



Fluoride ion-promoted hydrothermal synthesis of oxygenated $g\text{-C}_3\text{N}_4$ with high photocatalytic activity

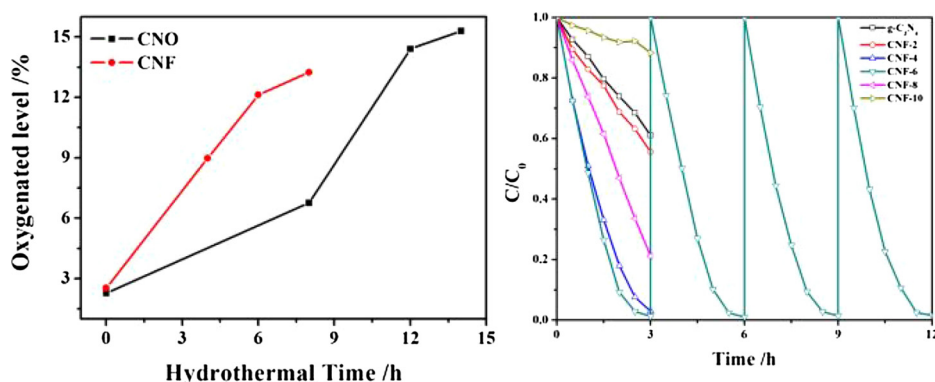
Lufei Ming, Na Sun, Liming Xu, Feng Chen*

Key Laboratory for Advanced Materials and Institute of Fine Chemicals, School of Chemistry and Molecular Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, PR China



GRAPHICAL ABSTRACT

The presence of fluoride ion can help to promote the hydrothermal synthesis of oxygenated $g\text{-C}_3\text{N}_4$, of which the photocatalytic activity is greatly improved.



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ABSTRACT

Fluoride ion, as a very nucleophilic anion, was introduced into the hydrothermal treatment of $g\text{-C}_3\text{N}_4$ for the synthesis of oxygenated $g\text{-C}_3\text{N}_4$. The existence of F⁻ promotes the hydrothermal oxygenation process by enhancing the hydrolysis and condensation progress of $g\text{-C}_3\text{N}_4$ to form the oxygenated $g\text{-C}_3\text{N}_4$ (CNFs). Plenty of the oxygen-containing groups like C=O, C–O and N–O were formed during the hydrothermal treatment of $g\text{-C}_3\text{N}_4$, accompanying with the stepwise fragmentization of $g\text{-C}_3\text{N}_4$ skeleton, which help to lower the valence band level, enhance the electron-hole separation efficiency under irradiation, and lower the impedance of $g\text{-C}_3\text{N}_4$. Specifically, CNF-6 shows the maximal photoresponse and the highest photocatalytic activity for the degradation of AO7 under visible irradiation.

1. Introduction

Graphite carbon nitride ($g\text{-C}_3\text{N}_4$) has been widely investigated as an organic semiconductor [1,2]. $g\text{-C}_3\text{N}_4$ possesses a graphitic structure with large surface area and good electron transfer ability; meanwhile, its organic skeleton provides much convenience to be chemically

modified [2]. Recently, more attention has been paid to the $g\text{-C}_3\text{N}_4$, mainly for its photocatalytic applications such as organic degradation [3–5], water splitting [6–11], H_2O_2 synthesis [12], and selective oxidation [13,14]. In order to improve its photocatalytic performance, many efforts have been set out, such as morphology control [15–17], impurity doping [9,18,19], semiconductor composite [2,20,21], noble

* Corresponding author.

E-mail addresses: minglufei@163.com (L. Ming), sunnakkxx@163.com (N. Sun), xlm890104@163.com (L. Xu), fengchen@ecust.edu.cn (F. Chen).

metal deposition [22,23] and nanostructures/isotype heterojunction [24–27].

Our previous work [28] found that the photocatalytic activity of $g\text{-C}_3\text{N}_4$ can be significantly modulated by introducing oxygen into the $g\text{-C}_3\text{N}_4$ skeleton to form an oxygenated $g\text{-C}_3\text{N}_4$ (CNO) with a mild hydrothermal treatment. Briefly, the energy band structure of the $g\text{-C}_3\text{N}_4$ is regulated by the introduction of oxygen-containing functional groups, which are relatively electron-withdrawing and thus benefit the separation efficiency of photoelectrons and holes. Further, the photo-oxidation capability of CNO is also enhanced as its valence band level is lowered down due to the interaction of the electron-withdrawing groups. Generally, the oxygenation of $g\text{-C}_3\text{N}_4$ under the hydrothermal condition is carried out with the nucleophilic attacking of hydroxyl anion (or water molecule) to the organic skeleton of $g\text{-C}_3\text{N}_4$, which leads to the transformation of C-NH_2 into C-OH . Meanwhile, the hydrothermal condition favors the hydrolysis and condensation of C=N-C skeleton of $g\text{-C}_3\text{N}_4$ to give C=O and C-O-C groups [29]. As we know, F^- is a very nucleophilic anion, and has been frequently used in material preparation for modulating the morphology, phase transition, as well as improving the crystallinity. For instance, F^- can promote the formation of high energy {001} facet for anatase TiO_2 , as the {001} facet can be stabilized via the formation of surface Ti-F bond [30]. F^- can play an important role in the phase transition of TiO_2 from titanate, in which F^- promotes the Ti-OH condensation to Ti-O-Ti by the formation of Ti-F bond [30]. In the synthesis of MCM-48 mesoporous molecular sieves, Rabinovich et al. [31] suggested that Si-F bond would be formed in the presence of F^- . The existence of Si-F bond increases the condensation rate of Si-OH , and is in favor of phase transformation and crystallinity enhancement; therefore, shortens the reaction time for MCM-48 synthesis. Due to the similar radius to the hydroxyl and a stronger electronegativity, F^- was found increase the hydrolysis and condensation progress of silicate by the formation of Si-F bond in Wang's work [32–34]. Since F^- is suggested play an important role in the hydrolysis and condensation of M-O-M (M represents Ti, Si, and etc.) bond, it was introduced into the hydrothermal system for oxygenating of $g\text{-C}_3\text{N}_4$ in this work. It is supposed that the stronger electronegativity of F^- made it a better nucleophile to attack the α -site of the tertiary amine in the skeleton of $g\text{-C}_3\text{N}_4$ or by substituting the C-OH to accelerate the hydrolysis/condensation process under hydrothermal condition.

2. Experimental section

2.1. Preparation of $g\text{-C}_3\text{N}_4$

Crude $g\text{-C}_3\text{N}_4$ was prepared according to our previous work [28]. The $g\text{-C}_3\text{N}_4$ material was prepared by directly heating the mixture of melamine and thiourea in this work. It is reported that the presence of sulfur containing precursor affects the polymerization/condensation of carbon nitride by optimizing its textural, electronic and optical properties, and thus benefits the photocatalytic performance of $g\text{-C}_3\text{N}_4$. Therefore, thiourea was used instead of urea. Briefly, 3.0 g melamine and 7.0 g thiourea were mixed mechanically by grinding. Then the mixture was heated at 530°C for 4.0 h with a heating-up rate of $2^\circ\text{C}/\text{min}$. According to the literatures, the precursors were thus condensed to form $g\text{-C}_3\text{N}_4$.

2.2. Hydrothermal oxygenation of $g\text{-C}_3\text{N}_4$ in the presence of fluoride ion

The hydrothermal treatment would lead to a partial hydrolysis of $g\text{-C}_3\text{N}_4$, with NH_4^+ and CO_3^{2-} as the by-products. Therefore, NH_4F is used to be added into the hydrothermal system to observe the impact of F^- ion to the synthesis of oxygenized $g\text{-C}_3\text{N}_4$, as the additional NH_4^+ counter ion has a minimal impact on the hydrothermal system.

A certain amount (0.2 g) of as-prepared $g\text{-C}_3\text{N}_4$ and 1.07 g NH_4F were mixed with 75 mL water and put into a stainless autoclave with a

100 mL-volume Teflon-inner-liner. Sonicated for 30 min, the autoclave was sealed and kept at 180°C for desired times. Then the solid samples were collected by centrifugation, washed several times with water and dried at 60°C overnight under vacuum. According to the hydrothermal times of 2.0, 4.0, 6.0, 8.0, 10.0 and 12.0 h employed, the as-obtained oxygenized $g\text{-C}_3\text{N}_4$ samples (CNF) were marked as CNF-2, CNF-4, CNF-6, CNF-8, CNF-10 and CNF-12, respectively.

Similarly, the oxygenized $g\text{-C}_3\text{N}_4$ samples (CNO) were also hydrothermally prepared from the crude $g\text{-C}_3\text{N}_4$ in the absence of F^- [28].

2.3. Catalyst characterization

To investigate the structure and chemical composition of the $g\text{-C}_3\text{N}_4$ and CNF, powder X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET), scanning electron microscopy (SEM), Fourier transform infrared spectra (FTIR), X-ray photoelectron spectroscopy (XPS), photocurrent measurement, and elemental analysis were used. The powder XRD was performed using a powder diffraction meter (Rigaku Ultima IV) operating (Cu $K\alpha$). The BET surface area was tested by ASAP 2020 (Micromeritics). The morphology of the samples was pictured with SEM (Tescan VEGA 3 SBU) observations. FTIR spectra were collected with a Nicolet 380 (Thermo Fisher Scientific). The instrument employed for XPS studies was a Thermo Fisher ESCALAB 250Xi system with Al $K\alpha$ radiation (photon energy 1361 eV), and calibrated internally by carbon deposit C1s binding energy (BE) at 284.8 eV. Photoluminescence spectra (PL) were collected using 365 nm radiation as the excitation light at room temperature with a fluorescence spectrometer (Shimadzu, RF-5301PC). Elemental analysis was measured by vario EL III (Elementar). Photocurrent and electrochemical impedance spectroscopy (EIS) were measured in a standard three-electrode system with a Cimp photo-electrochemical workstation (Zahner Co, Germany), using the prepared sample as the working electrode, a Pt wire as the counter electrode, and saturated calomel electrode (SCE; Ag/AgCl saturated KCl) as a reference electrode. A visible-light irradiation (300 W Xe lamp with a UV cutoff filter, $\lambda > 420$ nm) was used as the light source, and 0.5 M Na_2SO_4 aqueous solution was employed as the electrolyte. The working electrode was prepared by coating the sample powders on the FTO (F-SnO_2) glass via copper foil tape with conductive adhesive (3 M).

2.4. Photocatalytic activity test

In order to study the photocatalytic activities of the as-prepared $g\text{-C}_3\text{N}_4$ and CNF samples, AO7 (acid orange 7, 20 mg/L) was selected as a representative organic pollutant. The reaction was carried out in a self-made reactor. A 35 W metal halide lamp (Philips, HID-CV 35/S CDM) with a UV cutoff filter ($\lambda > 420$ nm) was used as the visible light source. Before the irradiation, 40 mL AO7 solution and 40 mg photocatalyst were put into a quartz tube with magnetic stirring in the dark for 1.0 h to achieve an adsorption-desorption equilibrium. During the reaction, a small amount (ca. 3 mL) of liquid was sampled every half an hour, centrifuged to remove the photocatalyst powders. The concentration of AO7 was then measured by recording the absorbance of AO7 at 484 nm using a UV-vis spectrophotometer (Shimadzu UV-2600).

The cyclic runs of photocatalyst for AO7 degradation was also carried out to verify the stability of CNF. After each cycle, the catalysts were collected by centrifugation, and then re-used in the next cycle without weighing.

3. Results and discussion

3.1. Component and morphology of electrodes

As presented in Fig. 1, XRD patterns of all the samples have a similar diffraction peak at 27.7° which represents the stacking of the conjugated aromatic groups corresponding to the (002) facets of $g\text{-C}_3\text{N}_4$

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