Engineering the nanoarchitecture and texture of polymeric carbon nitride semiconductor for enhanced visible light photocatalytic activity

Fan Dong [a,*], Zhenyu Wang [a], Yanjuan Sun [a], Wing-Kei Ho [b], Haidong Zhang [a]

[a] Chongqing Key Laboratory of Catalysis and Functional Organic Molecules, College of Environmental and Biological Engineering, Chongqing Technology and Business University, Chongqing 400067, PR China
[b] Department of Science and Environmental Studies, The Hong Kong Institute of Education, Tai Po, N.T., Hong Kong, China

ABSTRACT

In order to develop g-C_3N_4 for better visible light photocatalysis, g-C_3N_4 nanoarchitectures was synthesized by direct pyrolysis of cheap urea at 550 °C and engineered through the variation of pyrolysis time. By prolonging the pyrolysis time, the crystallinity of the resulted sample was enhanced, the thickness and size of the layers were reduced, the surface area and pore volume were significantly enlarged, and the band structure was modified. Especially for urea treated for 4 h, the obtained g-C_3N_4 nanosheets possessed high surface area (288 m^2/g) due to the reduced layer thickness and the improved porous structure. A layer exfoliation and splitting mechanism was proposed to explain the gradual reduction of layer thickness and size of g-C_3N_4 nanoarchitectures with increased pyrolysis time. The as-synthesized g-C_3N_4 samples were applied for photocatalytic removal of gaseous NO and aqueous RhB under visible light irradiation. It was found that the activity of g-C_3N_4 was gradually improved as the pyrolysis time was prolonged from 0 min to 240 min. The enhanced crystallinity, reduced layer thickness, high surface area, large pore volume, enlarged band gap, and reduced number of defects were responsible for the activity enhancement of g-C_3N_4 sample treated for a longer time. As the precursor urea is very cheap and the synthesis method is facile template-free, the as-synthesized g-C_3N_4 nanoscale sheets could provide an efficient visible light driven photocatalyst for large-scale applications.

1. Introduction

Over the past decades, visible light driven photocatalysis attracted intensive research interest worldwide due to their potential applications in environmental pollution control and solar energy conversion [1–8]. Various types of visible light photocatalytic materials have been developed. These photocatalytic materials can be divided into four types depending on their composition and band structure, including metal/nonmetal doped semiconductors with large band gap (such as C/N-doped TiO_2, N-doped $(BiO)_2CO_3$) [9–13], metal containing semiconductors with narrow band gap (such as Bi_2WO_6, Bi_3NbO_7, BiOBr) [14–17], plasmonic noble metals (such as Au, Pt) [18,19], and more recently discovered metal-free polymeric semiconductors (such as g-C_3N_4, red phosphorus and α-S_8) [20–22]. The different types of photocatalytic materials could be coupled to further enhance the activity on the basis of band gap engineering [23,24].

The discovery of polymeric graphitic carbon nitride (g-C_3N_4) as visible light driven metal-free photocatalyst was first reported by Wang et al. [20]. It was found that g-C_3N_4 is a multifunctional cat-

alyst and has been applied in broad areas owing to its high stability, appealing electronic structure and medium band gap [20]. Generally speaking, g-C_3N_4 can be synthesized by pyrolysis of nitrogen-rich precursors via polycondensation or pyrolysis. The typical precursors include cyanamide, dicyandiamide, trithiocyanuric acid, melamine, triazine, heptazine derivatives, and more recently discovered urea and thiourea [20,25–36]. The types of precursors have significant influence on the texture, electronic structure, and performance of g-C_3N_4 due to the different formation processes and degree of condensation [25–36]. Very recently, urea, as a very cheap and abundant industrial agent, is found to be a superior precursor [36,37]. The g-C_3N_4 prepared via pyrolysis of urea has relatively large surface area and thus high photocatalytic activity [36,37].

To increase the reactivity of g-C_3N_4, many strategies have been employed to modify g-C_3N_4, such as texture tuning by template, band gap modification by heteroatoms doping, post-functionalization, and coupling with other semiconductors [38,39]. The modified g-C_3N_4-based photocatalysts with favorable structure have shown encouraging activity enhancement. In general, a high surface area is desirable in order to improve the photocatalytic activity, which could provide more active sites for adsorption and reaction [38,39]. To achieve a high surface area, templates are

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* Corresponding author.
  E-mail address: dfctbu@126.com (F. Dong).

usually employed to introduce pores in various types of photocat-alytic materials. Wang et al. synthesized g-C_3N_4 with large surface area (239 m^2/g) by pyrolysis of cyanamide/ammonium thiocyanate templated by silica [40]. Xu et al. synthesized g-C_3N_4 with surface area of 128 m^2/g via silica template from pyrolysis of thiourea [41]. Yuliati et al. also applied templating strategy to increase the surface area of g-C_3N_4 (224 m^2/g) using urea as precursor [42]. The resultant g-C_3N_4 showed markedly enhanced visible light pho-tocatalytic activities toward hydrogen evolution or pollutants deg-radation [40–42]. Recent works for achieving high density and close-packed silica templates by directed self-assembly could also be potentially applied in template synthesis of g-C_3N_4 [43,44].

Recently, we have synthesized g-C_3N_4 with high visible light photocatalytic activity by pyrolysis of urea or thiourea in the ab-sence of template [33,36]. Under the same pyrolysis conditions, the surface area of g-C_3N_4 sample (75 m^2/g) from urea is higher than that of samples prepared directly from thiourea (27 m^2/g) and other precursors. However, it is still lower than the ones that were prepared in the presence of templates.

In the present work, we engineer the nanoarchitecture and the texture of g-C_3N_4 prepared by urea by a facile template-free. The effects of pyrolysis time on the microstructure and activity of g-C_3N_4 are systematically investigated. Unexpectedly, we find that the surface areas of g-C_3N_4 can be significantly increased to 288 m^2/g by just prolonging the pyrolysis time to 240 min under 550 °C. The surface area is even higher than that of g-C_3N_4 synthe-sized via templating method, further demonstrating the great advantages of using urea as precursor. A new layer exfoliation and splitting mechanism was proposed to account for this unex-pected interesting result. To the best of our knowledge, there is no report on template-free synthesis of g-C_3N_4 materials with such high surface areas. It is also interesting to note that the crystallinity of g-C_3N_4 increases with prolonged pyrolysis time. Through the present way, the enhancement of crystallinity and the increase in surface areas can be achieved simultaneously, which are two favor-able factors for promoting the photocatalytic activity of g-C_3N_4. The as-synthesized g-C_3N_4 material with high surface area is fur-ther employed for photocatalytic removal of gaseous NO and aque-ous RhB and showed efficient activity under visible light irradiation.

2. Materials and method

2.1. Synthesis of g-C_3N_4 from urea

The g-C_3N_4 was synthesized from urea by a facile template-free method [36]. In a typical synthesis, 10 g of urea powder was put into an alumina crucible with a cover and then heated to 550 °C in a muffle furnace for a certain time at a heating rate of 15 °C/min. The resulted powder was collected for use without further treatment. In order to investigate the effects of pyrolysis time, g-C_3N_4 was synthesized at 550 °C for 0, 15, 30, 60, 120 and 240 min, respectively. The resulted samples were labeled as CN-0, CN-15, CN-30, CN-60, CN-120 and CN-240, respectively. Note that the pyrolysis time does not include the time the furnace spent to raise the temperature to 550 °C. All the as-prepared samples were pale yellow.

2.2. Characterization methods

The crystal phase was analyzed by X-ray diffraction with Cu Kα radiation (XRD: model D/max RA, Japan) at a scan rate of 0.01° 2θ/s. The scan range of 2θ was 5–80°. To perform the thermogravimet-ric-differential scanning calorimetry analysis (TG-DSC: NETZSCH STA 409 PC/PG), 20 mg dry sample was sealed in an Al_2O_3 crucible

with a lid and scanned at a rate of 20 °C/min. FT-IR spectra were recorded on a Nicolet Nexus spectrometer on samples embedded in KBr pellets. A scanning electron microscope (SEM, JEOL model JSM-6490, Japan) was used to characterize the morphology of the samples. The UV–vis diffuse reflection spectra were obtained for the dry-pressed disk samples using a Scan UV–vis spectrophotom-eter (UV–vis DRS: UV-2450, Shimadzu, Japan) equipped with an integrating sphere assembly, using $BaSO_4$ as reflectance sample. Nitrogen adsorption–desorption isotherms were obtained on a nitrogen adsorption apparatus (ASAP 2020, USA) with all samples degassed at 150 °C for 12 h prior to measurements. The photolumi-nescence spectra were measured with a fluorescence spectropho-tometer (F-7000, Japan) using a Xe lamp as excitation source with optical filters. The detection of hydroxyl radicals during pho-tocatalysis was conducted to according to reported method [45].

2.3. Visible light photocatalytic activity

2.3.1. Degradation of gaseous NO

The photocatalytic activity was investigated by removal of NO at ppb levels in a continuous flow reactor at ambient temperature. The volume of the rectangular reactor, made of stainless steel and covered with Saint-Glass, was 4.5 L (30 cm × 15 cm × 10 cm). A 150 W commercial tungsten halogen lamp was vertically placed outside the reactor. A UV cutoff filter (420 nm) was adopted to re-move UV light in the light beam. Photocatalyst (0.1 g) was coated onto a dish with a diameter of 12.0 cm. The coated dish was then pretreated at 70 °C to remove water in the suspension. The NO gas was acquired from a compressed gas cylinder at a concentra-tion of 100 ppm of NO (N_2 balance, BOC gas). The initial concentra-tion of NO was diluted to about 600 ppb by the air stream. The desired relative humidity (RH) level of the NO flow was controlled at 50% by passing the zero air streams through a humidification chamber. The gas streams were premixed completely by a gas blender, and the flow rate was controlled at 2.4 L/min by a mass flow controller. After the adsorption–desorption equilibrium was achieved, the lamp was turned on. The concentration of NO was continuously measured by a chemiluminescence NO analyzer (Thermo Environmental Instruments Inc., 42i-TL), which monitors NO and NO_2 with a sampling rate of 1.0 L/min. The removal ratio (η) of NO was calculated as $\eta(\%) = (1 - C/C_0) \times 100\%$, where C and C_0 are concentrations of NO in the outlet steam and the feeding stream, respectively.

2.3.2. Degradation of aqueous RhB

Photocatalytic activity of g-C_3N_4 polymer for degradation of aqueous Rodamine B (RhB) was evaluated in a quartz glass reactor. 0.05 g of g-C_3N_4 was dispersed in RhB aqueous solution (55 mL, 5 mg/L). The suspension was stirred intensively to eliminate the influence of mass transfer. The light irradiation system contains a 500 W Xe lamp with a jacket filled with flowing and thermostatted aqueous $NaNO_2$ solution (1 M) between the lamp and the reaction chamber as a filter to block UV light (λ < 400 nm) and eliminate the temperature effect. Before irradiation, the suspension was allowed to reach equilibrium with continuous stirring for 60 min. The deg-radation efficiency of RhB was evaluated using the UV–vis absorp-tion spectra to measure the peak value of a maximum absorption of RhB solution. During the irradiation, 5 mL of suspension was continually taken from the reaction cell at given time intervals for subsequent dye concentration analysis after centrifuging. The maximum absorption of RhB is at wavelength of 552 nm. The re-moval ratio (%) can be calculated as $\eta(\%) = (C_0 - C)/C_0 \times 100\%$, where C_0 is the initial concentration of RhB considering RhB adsorption on the catalyst and C is the revised concentration after irradiation.