Catalysis Communications 59 (2015) 131–135

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

Tetraethylorthosilicate induced preparation of mesoporous graphitic carbon nitride with improved visible light photocatalytic activity

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ARTICLE INFO

Article history:
Received 24 September 2014
Received in revised form 14 October 2014
Accepted 17 October 2014
Available online 23 October 2014

Keywords:
Photocatalyst
Mesoporous g-C_3N_4
Tetraethylorthosilicate
Visible light
Dye

ABSTRACT

Mesoporous graphitic carbon nitride (mg-C_3N_4) has been prepared by the in situ formed silica from tetraethylorthosilicate (TEOS) as a mesoporous template. The resultant mg-C_3N_4 possessed a large surface area (152 m^2 g^{-1}), and enhanced photodegradation performance for Rhodamine B pollutant when energized with visible light. Moreover, mg-C_3N_4 also exhibited good stability after three recycles. The significant enhancement in photodegradation activity over mg-C_3N_4 catalyst could be ascribed to the large surface area, high adsorption ability to dye and enhanced separation efficiency of photogenerated electron-hole pairs. The simple strategy for the fabrication of mg-C_3N_4 may facilitate its wide applications in various fields.

1. Introduction

Semiconductor photocatalysts have drawn great attention owing to their outstanding performance in the conversion of solar energy. For the purpose of taking full advantage of solar energy, a great number of semiconductor materials with visible light activities have been exploited [1–3]. As a typical metal-free polymeric semiconductor material, graphitic carbon nitride (g-C_3N_4), has attracted great scientific interest due to its suitable band gap to absorb the visible light and unique properties, such as excellent performance of hydrogen production from water splitting and degradation of organic pollutants under visible light irradiation [4–13]. Unfortunately, the efficiency of bulk g-C_3N_4 was still restricted due to the high recombination rate of photogenerated electron–hole pairs and low surface area (less than 10 m^2 g^{-1}). To overcome these problems, many strategies have been employed to improve the photocatalytic activity, including non-metal doping [14], metal modifying [15], coupling with semiconductor composite [16] and controlling morphology [17]. Nevertheless, the improvement of highly efficient g-C_3N_4 with large surface area is still a significant challenge.

Recently, mesoporous g-C_3N_4 has drawn much attention. Compared with bulk g-C_3N_4, mesoporous g-C_3N_4 had higher porosity and larger specific surface area, which could enhance its mass transfer ability, enrich the pollutants on catalyst, suppress the recombination of photo-induced electron–hole pairs and hence result in the improvement of photocatalytic quantum efficiency [18].

In general, silica-templating method is an ordinary pathway to obtain mesoporous g-C_3N_4. Mesoporous g-C_3N_4 arranged in non-regular formation with high surface area and the same pore width to SiO_2 at 7 to 12 nm was prepared by direct use of silica nanoparticle templates [19,20]. Ordered mesoporous g-C_3N_4 with 2D hexagonal pore structure with relatively large mesochannels has been reported using SBA-15 as templates [21,22]. Besides, other mesoporous silicas were also introduced as templates for the synthesis of mg-C_3N_4 [23–25]. However, in the pioneering work, silica was prepared in advance as the templates of mg-C_3N_4, which was troublesome and time-consuming. Herein, silica was synthesized in situ by tetraethylorthosilicate (TEOS) precursor then silica was used directly as the mesotemplates in the synthesis of g-C_3N_4 from cyanamide (CA) precursor. After silica was removed, mesoporous g-C_3N_4 (mg-C_3N_4) was obtained with large surface area (152 m^2 g^{-1}), small pore width (5 nm), high adsorption capacity of Rhodamine B (RhB) and the reduced recombination rates of photoinduced electrons and holes, which made the obtained mg-C_3N_4 exhibit enhanced photocatalytic performance for the degradation of RhB under visible light irradiation.

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http://dx.doi.org/10.1016/j.catcom.2014.10.014
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2. Experimental

2.1. Synthesis of mg-C_3N_4

3 g of 50 wt.% cyanamide (CA) solution was mixed with 5 g ethanol, and the pH of the mixture was adjusted to 2 with 0.2 M HCl solution, then 2 mL TEOS was dropped into the abovementioned solution. After stirring for 2 h, the solution was transferred into the 25 mL Teflon-sealed autoclave at 110 °C for 20 h. Then the gel was obtained and transferred to the crucible with a cover after it was dried at 60 °C for 6 h. The crucible was heated at 550 °C for 4 h at a heating rate of 3 °C min^{-1} then cooled to room temperature. Subsequently, the as-prepared composites were stirred in 10% hydrofluoric acid for 24 h, then collected by filtration, washed by water and dried at 80 °C for 12 h, finally mg-C_3N_4 was obtained. For comparison, bulk g-C_3N_4 was prepared by heating 3 g cyanamide at 550 °C for 4 h at a heating rate of 3 °C min^{-1}.

2.2. Material characterizations

The patterns of X-ray diffraction were carried out on a Bruker D8 Advance X-ray powder diffractometer with Cu Kα radiation (40 kV, 40 mA) for phase identification. Fourier transform infrared spectroscopy (FTIR) was recorded in transmission mode from 4000 to 400 cm^{-1} on a Perkin Elmer spectrum 100 FTIR spectrometer using KBr discs. The morphology of the sample was examined by transmission electron microscopy (TEM, Tecnai G2 Spirit). N_2 adsorption–desorption isotherms were collected at 77 K using a Quantachrome NOVA 2000 surface area and porosity analyzer. Samples were outgassed at 150 °C for 12 h prior to measurements. X-ray photoelectron spectroscopy (XPS) measurements were recorded on Thermo Fisher Scientific ESCALAB 250Xi. Elemental analyses (EA) for the carbon and nitrogen contents were performed on a Vario Microcube CHN analyzer. The UV–vis diffuse reflectance spectra (DRS) were measured by a Perkin Elmer Lambda 750 UV–vis spectrometer. The photoluminescence spectra (PL) were obtained by a Perkin Elmer LS55 spectrometer with an excitation wavelength of 325 nm.

2.3. Photocatalytic testing

The photocatalytic performance of the sample was evaluated through degrading RhB dye under visible light. A 300 W Xe lamp with a 400 nm cutoff filter was used as the light source to provide visible light irradiation. A 50 mg mg-C_3N_4 sample was dispersed into a 100 mL 5 mg·L^{-1} RhB solution for photocatalytic examination under magnetic stirring. Prior to the light irradiation, the dispersion was kept in the dark for 60 min under magnetic stirring to reach the adsorption–desorption equilibrium. Solutions were collected after irradiation every 5 min and centrifuged to remove the catalyst then analyzed on a UV–vis spectrometer. For comparison, the photodegradation reactions were also carried out in the presence of bulk g-C_3N_4 powder and in the absence of any catalyst. The efficiency of degradation was calculated by C/C_0, wherein C is the concentration of the remaining dye solution at each irradiated time, and C_0 is the initial concentration.

3. Results and discussion

The X-ray diffraction patterns of the obtained mg-C_3N_4 and bulk g-C_3N_4 were shown in Fig. 1A. The peaks at 27.3° and 13.1°, corresponding to (002) and (100) planes of hexagonal g-C_3N_4 (JCPDS card no. 87-1526), indicated the graphite-like stacking of the conjugated aromatic units of CN and an in-plane structural packing motif, respectively. Compared with the bulk g-C_3N_4 sample, the as-prepared mg-C_3N_4 samples exhibited broader and lower diffraction intensity. The phenomenon was possibly explained that the existence of silica prevented the formation of extended graphitic layers during the thermal condensation process of CA, thus leading to lower crystallinity than the bulk g-C_3N_4 sample [20]. Fig. 1B exhibited the FTIR spectra of as-prepared mg-C_3N_4 and bulk g-C_3N_4. The absorption peak at 810 cm^{-1} was attributed to the out-of-plane skeletal bending modes of the triazine cycles [11], and the absorption bands in the range of 1200–1700 cm^{-1} were assigned to the typical stretching modes of CN heterocycles [10]. In the range of the 3000–3500 cm^{-1} region, the broad band centered at 3181 cm^{-1} was attributed to NH_2 or NH groups, which were originated from the incomplete condensation thus the residual hydrogen atoms bound to the edges of the graphene-like C–N sheet in the form of C–NH_2 and 2C–NH bonds [26].

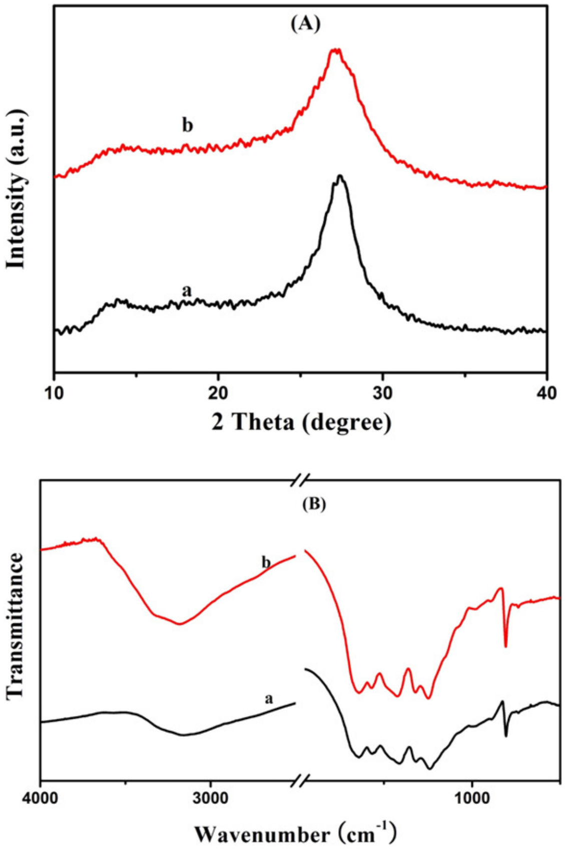

Fig. 1. (A) X-ray diffraction patterns and (B) FTIR spectra of (a) bulk g-C_3N_4 and (b) mg-C_3N_4.

To observe fine morphology of the as-prepared mg-C_3N_4 sample, TEM images with different magnifications for mg-C_3N_4 were displayed in Fig. 2. It was obviously seen that a great number of mesopores (labeled by red circles) were formed in the mg-C_3N_4 sample. The pore diameter was approximately 5 nm, which was in agreement with the result of BJH pore size distributions in Fig. S1B. And the surface area of the as-made mg-C_3N_4 was high up to 152 m^2 g^{-1} (Fig. S1A).

Fig. 2 C illustrated the detailed synthesis process of mesoporous carbon nitride. Firstly, CA and TEOS were mixed in an acidified mixture of water and ethanol (pH = 2). After a period of stirring, a clear homogeneous solution was formed, which suggested CA, TEOS and subsequently the formed silicic acid were completely dissolved in the mixture. Then the solution was placed in Teflon-sealed autoclave for crystallization to obtain the gel. After the gel was kept at 60 °C to evaporate the solvent, the obtained solid materials were thermally treated at 550 °C. Thus, g-C_3N_4 incorporating SiO_2 composites were obtained, in which TEOS generated SiO_2 and CA formed g-C_3N_4. During the process, CA acted as the base, preventing the aggregation of silica. After the silica removal by HF solution, the small mesopore widths of mg-C_3N_4 were obtained.

The XPS data for mg-C_3N_4 further supported the results obtained from the FTIR spectra. In C1s spectra, two peaks could be distinguished to be centered at 284.7 and 288.4 eV. The major peak at 284.7 eV was