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Original article

Etching graphitic carbon nitride by acid for enhanced photocatalytic activity toward degradation of 4-nitrophenol

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ABSTRACT

Graphitic carbon nitride (g-C_3N_4) with high photocatalytic activity toward degradation of 4-nitrophenol under visible light irradiation was prepared by HCl etching followed by ammonia neutralization. The structure, morphology, surface area, and photocatalytic properties of the prepared samples were studied. After treatment, the size of the g-C_3N_4 decreased from several micrometers to several hundred nanometers, and the specific area of the g-C_3N_4 increased from 11.5 m^2/g to 115 m^2/g. Meanwhile, the photocatalytic activity of g-C_3N_4 was significantly improved after treatment toward degradation of 4-nitrophenol under visible light irradiation. The degradation rate constant of the small particle g-C_3N_4 is 5.7 times of that of bulk g-C_3N_4, which makes it a promising visible light photocatalyst for future applications for water treatment and environmental remediation.

1. Introduction

In the past decades, the development of human society has caused tremendous environmental problems. Tons of organic pollutants were discarded into the lakes and rivers everyday which resulted in serious water contamination. The polluted water is harmful for human beings and other living things. Among those organic pollutants, the aromatic compound, 4-nitrophenol, from the raw material to manufacture drugs, pesticides, and dyes, is one of the primary organic pollutants in water. This chemical may cause a blood disorder [1,2]. It is difficult to remove the 4-nitrophenol by traditional biological and adsorption methods due to its high stability in water. Fortunately, Fujishima and Honda first reported the photocatalyst TiO_2 for splitting water to generate hydrogen gas in 1972 [3]. This novel photocatalytic technology becomes a promising way to degrade organic pollutants, which has attracted intense research interest all over the world in the past decades due to its environmentally friendly and economical advantages [4,5].

Although TiO_2 shows high photocatalytic activity for the degradation of many pollutants, it can only respond to the UV light irradiation due to its wide bandgap (3.2 eV). Unfortunately, the solar light contains only about 4% UV light. In order to improve the utilization of the solar light, to explore efficient visible light driven photocatalysts is greatly demanded. Many visible light driven photocatalysts have been reported in recent years [6–12]. Among these photocatalysts, the graphitic carbon nitride (g-C_3N_4), a metal free visible light driven photocatalyst, has attracted intense interest due to its unique properties such as high stability, non-toxicity, easy modification and outstanding electrical property [12,13]. Efforts have been devoted on using g-C_3N_4 as a photocatalyst for degradation of pollutants and production of hydrogen [12–20]. However, the photocatalytic activity of the as-prepared g-C_3N_4 is low. In order to improve the photocatalytic activity of g-C_3N_4, attempts have been made on increasing its surface area including using a template to prepare porous g-C_3N_4, or treated g-C_3N_4 by alkali or acid [14–17]. By using silica microballs as templates, the specific surface area of the g-C_3N_4 reached to 373 m^2/g [14]. However, hydrofluoric acid must be used in this method to remove the templates. This process is not environment friendly and costly. Other approaches, like HCl or alkali treatment, can improve the specific surface area of the g-C_3N_4 to several tens square meters per gram [16,17].

In this contribution, we are reporting a simple method of preparing high specific surface area g-C_3N_4 without any template. After etching, the surface area of the g-C_3N_4 increased from 11.5 m^2/g to 115 m^2/g, and the size of the g-C_3N_4 particle also decreased significantly. It shows excellent photocatalytic activity toward degradation of 4-nitrophenol compared with the pristine g-C_3N_4 under visible light irradiation.

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2. Experimental

Melamine ($C_3H_6N_6$) was purchased from Tianjin Kemiou Chemical Co., Ltd. $NH_3{\cdot}H_2O$ (25%) and HCl (37%) were purchased from Guangzhou Chemical Co., Ltd. All reagents used in this study are analytical grade and used without further purification. The g-C_3N_4 was synthesized by heating melamine to 550 °C for 2 h in a muffle. The as-prepared g-C_3N_4 was ground to powder using an agate mortar. g-C_3N_4 powder (0.95 g) was added into 40 mL HCl solution (1.0 mol/L) under magnetic stirring for 0.5 h. Then, the mixture was translated to a Teflon-lined autoclave (50 mL) and heated at 150 °C for 5 h. After being cooled down to the room temperature naturally, the product was collected by filtration followed by further dispersed in 40 mL ammonia solution (2.0 mol/L), and stirred for 0.5 h. After that, the product was washed with distilled water and ethanol for several times, and then dried at 80 °C for 10 h. Finally, the product was heated at 400 °C for 1 h in air to remove ammonia. The obtained product was named as g-C_3N_4-T.

Phase and structural of the samples were characterized by X-ray diffractometer (XRD, D8 Focus X-ray diffractometer, Bruker, Germany) using Cu Kα (λ = 0.154184 nm) as a radiation source. The Fourier transform infrared spectra (FTIR) of the products were recorded on IR Affiniy-1 FTIR spectrometer. The morphology of the samples was observed using a field emission scanning electron microscope (FESEM, JSM-6330F, JEOL, Japan). The specific surface areas were measured at 77 K using a 3H-2000PSI instrument and estimated by Brunauer–Emmett–Teller method. The UV–vis diffuse reflectance spectroscopy (UV–vis DRS) was conducted on a UV-2550 spectrophotometer using $BaSO_4$ as a reference. The photocatalytic reaction samples were analyzed by high performance liquid chromatography (HPLC, DIONEX, TCC-100) with ultimate 3000 variable wavelength detector. A C18 column (Ecosil EC5-3237, 250 mm × 4.6 mm) was used to separate the degradation products.

The photocatalytic activity of the samples was evaluated by degradation of 4-nitrophenol under irradiation of visible light using a 500 W Xe lamp (λ: 300–800 nm) as light source using sodium nitrite solution (5.0 g/L) as the UV light filter. For the photocatalytic degradation reaction, 0.40 g of the prepared photocatalyst was dispersed in 400 mL 4-nitrophenol solution (8 mg L^{-1}, pH 4). A small air pump (2.5 W) was used to blow air into the 4-nitrophenol solution. Before irradiation, the suspensions were stirred for 0.5 h in dark in order to reach an adsorption–desorption equilibrium between the 4-nitrophenol and photocatalyst. Then, the solution was exposed to Xe lump irradiation under magnetic stirring. At every 1 h interval, 7 mL solution was extracted from the reactor. The concentration of 4-nitrophenol was determined by measuring the absorption at λ = 317 nm. The solution samples were also analyzed by HPLC after filtered with a 0.22 μm cellulose membrane filter. The mobile phase of methanol:water (60:40, v/v), flow rate of 1.0 mL/min and detection at the wavelength of 224 nm were used.

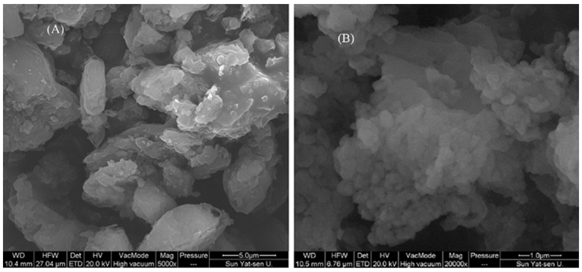

Fig. 1. FESEM images of (A) g-C_3N_4 and (B) g-C_3N_4-T.

3. Results and discussion

The FTIR spectrum of g-C_3N_4-T is almost the same as that of the as-prepared g-C_3N_4, indicating that they are the same structure (Fig. S1 in Supporting information). The typical IR characteristic peaks of graphitic carbon nitride can be found in both samples, and no other impurity peak was found in both samples. The peak in the region 801 cm^{-1} can be attributed to the triazine units, which are the units for forming graphitic carbon nitride. Meanwhile, several other strong peaks range from 1200 cm^{-1} to 1650 cm^{-1} can be ascribed to the typical stretching mode of CN heterocycles in g-C_3N_4. A broad peak ranges from 2800 cm^{-1} to 3400 cm^{-1} can be assigned to the N–H stretching vibration mode [20].

FESEM was used to observe the morphology of g-C_3N_4-T and g-C_3N_4. Fig. 1A shows the pristine g-C_3N_4 sample. The size of g-C_3N_4 is about several micrometers. After treatment, g-C_3N_4-T was corroded by HCl to several hundred nanometers, as shown in Fig. 1B. The specific surface area of the samples, an important factor affecting the activity of a photocatalyst, was also examined. Fig. 2A shows the nitrogen adsorption–desorption isotherms of g-C_3N_4 and g-C_3N_4-T, both of the isotherms are of type IV (BDDT Classification), suggesting the presence of mesopores in all samples [24]. The result reveals that the specific surface area of g-C_3N_4-T increases to 115 m^2/g after treatment, which is 10 times of that of the pure g-C_3N_4 (11.5 m^2/g). Fig. 2B is the pore size distribution curve, which reveals that the pore size of g-C_3N_4-T increased because of the acid etching. The increased surface area of g-C_3N_4-T can be attributed to the decreasing size of the particles,

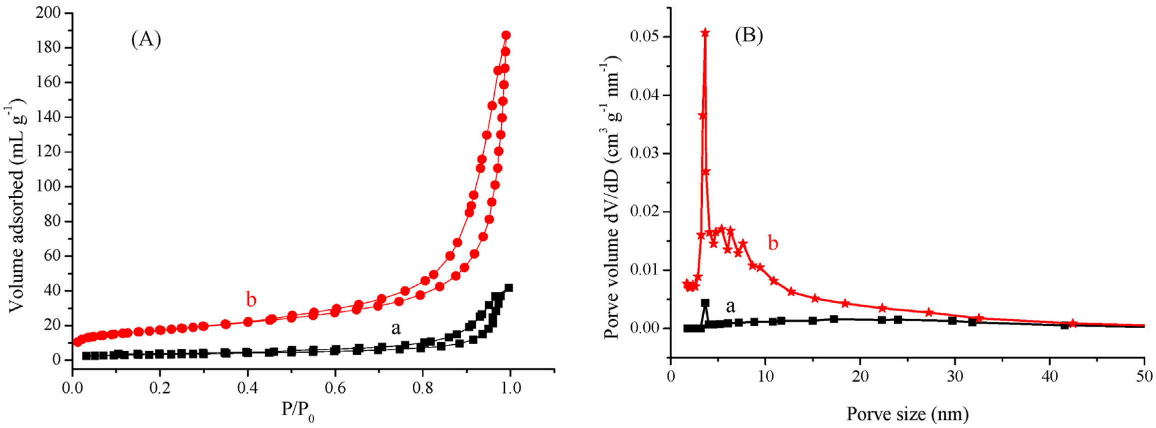

Fig. 2. (A) The nitrogen adsorption/desorption isotherms of (a) g-C_3N_4 and (b) g-C_3N_4-T. (B) The pore-size distribution of (a) g-C_3N_4 and (b) g-C_3N_4-T.