



Facile synthesis of nitrogen deficient g-C₃N₄ by copolymerization of urea and formamide for efficient photocatalytic hydrogen evolution

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ABSTRACT

It is noted that appropriate amount of nitrogen defects in g-C₃N₄ are beneficial to the photocatalytic reaction. In this study, a facile approach for the preparation of nitrogen deficient g-C₃N₄ was developed by polymerization of urea with a small amount of formamide. The obtained g-C₃N₄ displays extended optical absorption and enhanced migration and separation of photogenerated charge carriers, which result in efficient photocatalytic hydrogen evolution. The hydrogen evolution rates of the optimized sample matched well with the extended optical absorption along with different wavelength. Density functional theory calculations further certified the proposed scheme of nitrogen defects. This work provides a feasible process using organic chemical protocols to synthesize polymeric photocatalysts. In addition, the importance of nitrogen defects on the photocatalytic performance of g-C₃N₄ was discussed based on experimental results. The work opens a new pathway for the development of highly active g-C₃N₄ for the application.

1. Introduction

Artificially mimicking photosynthesis is an attractive pathway to directly capture, convert, and store solar energy [1–5]. It is meaningful to search for powerful multifunctional materials as photocatalysts working under visible light. Recently, graphitic carbon nitride (g-C₃N₄), a polymeric π -conjugated semiconductor, has raised intensive research interest as a metal-free photocatalyst, because of its sustainable utilization of solar energy [6–10]. Nevertheless, the activity of pristine g-C₃N₄ remains moderate. The intrinsic drawbacks of fast charge recombination and lack of visible light absorption above 460 nm, seriously limit the photocatalytic activity of g-C₃N₄ [11–13]. Therefore, fine-tuning intrinsic electronic structures of the g-C₃N₄ conjugated system, especially to extend its visible light adsorption and to reduce recombination rate of photogenerated electrons and holes, is supposed to be an effective pathway to improve the photocatalytic performance [14–17]. Taking into account the organic nature of the π -electron aromatic system, molecular design and synthesis of conjugated carbon nitride (CN)-based photocatalysts is indeed feasible. The diversity of organic chemistry will broaden the pathways of creating supermolecules using CN precursors and co-monomers for preparation of modified g-C₃N₄. Indeed, incorporation of various functional groups into g-C₃N₄ conjugated system by copolymerization has already been reported to optimize the surface properties, textures and electronic structures [18–22]. For example, the electronic and optical properties

of g-C₃N₄ were modified by copolymerization of urea with phenylurea, resulting in about 9 times improvement in hydrogen evolution rate [23]. In another report, with the fusion of electron-rich thiophene into the conjugated framework of g-C₃N₄, the electronic property and bandgap were optimized, and the migration and separation of charge carriers were improved effectively because of the formation of surface dyadic structures [24].

Although fusion of aromatic motifs into conjugated carbon nitride framework has been discussed a lot, little design is proposed for the introduction of nitrogen defects in g-C₃N₄ by copolymerization of comonomers with CN precursors.

Nitrogen defects in g-C₃N₄ were reported to be favorable for photocatalytic reactions. The defects can manipulate the electronic structure and probably act as active sites for reactive molecules. At present, there are some tries to obtain nitrogen defects in g-C₃N₄ [25,26]. For example, concentrated hydrochloric acid-treated g-C₃N₄ exhibited outstanding nitrogen photofixation ability under visible light, which is 13.4-fold of that of the bulk g-C₃N₄ [27]. However, in addition to the effect of nitrogen defects in g-C₃N₄, the improved factors can mainly be attributed to smaller particle size, larger surface area. In another case, the nitrogen deficient g-C₃N₄ with slight change in morphology by controlling the polycondensation temperature of dicyandiamide, displayed only 1 times higher than the pristine g-C₃N₄ for degradation of RhB under visible light [28]. In another report, the nitrogen-deficient g-C₃N_{4-x}, which was prepared by hydrothermal treatment using oxidant

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ammonium thiosulfate, exhibited about 3 times higher than the pristine $g\text{-C}_3\text{N}_4$ for H_2 production [29]. Although some photocatalysts based on nitrogen deficient $g\text{-C}_3\text{N}_4$ have been developed, the introduction of nitrogen defects in $g\text{-C}_3\text{N}_4$ by copolymerization of small molecules with CN precursors is scarcely reported.

In this study, we design the nitrogen deficient $g\text{-C}_3\text{N}_4$ by polymerization of urea and formamide. The chemical and physical properties of the functional $g\text{-C}_3\text{N}_4$ materials were fully analyzed to explore the influence of formamide doping on their optical, morphology, and electronic properties. The hydrogen evolution performance of the visible light driven photocatalyst was investigated in detail. In addition, the influence of thermally polymerized time on the performance of the prepared samples was discussed. The structure of the resultant sample was also analyzed by density functional theory (DFT) calculations. The facile design based on reactions of small organic molecules will open a pathway to synthesis $g\text{-C}_3\text{N}_4$ with high performance.

2. Experimental

2.1. Preparation of photocatalysts

The molecular structures of formamide and urea are similar. According to the mechanism by direct polymerization of urea [30], previous experimental studies [31,32] and ab initio calculations [33,34], the possible polymerization mechanism is illustrated in Scheme 1. First, 10.0 g urea and different amount of formamide (0.05, 0.08, 0.1, 0.13 and 0.2 mL) were homogeneously mixed and put in a semiclosed reactor, and then heated to 550 °C in a muffle furnace for 2 h. For simplicity, the as-prepared samples were denoted as UCNF x . For example, UCNF005 was prepared by adding 0.05 mL formamide. For comparison, pure $g\text{-C}_3\text{N}_4$ was prepared by directly heating 10 g urea at 550 °C for 2 h [23], and the sample was denoted as UCN. In addition, mixtures of 10.0 g urea and 0.1 mL formamide were calcinated at 550 °C for 1, 2, 3 and 4 h, and the resulted samples were denoted as 1UCNF01, 2UCNF01, 3UCNF01, 4UCNF01, respectively. For comparison, $g\text{-C}_3\text{N}_4$ samples of 1UCN, 2UCN, 3UCN and 4UCN were also

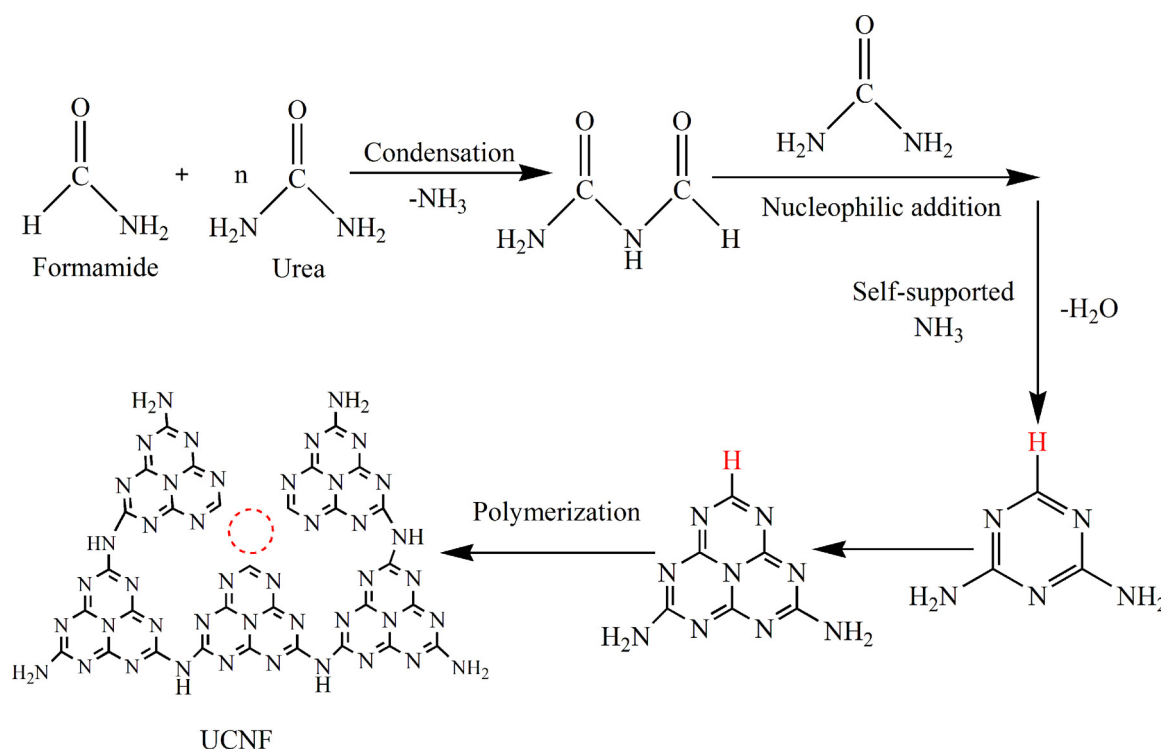
obtained by calcination of urea (10.0 g) at 550 °C for 1, 2, 3 and 4 h, respectively. Actually, it is easy to find UCNF01 and 2UCNF01, UCN and 2UCN are the same.

2.2. Characterization

X-ray diffraction patterns (XRD) of the samples were recorded on a Bruker GADDS powder X-ray diffractometer. FT-IR spectra were measured on an Affinity-1 FTIR spectrometer. Transmission electron microscopy (TEM) images were taken using a JEOL Model JEM 2100 EX instrument. UV–vis diffuse reflectance spectra (DRS) were recorded on a Hitachi U-3010 UV–vis spectrometer, with BaSO_4 as a reflectance standard. XPS analysis was performed on a Thermo Scientific ESCALAB 250 XPS photoelectron spectrometer employing Al K monochromatic X-ray radiation. N_2 adsorption-desorption isotherms were obtained with a Micromeritics TriStar II 3020 at 77 K. Elemental analysis was conducted using an elemental analyzer (VARIO EL CUBE microanalyzer). Photoluminescence (PL) spectra were obtained using an FLS-980 fluorescence spectrophotometer at room temperature. Electron paramagnetic resonance (EPR) measurements were performed using a Bruker model ER200-SRC spectrometer. The microwave frequency is 100.00 kHz, and the center field is 337.554 mT. The density functional theory (DFT) calculations using Gaussian09 program were adopted. To do that, B3LYP functions and 6–31 G (d, p) basis sets without any symmetry constraints were built.

2.3. Preparation of working electrode and photoelectrochemical measurements

Photoelectrochemical measurements were conducted on a CHI 660C electrochemical workstation operated in a conventional three-electrode cell, in which, an FTO electrode deposited with the prepared sample was used as the working electrode, with an Ag/AgCl electrode as the reference electrode, and a Pt plate as the counter electrode. To prepare a working electrode, 20 mg photocatalyst was ultrasonically dispersed in an ethical solution. Then, the resulting slurry was spread onto FTO



Scheme 1. Proposed mechanism of reaction paths for the formation of UCNF x .

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