



Facile fabrication of high-yield graphitic carbon nitride with a large surface area using bifunctional urea for enhanced photocatalytic performance



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ABSTRACT

Graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) has aroused intense expectations owing to its outstanding visible-light-response capability for hydrogen generation from water. However, the low-yield, low practical surface area and high photogenerated charge recombination rate severely limits its photocatalytic performance. Here, in this study high-yield synthesis of $g\text{-C}_3\text{N}_4$ with a large surface area has been achieved successfully through an in situ pyrolysis of cyanamide with the assist of the bifunctional urea. During the synthesis process, urea may decompose into a lot of ammonia and carbon dioxide, which acts as the supplementary-nitrogen-source and bubble-generating template respectively. It is found that the surface area and photocatalytic activity can be controlled by adjusting the addition of the environmentally friendly bifunctional urea. The as-prepared $g\text{-C}_3\text{N}_4$ exhibits unique optical activity as well as photoelectrochemical activity for solar-to-chemical conversion, and this simple bifunctional method may open a new pathway for designing and optimizing of photocatalysts.

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1. Introduction

Utilization of renewable and clean energy resources and development of eco-friendly practical systems for environmental remediation have evoked much attention owing to the decline in fossil-fuel production and increasing concern on environmental issues [1–4]. In particular, photocatalytic water splitting using photocatalysts represents a highly attractive way to convert solar energy, which is the most abundant and universally available source of renewable energy, into hydrogen that is considered as an ideal fuel for future energy sustainability [5–8]. Therefore, searching and optimizing highly efficient photocatalysts for photocatalytic hydrogen evolution reaction (HER) is of great significance. Amongst all existing semiconductor photocatalysts being thermodynamically capable of HER, graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) has stimulated particular interests because of its high in-plane nitrogen content, excellent chemical and thermal stability, and appealing electronic structure [9–15]. Unfortunately, the low specific surface area, low-yield and insufficient solar-light absorption severely limit the photocatalytic performance of conventional bulk $g\text{-C}_3\text{N}_4$

[16–19]. In this context, considerable and continuing effort has been devoted to improve the activity of $g\text{-C}_3\text{N}_4$ based photocatalysts.

To improve the photocatalytic performance of $g\text{-C}_3\text{N}_4$, several strategies, such as nanostructuring [20–22], doping [23–25], cocatalyzing [26–28], copolymerization [29–31] and exfoliation [32–34], have been exploited. The high-yield synthesis of $g\text{-C}_3\text{N}_4$ with high surface area is of particular interest because a larger surface area can be favourable for photocatalytic reaction by providing more surface reactive sites and increasing the mass transfer [18,35]. Generally, $g\text{-C}_3\text{N}_4$ with a large surface area is obtained by a template-induced method. One is the “hard template” method [36,37]. By utilizing this method, the surface areas can be controlled by different silica or anodic aluminium oxides templates. However, the removal of the host matrices by aqueous ammonium bifluoride or hydrogen fluoride may result in some impurity residues, and the removal process is also complex and time-consuming [17,32]. The other is the “soft-template” method, but this method may result in some carbon residue and nitride loss [38–40]. Besides, the commonly used one-step method for the bulk $g\text{-C}_3\text{N}_4$ preparation suffers from a very low yield (~6%), because the polymerization temperature is higher than the sublimation point of the reagent and the gas intermediate product (ammonia) is also participate in the later polymerization [41]. Hence, it is of great urgency to develop a

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facile and economic synthesis method of high-yield g-C₃N₄ with a large surface area for the industrial and practical applications.

Here, we demonstrated an efficient method that high-yield g-C₃N₄ with a large surface area can be developed by in situ direct pyrolysis of cyanamide with the assist of the bifunctional urea. The dissolution of the urea into the molten cyanamide at the temperature of 60 °C can result in the formation of intermolecular hydrogen bonds network. During the synthesis process of g-C₃N₄, urea may decompose into a lot of ammonia (NH₃) and carbon dioxide (CO₂), which serves as the nitrogen-source supply and the bubble-generating template respectively. Since the hydrogen bonds network can suppress the escape of the NH₃, a high yield (60–70%) production of g-C₃N₄ is achieved. The surface area structure and photocatalytic activity can be easily controlled by adjusting the mass ratio of urea to cyanamide. The resultant g-C₃N₄ provides a large accessible surface area, and exhibits significantly improved optical and electronic properties.

2. Experimental

2.1. Synthesis of photocatalysts

Typically, 2 g of the different mass ratios of cyanamide and urea powders were added into a covered crucible, and then the mixture was heated in an oil bath at 60 °C for 30 min. After it turned into the molten state, the crucible was then taken out from the oil bath to cool down to the room temperature. Then, the resultant powders were calcined at 550 °C for 2 h in air, and the final samples were obtained. According to the mass content of urea, the as-prepared samples were named as CN, CN-0.5, CN-1, CN-1.5 and CN-2, respectively.

2.2. Material characterization

The structures of the powder samples were investigated by X-ray diffractometer (XRD, Bruker D8 Advanced Diffractometer operating with Cu K α radiation). The angular range was $2\theta = 5\text{--}55^\circ$, with a speed of $6^\circ/\text{min}$. Infrared transmission was obtained with a Fourier transform infrared (FTIR) spectrophotometer Spectrum (Nicolet). The optical absorbance spectra of the samples were performed on using a UV–vis spectrometer (CARY 300). Element analysis (EA) was conducted by an elemental analyzer (vario ELII; Elementar Analysensysteme, Germany). The photoluminescence (PL) measurements were performed in an Edinburgh instruments (FLSP 920) system operated at room temperature. Brunauer–Emmett Teller (BET) surface areas were determined by a TriStar 3020 nitrogen sorption isotherm apparatus. Transmission electron microscopy (TEM, JEM 2100, 200 kV) were used to characterize the morphology and structure of the obtained products.

2.3. Photocatalytic experiments

The photocatalytic reaction was performed in a pyrex glass cell connected to a glass closed gas circulation system. The deposition of 3 wt% Pt was conducted by directly immersing the products into H₂PtCl₆ ethanol solution and calcinated at 180 °C for 30 min (ramp: 2°C min^{-1}). H₂ evolution analysis was performed by dispersing 50 mg of catalyst powder in an aqueous solution containing triethanolamine (100 mL, 10 vol.%) as the sacrificial electron donor. The reactant solution was evacuated several times to remove air completely before the reaction. A 300 W Xe lamp with a 420 nm cutoff filter was used as the light source. A flow of cooling water was used during the reaction to maintain the temperature of the reactant solution at 15 °C. The amount of evolved H₂ evolved was analyzed by gas chromatography (TECHCOMP, 7890 II).

2.4. Photoelectrochemical measurements

Photocurrent was conducted with an electrochemical analyzer (CHI660E Instruments) in a standard three-electrode system using the prepared samples as the working electrodes, using a Pt gauze electrode and Ag/AgCl (saturated KCl) as the counter electrode and reference electrode, respectively. The working electrodes were immersed in the electrolyte (0.2 M Na₂SO₄ aqueous solution) for 60 s before any measurements were taken.

The working electrode was prepared on fluoride tin oxide (FTO) conductor glass, which was cleaned by sonication in acetone and ethanol for 10 min each. 10 mg of powder was mixed with 0.2 mL DMF and 0.05 mL Liquion solution to make a slurry. The slurry was then injected onto the FTO glass, whose sides were previously covered with Scotch tape and the exposed area of electrodes was 0.785 cm². These electrodes were dried at 120 °C for 30 min in air to improve adhesion.

3. Results and discussion

Cyanamide is an organic precursor with a low melting point, usually below 50 °C. When the mixture of cyanamide and urea was heated in an oil bath at 60 °C for 30 min, the urea would dissolve into the molten cyanamide and the intermolecular hydrogen bonds network might formed on account of the existence of the electronegative atoms such as nitrogen and oxygen [42,43]. For a better understanding of the different reaction processes of CN-x samples, thermogravimetric analysis (TGA) was carried out. All the precursors were heated from room temperature to 1000 °C at a rate of $10^\circ\text{C min}^{-1}$ in air, and the TGA curves are shown in Fig. 1. As evidenced by TGA, the addition of urea might obviously increase the 2nd stage reaction time between 200 °C to 400 °C, indicating that partial generated NH₃ re-participate in the pyrolysis process due to the hydrogen bonds network. Fig. 2 shows the TEM image of as-synthesized CN, CN-1.5 and CN-2 samples. A layered and plate-like surface morphology consisting of wrinkles is exhibited on CN-1.5. Some breakage of the plate which is induced by the bubble templates can be found, which make the CN-1.5 possess a large specific surface area. As can be seen from the N₂ adsorption-desorption isotherms of the as-prepared CN-x samples (Fig. 3), the surface area of CN-1.5 was about 59.9 m² g⁻¹, more than five times larger than CN which is synthesized without the assist of urea. This indicates that CO₂ gas generated from the pyrolysis of urea can act as the bubble template.

The structure of the as-prepared samples was detected by XRD. All XRD patterns in Fig. 4a exhibit two distinct peaks at round 27.4°

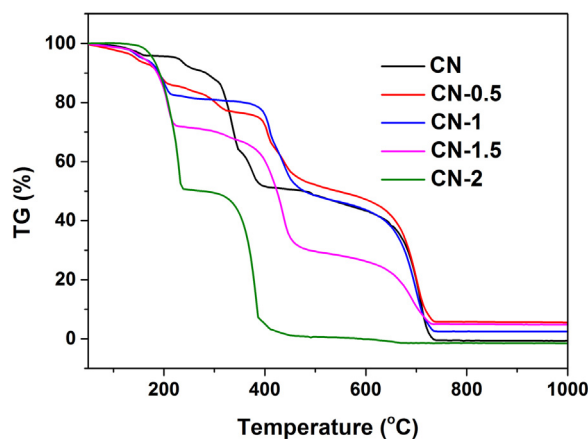


Fig. 1. Thermogravimetric analysis (TGA) curves of CN and CN-x (x = 0.5, 1, 1.5 and 2) samples.

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