

A facile pyrolysis method for g – C₃N₄ synthesizing: photocatalytic degradation of methylene blue under visible light

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The bulk g – C₃N₄ had been synthesized by a facile chemical pyrolysis method, which is based on the self–condensation of cyanamide, dicyandiamide, and melamine to generate g – C₃N₄. These materials were also characterized by XRD, UV – vis spectra and FT – IR, and elemental analysis. Photocatalytic activity of g – C₃N₄ was evaluated by the photodegradation of methylene blue (MB). The experiments compared the photocatalytic activity of g – C₃N₄, which was synthesized from the varying precursors at 520 °C. The results indicated that the g – C₃N₄ obtained from dicyandiamide exhibited high photodegradation activity. Based on our comparison experiments, a possible mechanism for g – C₃N₄ photocatalysis system was proposed.

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1. Introduction

The heterogeneous photocatalysis eliminating an organic pollutant from water or air has numerous potential applications to resolve serious environmental pollution. In recent years, researchers have devoted extensive efforts to prepare semiconductors for photocatalytic reaction with a suitable band gap, such as metal – containing oxide, sulfide, and oxynitride [1 – 7]. Very recently, a novel metal – free semiconductor photocatalyst, carbon nitride (C₃N₄), was found to have good performance in the photooxidation of methyl orange (MO), the developed g – C₃N₄ metalincluding compounds could effectively degrade MO dyes [8 – 9]. Wang et al. also reported that g – C₃N₄ with a band gap of 2.7 eV achieved functionality as a stable photocatalyst for H₂ evolution from water under visible light irradiation [10 – 12]. Covalent carbon nitrides have attracted much attention since the theoretical prediction of their remarkable mechanical and electronic properties of some phases [13 – 14], for example, g – C₃N₄ was used as catalyst or carrier due to its excellent stability at an ambient condition [15]. In the most case, g – C₃N₄ powder was prepared by a facile pyrolysis method using amine precursors [16 – 23]. However, the obtained g – C₃N₄ from varying amine precursors may present the discrepant photocatalytic properties. To develop a highly efficient photocatalytic system, it is interesting to know the photocatalytic properties of g – C₃N₄ depending on precursors. The detailed investigation on g – C₃N₄ will provide useful information for its photocatalysis application.

Here, the g – C₃N₄ powder was prepared by directly heating cyanamide, dicyandiamide, and melamine respectively. The photocatalytic activity of g – C₃N₄ powder was evaluated by photodegradation of methylene blue (MB). The results suggest that obtained the g – C₃N₄ has photocatalytic activity. The photocatalytic property of g – C₃N₄ depending on amine precursors was provided.

2. Experimentals

The samples were characterized by X – ray diffraction (XRD) for phase identification on a DX – 2000 diffractometer (Cu K α irradiation). The Fourier transformed infrared (FT – IR) spectra were recorded in a Thermo Nicolet Avatar 360 infrared spectrophotometer. UV – vis diffuse reflection spectra were measured using an UV – vis spectrophotometer (Jasco UV – 550, Japan). The C/N ratios were measured with a Vario EL III analyzer (Elementar Germany).

Photocatalytic activity of g – C₃N₄ for methylene blue (MB) degradation was evaluated in a Pyrex glass cylindrical reactor with the diameter of 50 mm and effective volume of 100 mL, 50 mg of g – C₃N₄ was dispersed in MB aqueous solution (50mL, 50mg L⁻¹). Photodegradation of MB was preformed under a 300 W Xe lamp with a water filter and cutoff filter for visible light ($\lambda > 420$ nm). At an hour interval, 2ml suspension was removed, and then the concentration of MB was analyzed using the UV – vis spectrophotometer at 648 nm.

3. Results and discussion

The results show the typical feather of $g-C_3N_4$ with two peaks resulting from graphite structure and tri-s-triazine units in the Fig. 1, which is similar to the previous reports [8–9, 17]. The strongest peak at 27.3° is due to the stacking of the conjugated aromatic system, corresponding to the 002 crystal face and the interplanar distance of aromatic units of 0.326 nm, as well as a peak at 13.2° , resulting from the periodic arrangement of the condensed tri-s-triazine units in the sheets, corresponding to interplanar distance of 0.670 nm. This distance is smaller than one tri-s-triazine unit (ca. 0.73 nm), presumably owing to the presence of small tilt angularity in the structure.

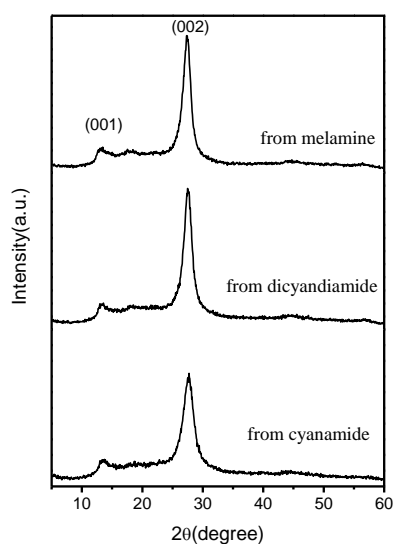


Fig. 1. XRD patterns for $g-C_3N_4$ fabricated from varying precursors.

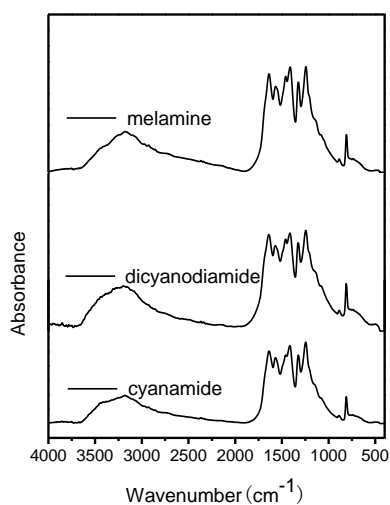


Fig. 2. FT-IR spectra for $g-C_3N_4$ fabricated from varying precursors.

The Fourier transformed infrared (FT-IR) spectra of samples are shown in Fig. 2. We can see three regions in the spectra: 810 cm^{-1} , $1240-1643\text{ cm}^{-1}$ and 3200 cm^{-1} . It is well known that the bands at 810 cm^{-1} corresponds to the characteristic breathing mode of the triazine units. Several strong bands in the $1240-1643\text{ cm}^{-1}$ region are the stretching modes of CN heterocyclics [18–21]. More than that, the sharp peak at 1643 cm^{-1} can be deemed as an indication of good crystallinity of $g-C_3N_4$. Additionally, a broad band at around 3200 cm^{-1} is indicative of NH stretching vibration modes. Indeed, as reported, the residual hydrogen atoms bind to the edges of the graphene-like C-N sheet in the form of C-NH₂ and 2 C-NH bonds [21].

The UV-vis diffuse reflectance spectroscopy showed that the absorption edges of all samples are close to 460 nm, and weak absorption tails were seen due to the structure defects in the heated samples, which may improve the visible absorption of materials.

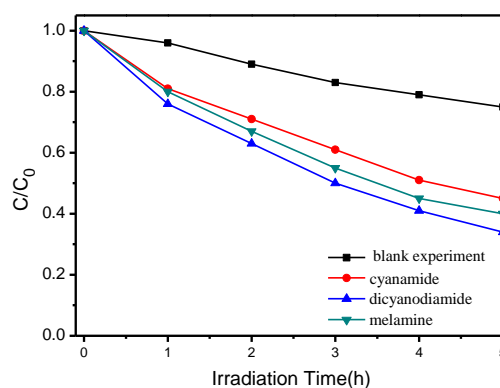


Fig. 3. Photodegradation of MB over the $g-C_3N_4$ prepared from varying precursors.

The photocatalytic activities of the samples for methylene blue (MB) photodegradation were evaluated under visible light irradiation, as shown in Fig. 3. A blank (without a catalyst) was also given for comparison. Results show that 25%, 55%, 66%, 60% MB was photodegraded after 5 h irradiation for the blank, $g-C_3N_4$ obtained from cyanamide, dicyandiamide, and melamine, respectively. No clearly distinction was shown for the $g-C_3N_4$ properties according to the front results, such as the phase and covalent bond of carbon nitride. However, the result of elemental analyses is an exception, which proposed that the different precursors affect on the structural integrality for the final carbon nitride, the average value of the C/N molar ratio is 0.671, 0.685, and 0.676 for cyanamide, dicyandiamide, and melamine respectively, for all cases are lower than the theoretical value of 0.75. The results are in agreement with the FT-IR, and due to the defects, surface termination effects by uncondensed amino functions. The C/N molar ratio and the degree of condensation are consistent with the photocatalytic activity. The samples from dicyandiamide showed the high photo oxidation ability. Higher C/N

ratio and degree of condensation make the photocatalytic activity increase.

4 Conclusions

Three bulk $g-C_3N_4$ samples have been synthesized successfully by the self-condensation of cyanamide, dicyandiamide, and melamine in this work. All of $g-C_3N_4$ was provided with the analogical properties such as the phase, covalent bond and the absorption edges under UV – visible light. However, the C / N molar ratio and the structural integrality of carbon nitride is discrepant, the average value of the C / N ratio is 0.671, 0.685, and 0.676 for cyanamide, dicyandiamide, and melamine respectively. The $g-C_3N_4$ synthesized by dicyandiamide exhibited the photodegradation activity. Higher C / N molar ratio and degree of condensation make the photocatalytic activity more increase.

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