C₃N₄复合材料具有相当高的可见光光催化活性。结果还显示, 所制复合材料具有很高的稳定性, 连续使用4次均保持相似的活性。作为一种可见光催化剂, 所制Pt/pg-C₃N₄复合材料有望广泛应用于水中持久性有机污染物的降解以及光催化裂解水产氢、NO分解和CO₂还原等领域。

关键词: 光催化作用; 多孔氮化碳; 光还原; 铂沉积; 4-氟苯酚

收稿日期: 2016-09-17. 接受日期: 2016-11-06. 出版日期: 2017-01-05.

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基金来源: 国家自然科学基金(51568049, 51208248, 51468043, 21366024); 国家优秀青年科学基金(51422807); 江西省自然科学基金(20161BAB206118, 20114BAB213015); 江西省教育厅科技项目(GJJ14515, GJJ12456).

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