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Article

Fabrication of porous g-C₃N₄ and supported porous g-C₃N₄ by a simple precursor pretreatment strategy and their efficient visible-light photocatalytic activity

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ABSTRACT

Porous g-C₃N₄ and supported porous g-C₃N₄ were fabricated for the first time by a simple strategy using pretreated melamine as a raw material and pretreated quartz rod as a substrate. The formation of a richly porous microstructure can be attributed to the co-existence of different pore-fabricating units in the preparation system for porous g-C₃N₄. The richly porous microstructure endowed the as-prepared porous g-C₃N₄ with an excellent photocatalytic activity. The as-prepared supported porous g-C₃N₄ exhibited considerable stability because of the existence of chemical interaction between porous g-C₃N₄ and the quartz rod substrate. The photocatalytic activity of the supported porous g-C₃N₄ was competitive with that of porous g-C₃N₄ in powder form because neither the surface migration of photogenerated electrons nor the diffusion of the target organic pollutant were affected by the construction of the quartz rod reactor. The photocatalytic activity of the as-prepared porous g-C₃N₄ and supported porous g-C₃N₄ was preliminarily evaluated by the treatment of single-component organic wastewater under visible-light irradiation. Subsequently, the as-prepared porous g-C₃N₄ was further applied in conventional hydrogen evolution and a new system for simultaneous hydrogen evolution with organic-pollutant degradation. The hydrogen yield and degradation efficiency both increased with increasing photocatalytic activity of the as-prepared materials in the system for simultaneous hydrogen evolution with organic-pollutant degradation.

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1. Introduction

As a metal-free semiconductor photocatalyst, graphitic carbon nitride (g-C₃N₄) has been widely used in many photocatalytic applications, such as the removal of aqueous organic pollutants, evolution of hydrogen by water-splitting, reduction of

carbon dioxide into hydrocarbon fuels, and synthesis of organic target compounds by selective oxidation [1–10]. However, its bulk layered structure and powder physical state severely limit the practical application of g-C₃N₄ in heterogeneous photocatalytic reactions [11–17]. On the one hand, the bulk layered structure of g-C₃N₄ limits the surface migration of photogenerated

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ated carriers and increases the mass transfer resistance in photocatalytic reactions. On the other hand, the powder physical state of $g\text{-C}_3\text{N}_4$ is inconvenient for practical application because of the additional solid-liquid separation step. Therefore, several studies have been conducted to develop a morphologically controlled synthesis and supporting material for $g\text{-C}_3\text{N}_4$ to overcome these disadvantages [18–24].

The construction of a porous microstructure is a promising strategy for the synthesis of $g\text{-C}_3\text{N}_4$ with enhanced photocatalytic activity [25]. Dong et al. [26,27] synthesized porous $g\text{-C}_3\text{N}_4$ using hydrochloric acid-pretreated melamine as a precursor. In the present study we show that melamine pretreated with either hydrochloric acid or ethylene glycol (EG) can be used as a precursor for the preparation of porous $g\text{-C}_3\text{N}_4$. Interestingly, the present work also shows that porous $g\text{-C}_3\text{N}_4$ prepared using melamine co-pretreated with both of these reagents exhibits a more abundant porous microstructure than porous $g\text{-C}_3\text{N}_4$ prepared using melamine singly pretreated with just one of these reagents, which is attributed to the co-existence of different pore-fabricating units in the preparation system of the former.

In contrast to the preparation of supported titanium dioxide, supported $g\text{-C}_3\text{N}_4$ is difficult to fabricate because of the lack of a suitable sol-gel process [28–32]. Moreover, the practical application of $g\text{-C}_3\text{N}_4$ supported on a substrate of fluorine-tin oxide (FTO) suffers from several drawbacks. First, the sheet-shaped physical structure of the FTO substrate is not conducive to the diffusion of reactants. Second, the absorption of light by the FTO substrate reduces the amount of light available for the photocatalyst. Therefore, $g\text{-C}_3\text{N}_4$ can only be coated on one side of the substrate. Third, no chemical bonds are formed between $g\text{-C}_3\text{N}_4$ and the FTO substrate. Therefore, the loss of $g\text{-C}_3\text{N}_4$ is inevitable in the course of the photocatalytic reaction.

To solve these drawbacks of $g\text{-C}_3\text{N}_4$ in practical applications, porous $g\text{-C}_3\text{N}_4$ and supported porous $g\text{-C}_3\text{N}_4$ were fabricated for the first time using melamine co-pretreated with hydrochloric acid and EG as a raw material and a quartz rod co-pretreated with hydrofluoric acid and (3-aminopropyl)trimethoxysilane as a substrate. The as-prepared porous $g\text{-C}_3\text{N}_4$ showed excellent photocatalytic activity because of its richly porous microstructure. The as-prepared supported porous $g\text{-C}_3\text{N}_4$ exhibited considerable stability because of the chemical interaction between porous $g\text{-C}_3\text{N}_4$ and the quartz rod substrate. In addition, the photocatalytic activity of the supported porous $g\text{-C}_3\text{N}_4$ was competitive with that of porous $g\text{-C}_3\text{N}_4$ in powder form because neither the surface migration of photogenerated carriers nor the diffusion of the target organic pollutant were affected by the construction of the quartz rod reactor.

The photocatalytic activities of the as-prepared porous $g\text{-C}_3\text{N}_4$ and supported porous $g\text{-C}_3\text{N}_4$ were preliminarily evaluated by the treatment of single-component organic wastewater under visible-light irradiation. Subsequently, the as-prepared porous $g\text{-C}_3\text{N}_4$ was further applied in conventional hydrogen evolution and a new system for simultaneous hydrogen evolution with organic-pollutant degradation. In the system for sim-

ultaneous hydrogen evolution with organic-pollutant degradation, both the hydrogen yield and the degradation efficiency were significantly decreased compared with conventional photocatalytic degradation and hydrogen evolution systems because of the difficulty of the redox reaction between water and the organic pollutant. However, both factors were found to increase with increasing photocatalytic activity of the as-prepared materials used in the system. The reason for this improvement was investigated.

2. Experimental

2.1. Chemicals and reagents

Melamine ($\text{C}_3\text{H}_6\text{N}_6$, CP grade) and chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, GR grade) were purchased from Sinopharm Chemical Reagent Co. Ltd. Quartz rods (2 mm $\times$ 10 cm, abbreviated QR) were purchased from Shenghui Quartz Products Co. Ltd. Hydrochloric acid (HCl, AR grade, 36%–38%), EG ($\text{C}_2\text{H}_6\text{O}_2$, AR grade), and hydrofluoric acid (HF, AR grade, $\geq 40\%$) were purchased from Xilong Chemical Co. Ltd. (3-Aminopropyl)trimethoxysilane ($\text{C}_6\text{H}_{17}\text{NO}_3\text{Si}$, 97%, abbreviated KH-540) and *p*-chlorophenol ($\text{C}_6\text{H}_5\text{OCl}$, GC grade, abbreviated PCP) were purchased from Aladdin Chemistry Co. Ltd. Rhodamine B ($\text{C}_{28}\text{H}_{31}\text{ClN}_2\text{O}_3$, AR grade, abbreviated RB), and triethylamine ($(\text{C}_2\text{H}_5)_3\text{N}$, AR grade, abbreviated TEA) were purchased from Shanghai Fine Chemical Technology Co. Ltd. All chemicals were used without further purification. Double-distilled water was used in the catalyst preparation and subsequent catalytic tests.

2.2. Preparation

2.2.1. Fabrication of porous $g\text{-C}_3\text{N}_4$ using HCl- and EG-co-pretreated melamine as a precursor

In a typical synthesis, 3 g of melamine was placed into a 100-mL beaker, followed by the addition of 10 mL of HCl, 10 mL of EG, and 3 mL of water. After stirring the white viscous suspension for 1 h at room temperature, the HCl- and EG-co-pretreated melamine precursor was obtained by washing, centrifugation, and drying. Subsequently, the HCl- and EG-co-pretreated melamine precursor was transferred to 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 further heated to 550 °C at a rate of 10 °C/min. After maintaining the temperature at 550 °C for 2 h, a sample of yellow porous $g\text{-C}_3\text{N}_4$ was obtained after natural cooling, which was denoted pg- C_3N_4 -(HCl + EG). For comparison, samples denoted pg- C_3N_4 -EG and pg- C_3N_4 -HCl were also prepared by the same method but in the absence of HCl or EG, respectively, in the course of melamine pretreatment, and with the addition of 20 mL of EG or HCl (rather than 10 mL) during synthesis. Bulk $g\text{-C}_3\text{N}_4$ was also prepared by the same method but using non-pretreated melamine as a precursor.

2.2.2. Fabrication of supported porous $g\text{-C}_3\text{N}_4$ using HF- and KH-540-co-pretreated quartz rod substrate

In a typical synthesis, the quartz rods were soaked in dilute HF for 20 min at room temperature and then washed with water several times. The HF-pretreated quartz rods were placed into a 25 mL test tube containing 1 mL of KH-540 and 20 mL of ethanol, and then heated at 60 °C for 24 h. After washing the HF- and KH-540-co-pretreated quartz rods with ethanol and water several times, the above-prepared HCl- and EG-co-pretreated melamine precursor was uniformly coated onto the surface of the quartz rods. The coated quartz rods were transferred to a ash pan (6 cm × 12 cm) after drying at 60 °C for 24 h and heated at 550 °C for 2 h. Finally, the quartz rod-supported porous g-C₃N₄ samples were obtained after natural cooling, and denoted QR-pg-C₃N₄.

2.3. Characterizations

Transmission electron microscopy (TEM) images were recorded on a JEOL JEM-2010 transmission electron microscope at an accelerating voltage of 200 kV. Scanning electron microscopy (SEM) images were recorded using a Quanta 200 environmental scanning electron 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 D8 ADVANCE 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. Photocatalytic tests

2.4.1. Photocatalytic treatment of single-component organic wastewater using pg-C₃N₄ and QR-pg-C₃N₄

A PLS-SXE 300 Xe lamp (300-W, Beijing PerfectLight Co. Ltd., China) with an output wavelength $\lambda > 320$ nm served as the light source. The UV component of the irradiation from the lamp was removed using a 420-nm-cutoff filter, so that only visible light with an output wavelength $\lambda > 420$ nm was retained. 100 mg of powder photocatalyst and 100 mL of single-component organic wastewater (containing 10 ppm RB or 20 ppm PCP) were poured into a beaker with a quartz cover. Additionally, 100 mg of supported photocatalyst and 100 mL of single-component organic wastewater (20 ppm PCP) were poured into a self-designed quartz rod reactor (Scheme 2). For the powder photocatalyst, the suspension was ultrasonicated for 10 min and stirred in the dark until adsorption-desorption equilibrium. For the supported photocatalyst, the reactor was left to stand until adsorption-desorption equilibrium was

reached. Subsequently, the light source was switched on, and fixed amounts of the reaction solution were extracted at pre-determined time intervals during irradiation. Changes in the RB concentrations were analyzed using a UNICO UV-2000 spectrophotometer at $\lambda = 554$ nm. Changes in the PCP concentrations were analyzed using an Agilent 1100 series high-performance liquid chromatography (HPLC) C₁₈ column and a UV detector ($\lambda = 277$ nm), with acetonitrile/water (60/40 v/v) used as the mobile phase at a flow rate of 1.0 mL/min.

2.4.2. Hydrogen evolution by water-splitting using TEA as an electron donor

100 mg of powder photocatalyst loaded with 3 wt% Pt co-catalyst and 100 mL of H₂O containing 10 vol% TEA were poured into a quartz reactor. The above suspension was ultrasonicated for 10 min and stirred in the dark for 1 h. Subsequently, the light source was switched on, and further stirring was performed. The temperature of the suspension was maintained at 35 ± 2 °C by circulation of water through an external cooling jacket. After irradiation under visible light with $\lambda > 420$ nm for 6 h, the generated hydrogen was analyzed in situ with a GC 7890-II TCD gas chromatograph (TECHCOMP) using an MS-5 A column, which was connected to a circulating gas line with an argon carrier. For comparison, the photocatalytic tests were also performed in a pure TEA system.

2.4.3. Simultaneous hydrogen evolution with organic-pollutant degradation

The above-described hydrogen evolution system, i.e., 100 mL of H₂O containing 10 vol% TEA, was replaced by 100 mL of an aqueous solution of an organic pollutant (50 ppm RB). After allowing the organic pollutant and the photocatalyst to reach adsorption-desorption equilibrium in preparation for the hydrogen evolution reaction, the saturated photocatalyst was separated and transferred to a new reaction solution. For comparison, the photocatalytic tests were also performed in a pure H₂O system. The generated hydrogen was analyzed in situ with a GC 7890-II TCD gas chromatograph. The change in the RB concentration was analyzed using a UNICO UV-2000 spectrophotometer at $\lambda = 554$ nm.

3. Results and discussion

3.1. Characterizations

3.1.1. Morphologies and textural properties

The morphologies of the as-prepared bulk g-C₃N₄, pg-C₃N₄-EG, pg-C₃N₄-HCl, and pg-C₃N₄-(HCl + EG) were characterized by TEM observation (Fig. 1(a)–(d)). As shown in Fig. 1(a), the bulk g-C₃N₄ exhibited a non-porous graphite-like layered microstructure. It can be clearly seen from Fig. 1(b) and (c) that samples of porous g-C₃N₄ with different pore geometries were successfully fabricated using melamine pretreated with EG or HCl, respectively. The different pore geometries of pg-C₃N₄-EG and pg-C₃N₄-HCl suggest the presence of different pore-fabricating units in the catalyst preparation systems.

Fig. 1. TEM images of bulk g-C₃N₄ (a), pg-C₃N₄-EG (b), pg-C₃N₄-HCl (c), and pg-C₃N₄-(HCl + EG) (d); (e) SEM images of QR-pg-C₃N₄; (f) random sampling photograph of QR-pg-C₃N₄.

Compared with pg-C₃N₄-EG and pg-C₃N₄-HCl, the formation of a more richly porous microstructure for pg-C₃N₄-(HCl + EG) can be attributed to the co-existence of different pore-fabricating units in the combined catalyst preparation system (Fig. 1(d)). Fig. 1(e) and (f) show an SEM image and a randomly sampled photograph of QR-pg-C₃N₄, respectively, demonstrating that porous g-C₃N₄ was successfully coated onto the quartz rod substrate with a uniform and stable morphology. The porous g-C₃N₄ coating had a thickness of about 20 μ m.

The textural properties of the as-prepared bulk g-C₃N₄, pg-C₃N₄-EG, pg-C₃N₄-HCl, and pg-C₃N₄-(HCl + EG) were characterized by measuring their nitrogen gas porosity (Fig. 2). As

shown in Fig. 2(a), the type-II isotherm of bulk g-C₃N₄ implies its non-porosity. The type-IV isotherms with H3-type hysteresis loops for pg-C₃N₄-EG, pg-C₃N₄-HCl, and pg-C₃N₄-(HCl + EG) are evidence of their porous microstructures. As shown in Fig. 2(b), the Barrett-Joyner-Halenda (BJH) pore-size distribution curves reveal that all of the tested materials exhibited a weak narrow peak in the range of 3–5 nm, which can be attributed to the released NH₃, which acted as a soft template in the course of melamine polycondensation. The strong, broad pore-size distribution peaks in the range of 5–120 nm for pg-C₃N₄-EG, pg-C₃N₄-HCl, and pg-C₃N₄-(HCl + EG) originate from the formation of porous microstructures. The Brunau-

Fig. 2. Nitrogen sorption isotherms (a) and pore-size distribution curves (b) of as-prepared powder photocatalysts.

Fig. 3. XRD patterns of as-prepared powder photocatalysts.

er-Emmett-Teller (BET) surface areas of pg-C₃N₄-EG, pg-C₃N₄-HCl, and pg-C₃N₄-(HCl + EG) were larger than that of bulk g-C₃N₄ because their porous microstructures resulted in more exposed geometrical surfaces compared with the bulk layered structure of the latter. The BET surface area of pg-C₃N₄-(HCl + EG) was larger than those of pg-C₃N₄-EG and pg-C₃N₄-HCl because of its more richly porous microstructure.

3.1.2. Compositional and structural information

The phase structures of the as-prepared bulk g-C₃N₄, pg-C₃N₄-EG, pg-C₃N₄-HCl, and pg-C₃N₄-(HCl + EG) were characterized by XRD analysis (Fig. 3). The bulk g-C₃N₄ exhibited a typical (002) interlayer-stacking peak at 27.5°, corresponding to an interlayer distance of $d = 0.33$ nm, and a (100) peak at 12.9° corresponding to an in-plane structural packing motif with a period of 0.675 nm. Compared with bulk g-C₃N₄, the weaker diffraction intensity of the (002) peaks for pg-C₃N₄-EG and pg-C₃N₄-HCl can be attributed to the reduced content of layered morphologies in the porous microstructures of the latter materials. For pg-C₃N₄-(HCl + EG), the diffraction intensity of the (002) peak was weaker still than those of pg-C₃N₄-EG and pg-C₃N₄-HCl because of its even more richly porous micro-

structure.

The changes in the chemical structure of the pretreated melamine were confirmed by FTIR spectral characterization. As shown in Fig. 4(a), the characteristic FTIR peaks of melamine and EG-pretreated melamine were very similar, indicating that the chemical structure of melamine remained intact after EG pretreatment. However, the characteristic peaks of HCl-pretreated and HCl/EG-co-pretreated melamine were shifted with respect to melamine but did not correspond to those of pure cyanuric acid. This result indicates the formation of hydrogen-bonded aggregates of melamine-cyanuric acid during the pretreatment of melamine by HCl [33]. The FTIR spectra of bulk g-C₃N₄, pg-C₃N₄-EG, pg-C₃N₄-HCl, and pg-C₃N₄-(HCl + EG) are shown in Fig. 4(b). For all the tested materials, the sharp peak at 813.5 cm⁻¹ is the typical bending vibration of *s*-triazine units, the series of peaks in the range of 1100–1700 cm⁻¹ is attributed to stretching modes, including C–N and C=N, in the CN heterocycles, and the broad absorption peaks in the range of 2900–3400 cm⁻¹ originate from the stretching vibrational modes of primary (–NH₂) and secondary (–NH) amines. Evidently, the FTIR spectra of pg-C₃N₄-EG, pg-C₃N₄-HCl, and pg-C₃N₄-(HCl + EG) were similar to that of bulk g-C₃N₄, indicating that these species retained the same chemical structure as bulk g-C₃N₄ after the formation of their porous microstructures. However, pg-C₃N₄-EG, pg-C₃N₄-HCl, and pg-C₃N₄-(HCl + EG) exhibited stronger FTIR modes compared with g-C₃N₄ because they contained greater amounts of exposed surface functional groups.

The surface composition and chemical state of the constituent elements of bulk g-C₃N₄ and pg-C₃N₄-(HCl + EG) were characterized by a high-resolution XPS probe technique (Fig. 5). As shown in Fig. 5(a), bulk g-C₃N₄ exhibited a peak in the C 1s binding-energy region centered at 285.0 eV, which is typically assigned to C–C and/or C=C, and originates from the adventitious reference carbon on the surface. The peak centered at 288.3 eV originates from *sp*²-hybridized C atoms bonded to N in an aromatic ring (N=C–(N)₂), while the peak centered at 289.1 eV is assigned to *sp*² C atoms in an aromatic ring attached to primary and secondary amines (N=C(N)–NH₂, N=C(N)–NH).

Fig. 4. FTIR spectra of pretreated melamine precursor (a) and as-prepared powder photocatalysts (b).

Fig. 5. High-resolution XPS of bulk g-C₃N₄ and pg-C₃N₄-(HCl + EG) in the C 1s (a) and N 1s (b) binding energy regions.

Compared with bulk g-C₃N₄, the XPS peaks of *sp*² C atoms for pg-C₃N₄-(HCl + EG) were more intense and shifted to higher binding energies because the formation of a porous microstructure increased the number of exposed surface functional groups, so that the original electronic environment of the *sp*² C atoms was perturbed by the increased presence of surface -NH₂ and -NH groups. The high-resolution XPS results for the N 1s binding-energy regions (Fig. 5(b)) are consistent with the C 1s results just described. For bulk g-C₃N₄, the peak centered at 398.8 eV is assigned to *sp*²-hybridized aromatic N atoms bonded to C atoms (C=N-C). The peak centered at 400.2 eV is related to either tertiary N 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 400.8 eV corresponds to N atoms bonded to three C atoms in an aromatic ring (N-(C)₃). The weak peak at 404.2 eV is attributed to charging effects or positive-charge localization in heterocycles [34]. For pg-C₃N₄-(HCl + EG), the XPS peaks of the N 1s binding-energy regions were more intense and shifted to higher binding energies compared with those of bulk g-C₃N₄ because of the increased number of exposed surface functional groups and the changes in the original electronic environment of the N atoms.

3.1.3. Optical and electronic properties

The light absorption properties of the as-prepared bulk g-C₃N₄, pg-C₃N₄-EG, pg-C₃N₄-HCl, and pg-C₃N₄-(HCl + EG) were studied by UV-Vis/DRS. As shown in Fig. 6(a), bulk g-C₃N₄ displayed typical semiconductor absorption within the region of 200–465 nm, originating from an induced electronic transition from the valence band (VB), populated by N 2*p* orbitals, to the conduction band (CB), formed by C 2*p* orbitals. Compared with bulk g-C₃N₄, the enhanced light absorption in the region of 200–465 nm for pg-C₃N₄-EG, pg-C₃N₄-HCl, and pg-C₃N₄-(HCl + EG) can be attributed to the increased efficiency of the electronic transition from VB to CB, because their porous microstructures are more favorable than the bulk layered structure for this transition.

The photocatalytic quantum efficiencies of the as-prepared bulk g-C₃N₄, pg-C₃N₄-EG, pg-C₃N₄-HCl, and pg-C₃N₄-(HCl + EG) were studied by PL measurements. As shown in Fig. 6(b), with an excitation wavelength of 330 nm and an operating voltage of 400 V, bulk g-C₃N₄ exhibited a broad fluorescence emission peak in the range of 400–600 nm. This finding suggests that the photoinduced e⁻-h⁺ pairs generated within the bulk g-C₃N₄ had a tendency to recombine. Compared with bulk g-C₃N₄, the suc-

Fig. 6. UV-Vis/DRS (a) and PL spectra (b) of as-prepared powder photocatalysts.

cessively decreasing PL intensities of pg-C₃N₄-EG, pg-C₃N₄-HCl, and pg-C₃N₄-(HCl + EG) indicate that their porous microstructures promoted the efficient separation and transportation of the photogenerated carriers.

3.2. Fabrication mechanism of porous g-C₃N₄ by precursor pretreatment strategy

To date, there are few reports of the fabrication of porous g-C₃N₄ by the use of a pretreated precursor. Dong et al. [27] suggested that pretreatment with HCl would alter the condensation behavior of melamine, and thus induced the formation of porous g-C₃N₄, through the protective neutralization of the amino groups by reaction with HCl, thus limiting the involvement of the amino groups in thermal condensation. From the above characterization results we conclude that the successful construction of the porous microstructures is attributed to the presence of pore-fabricating units in the preparation systems for porous g-C₃N₄. These pore-fabricating units effectively hindered the continuous polycondensation of melamine during bulk g-C₃N₄ formation. Therefore, a porous microstructure was formed in the regions where melamine polycondensation was terminated.

As shown in Scheme 1, for the EG-pretreated melamine sys-

tem, the pore-fabricating units were formed by hydrogen bonding interactions between melamine and EG. The EG-protected melamine was unable to self-react with the original melamine species, thus terminating melamine polycondensation. Eventually, a porous microstructure was formed in the terminal region of melamine polycondensation. In the case of HCl pretreatment, melamine and cyanuric acid co-existed in the preparation system because of the formation of the latter by the acid–base reaction between melamine and HCl. Typically, cyanuric acid exists in two isomeric forms, *s*-triazine-2,4,6-trione and *s*-triazine-2,4,6-triol. The trione form is unable to react with melamine by high-temperature polycondensation to produce pores. However, the triol form can react with melamine by intermolecular dehydration. Therefore, a porous microstructure was formed in the terminal region of the polycondensation of melamine and the *s*-triazine-2,4,6-triol form of cyanuric acid. For the HCl- and EG-co-pretreated melamine system, a more richly porous microstructure was fabricated because of the co-existence of different pore-fabricating units. Specifically, the three types of pore-fabricating units in this catalyst preparation system were EG-protected melamine, cyanuric acid in the *s*-triazine-2,4,6-trione form, and EG-protected cyanuric acid in the *s*-triazine-2,4,6-triol form. Compared with the singly EG- or HCl-pretreated melamine

Scheme 1. Fabrication mechanism of porous g-C₃N₄ by precursor pretreatment strategy.

systems, the HCl- and EG-co-pretreated melamine system contained not only more types of pore-fabricating units but a greater absolute amount of them. Therefore, a richly porous microstructure was fabricated in the terminal region of melamine polycondensation.

3.3. Photocatalytic tests

3.3.1. Photocatalytic treatment of single-component organic wastewater

Photocatalytic degradation tests were conducted in an aqueous solution containing oxygen from dissolved air. The photocatalytic activity of the as-prepared bulk $g\text{-C}_3\text{N}_4$, $\text{pg-C}_3\text{N}_4\text{-EG}$, $\text{pg-C}_3\text{N}_4\text{-HCl}$, and $\text{pg-C}_3\text{N}_4\text{-(HCl + EG)}$ was preliminarily evaluated by the degradation of aqueous RB. As shown in Fig. 7(a), the direct photodegradation experiment (i.e., in the absence of a catalyst) found that the RB concentration in the reaction system showed negligible changes under visible-light irradiation for 90 min. For the catalytic experiments, adsorption tests were performed to confirm that the adsorption–desorption equilibria had been reached prior to irradiation with the Xe lamp. The percentages of RB adsorbed on the bulk $g\text{-C}_3\text{N}_4$, $\text{pg-C}_3\text{N}_4\text{-EG}$, $\text{pg-C}_3\text{N}_4\text{-HCl}$, and $\text{pg-C}_3\text{N}_4\text{-(HCl + EG)}$ were 1.9%, 12.4%, 15.5%, and 18.6%, respectively. The photocatalytic activities of the as-prepared photocatalysts for the degradation of aqueous RB followed the order of bulk $g\text{-C}_3\text{N}_4 < \text{pg-C}_3\text{N}_4\text{-EG} < \text{pg-C}_3\text{N}_4\text{-HCl} < \text{pg-C}_3\text{N}_4\text{-(HCl+EG)}$. Compared with bulk $g\text{-C}_3\text{N}_4$, the increased photocatalytic activity of $\text{pg-C}_3\text{N}_4\text{-EG}$, $\text{pg-C}_3\text{N}_4\text{-HCl}$, and $\text{pg-C}_3\text{N}_4\text{-(HCl + EG)}$ can be attributed to their porous microstructures, which enlarged the BET surface areas, improved the light-absorption capacities, and increased the photocatalytic quantum efficiencies of these as-prepared materials. The photocatalytic activity of $\text{pg-C}_3\text{N}_4\text{-(HCl + EG)}$ was higher than those of $\text{pg-C}_3\text{N}_4\text{-EG}$ and $\text{pg-C}_3\text{N}_4\text{-HCl}$ owing to its more richly porous microstructure.

The stability and photocatalytic activity of the as-prepared QR- $\text{pg-C}_3\text{N}_4$ were evaluated by applying it for the degradation of aqueous PCP in three consecutive cycles. As shown in Fig. 7(b), the capacity of the as-prepared QR- $\text{pg-C}_3\text{N}_4$ for aqueous PCP degradation proved highly stable. We attribute this to the

Scheme 2. The designed route for fabrication of QR- $\text{pg-C}_3\text{N}_4$ and their application to the degradation of aqueous organic pollutants under visible-light irradiation.

chemical interaction between the quartz rod substrate and porous $g\text{-C}_3\text{N}_4$ (Scheme 2). The photocatalytic activity of QR- $\text{pg-C}_3\text{N}_4$ remained at a similar level to that of powder $\text{pg-C}_3\text{N}_4\text{-(HCl + EG)}$, indicating that the surface migration of photogenerated carriers and the diffusion of the target organic pollutant were not affected after the construction of the quartz rod reactor (Scheme 2). The stability and photocatalytic activity of the as-prepared QR- $\text{pg-C}_3\text{N}_4$ suggest its potential utility in the practical treatment of industrial wastewater.

3.3.2. Hydrogen evolution by water-splitting using TEA as an electron donor

TEA is commonly used as an electron donor in traditional photocatalytic hydrogen evolution systems. Therefore, the photocatalytic activities of bulk $g\text{-C}_3\text{N}_4$, $\text{pg-C}_3\text{N}_4\text{-EG}$, $\text{pg-C}_3\text{N}_4\text{-HCl}$, and $\text{pg-C}_3\text{N}_4\text{-(HCl + EG)}$ for hydrogen evolution by water-splitting were evaluated in a TEA aqueous solution (10 vol%) under visible-light ($\lambda > 420 \text{ nm}$) irradiation for 6 h in the presence of 3 wt% Pt co-catalyst. As shown in Fig. 8(a), the photocatalytic activities of the tested photocatalysts for hydrogen evolution by water-splitting followed the order of bulk $g\text{-C}_3\text{N}_4 < \text{pg-C}_3\text{N}_4\text{-EG} < \text{pg-C}_3\text{N}_4\text{-HCl} < \text{pg-C}_3\text{N}_4\text{-(HCl + EG)}$. Thus, $\text{pg-C}_3\text{N}_4\text{-(HCl + EG)}$ showed the highest hydrogen evolution

Fig. 7. (a) Photocatalytic degradation of aqueous RB over as-prepared powder photocatalysts; (b) stability study of as-prepared QR- $\text{pg-C}_3\text{N}_4$ toward aqueous PCP degradation.

Fig. 8. (a) Hydrogen evolution from water-splitting by using TEA as an electron donor over as-prepared powder photocatalysts; (b) simultaneous hydrogen evolution with RB degradation over as-prepared powder photocatalysts.

activity among the tested samples, presumably because of its richly porous microstructure. However, when tested in a pure TEA system, pg-C₃N₄-(HCl + EG) showed a much lower hydrogen evolution activity, presumably because of the absence of water. This verifies that the production of hydrogen originated from water-splitting rather than TEA decomposition.

3.3.3. Simultaneous hydrogen evolution with organic-pollutant degradation

In the system for simultaneous hydrogen evolution with organic-pollutant degradation, the hydrogen yield and degradation efficiency were both reduced compared with the respective conventional systems (Fig. 8(b)). In previous work [23] we showed that both photocatalytic degradation and hydrogen evolution were redox reactions and that the photocatalyst acted as an electron-transfer medium in the redox process. However, in the system for simultaneous hydrogen evolution with organic-pollutant degradation, the redox reaction between the organic pollutants and water was heavily disfavored because of the poor electron-donating ability of the pollutants, hence the decreased hydrogen yield and degradation efficiency. Interestingly, however, in the simultaneous system, the hydrogen yield and degradation efficiency both increased as the photocatalytic activity of the as-prepared materials used in the system increased. This indicates that enhancing the electron-transfer capability of the photocatalyst facilitated the redox reaction between organic pollutants and water. Additionally, because hydrogen evolution is a redox reaction, it was heavily disfavored in the pure H₂O or pure TEA systems because of the absence of a reducing agent (TEA) or oxidizing agent (H₂O), respectively. Therefore, the hydrogen yield was low in these cases.

4. Conclusions

Porous g-C₃N₄ and supported porous g-C₃N₄ were successfully fabricated by using HCl- and EG-co-pretreated melamine as a raw material and quartz rod as a substrate. The formation of a richly porous microstructure can be attributed to the

co-existence of different pore-fabricating units in the preparation system for porous g-C₃N₄. The as-prepared pg-C₃N₄-(HCl + EG) showed excellent photocatalytic activity because of the enlarged BET surface area, improved light-absorption capacity, and increased photocatalytic quantum efficiency resulting from its richly porous microstructure. The considerable stability of the as-prepared QR-pg-C₃N₄ can be attributed to the chemical interaction between the porous g-C₃N₄ and quartz rod substrate. The QR-pg-C₃N₄ and pg-C₃N₄-(HCl + EG) had similar photocatalytic activities, indicating that the surface migration of photogenerated carriers and the diffusion of the target organic pollutant were not affected after the construction of the quartz rod reactor. In a system for simultaneous hydrogen evolution with organic-pollutant degradation, the finding that both the hydrogen yield and the degradation efficiency increased with increasing photocatalytic activity of the as-prepared materials indicates that enhancing the electron-transfer capability of the photocatalyst facilitated the redox reaction between organic pollutants and water.

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Graphical Abstract

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Fabrication of porous g-C₃N₄ and supported porous g-C₃N₄ by a simple precursor pretreatment strategy and their efficient visible-light photocatalytic activity

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Porous g-C₃N₄ and supported porous g-C₃N₄ were fabricated for the first time by a simple precursor pretreatment strategy and applied in organic-pollutant degradation, hydrogen evolution, and simultaneous hydrogen evolution with organic-pollutant degradation under visible-light irradiation.

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一种简单前驱体预处理策略制备多孔氮化碳和负载型多孔氮化碳及其高效可见光光催化活性

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摘要: 作为一种非金属半导体光催化剂, 石墨相氮化碳($g-C_3N_4$)已广泛应用于水中有机污染物去除、劈裂水产氢、二氧化碳还原制碳氢化合物燃料以及选择性氧化有机合成等许多光催化领域。然而, 聚集态层状结构和粉末物理状态严重限制了 $g-C_3N_4$ 在非均相光催化反应中的实际应用。一方面, $g-C_3N_4$ 的聚集态层状结构限制了光生载流子的表面迁移并增加了光催化反应的传质阻力。另一方面, 由于附加的固-液分离步骤, 粉体 $g-C_3N_4$ 不便于实际应用。因此, 为解决 $g-C_3N_4$ 的上述缺点, 一些研究已经进行并集中于 $g-C_3N_4$ 的形貌控制合成及负载。

构建多孔微观结构是合成具有优异光催化活性 $g-C_3N_4$ 的有效途径之一。本文研究表明, 盐酸或乙二醇预处理的三聚氰胺均可用作制备多孔 $g-C_3N_4$ 的前驱体。有趣的是, 由于在多孔 $g-C_3N_4$ 制备体系中不同制孔单元的共存, 与通过盐酸或乙二醇单独预处理的三聚氰胺制备的多孔 $g-C_3N_4$ 相比, 通过二者共同预处理的三聚氰胺制备的多孔 $g-C_3N_4$ 具有更丰富的多孔微观结构。

与制备负载型二氧化钛不同, 由于在制备 $g-C_3N_4$ 过程中缺少溶胶-凝胶步骤, 因此负载型 $g-C_3N_4$ 较难制备。而且, 对于氟-锡氧化物(FTO)基底负载的 $g-C_3N_4$, 在实际应用中存在一些不足。首先, FTO基底的片状物理结构不利于反应底物的扩散。其次, FTO基底的吸光效应会导致光能损失, 因此 $g-C_3N_4$ 只能在FTO基底的单面负载。最后, 在 $g-C_3N_4$ 和FTO基底之间无化学作用, 因此在光催化反应过程中不可避免造成 $g-C_3N_4$ 的损失。

因此, 以盐酸/乙二醇共同预处理的三聚氰胺作原料, 氢氟酸/3-氨基丙基三甲氧基硅烷共同预处理的石英棒作基底, 首次制备了多孔 $g-C_3N_4$ 和负载型多孔 $g-C_3N_4$ 。丰富的多孔微观结构使得所制多孔 $g-C_3N_4$ 具有优异的光催化活性; 且由于多孔 $g-C_3N_4$ 与石英棒基底间存在化学作用, 因而具有相当高的稳定性。另外, 由于在构建石英棒反应器之后不影响光生载流子的表面迁移和目标有机污染物的扩散, 因此负载型多孔 $g-C_3N_4$ 的光催化活性与粉体多孔 $g-C_3N_4$ 相似。

所制备多孔 $g-C_3N_4$ 和负载型多孔 $g-C_3N_4$ 的光催化活性通过在可见光条件下单组份有机废水的处理进行初步评价。在有机污染物降解同时产氢系统中, 由于水和有机污染物之间的氧化还原反应难于进行, 因此与传统的光催化降解和产氢系统相比, 所制多孔 $g-C_3N_4$ 的氢气产率和降解效率均显著降低; 然而, 在有机污染物降解同时产氢系统中, 随着该材料光催化活性的提高, 氢气产率和降解效率同时提高。这是因为光催化剂电子传递能力的提高促进了有机污染物和水之间的氧化还原反应。

关键词: 多孔微观结构; 石墨相氮化碳; 基底; 降解; 产氢

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