



Lower treating temperature leading to higher air purification activity

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HIGHLIGHTS

- High yield and good photocatalytic activity carbon nitride was obtained.
- Melem/g-C₃N₄ were formed under temperature lower than 550 °C.
- Heterojunction between melem and g-C₃N₄ was beneficial for the activity enhancement.
- The ratio of melem and g-C₃N₄ around 1:1 bring about best performance.

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ABSTRACT

Polymeric graphitic carbon nitride is an efficient visible-light photocatalyst for NO removal which can be prepared by precursors rich in C and N elements, such as melamine, dicyandiamide, urea, and thiourea et al. The method of synthesizing carbon nitride from melamine and dicyandiamide has much higher yield and, whereas the photocatalytic efficiency of the product was lower than that of synthesizing from urea and thiourea. In present work, the photocatalytic performance of carbon nitride prepared from dicyandiamide was significantly improved; melem/g-C₃N₄ was prepared from dicyandiamide under lower temperature with superior performance on NO purification than pure carbon nitride (g-C₃N₄). Suitable depolymerization ratio and surface protonation status could bring about higher photocatalytic activity through XPS characterizations. Through the SEM images, two kinds of morphology nanorod carbon nitride and bulk carbon nitride cross each other together and the ratio variation are consistent with reaction temperature and time. The different band gap structure between g-C₃N₄ and melem could drive the photogenerated electron-hole separation due to the offsets and lead to higher NO removal efficiency. This heterojunction consisted of melem and g-C₃N₄ was developed here just by adjusting reaction temperature and time, which could open up a new possibility for air purification in a low cost way.

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1. Introduction

Photocatalysis technology are widely applied in the field of hydrogen evolution, organic contaminant removal in water, and air purification etc [1–5]. Screening for highly active photocatalysts has been one of the hottest research topics worldwide [6–8]. Various photocatalysts have been developed including conventional material TiO₂ [9,10], whereas the application of TiO₂ is restricted since it can be only motivated under ultraviolet light. Many methods have been proposed to overcome the limitation of TiO₂ [11–13]. However, these efforts are complicated and will raise the synthesis cost. Recently, graphitic carbon nitride (g-C₃N₄) has been intensively investigated for application as photocatalyst in various

fields owing to its optical band gap (2.4–2.8 eV) responding to visible light [14–18]. Thus, g-C₃N₄ has been considered as one of the most promising candidates for next generation photocatalyst due to its facile large-scale fabrication and stable chemical property compared to other visible-light photocatalyst [19]. g-C₃N₄ can be synthesized by condensing precursors rich of C and N elements such as cyanamide, dicyandiamide, melamine, urea and thiourea, etc [20–24]. Among these frequently-used precursors, the products of g-C₃N₄ prepared from urea and thiourea have superior photocatalysis performance than that prepared from dicyandiamide and melamine reported by Tang and Dong due to more completely depolymerization and increased surface areas [25,26]. Whereas, the yield mass ratio of g-C₃N₄ prepared with dicyandiamide and melamine (5–6 g/10 g, g-C₃N₄/ dicyandiamide or melamine) is much higher than that pyrolyzed from urea and thiourea (0.3–0.4 g/10 g, g-C₃N₄/urea) under the same reaction condition [25].

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In consequence, endeavoring to improve the photocatalytic performance of $g\text{-C}_3\text{N}_4$ pyrolyzed from dicyandiamide and melamine is meaningful for practical applications of the novel photocatalyst.

The photocatalytic efficiency of $g\text{-C}_3\text{N}_4$ is affected by many factors, such as the band gap structure of semiconductors, surface area, absorption range and morphology in a general way. Consequently, many methods have been developed to overcome these restrictions of $g\text{-C}_3\text{N}_4$, such as textural engineering [27], copolymerization [28], doping [29], cocatalyst deposition [30], heterostructure design [31], and thin-film fabrication [32]. Among them, higher recombination rate of photogenerated electron-hole pair is a dominant factor limiting $g\text{-C}_3\text{N}_4$ photo-current conversion efficiency [33–35]. Construction of heterojunction is an efficient way to improve the separation ratio of photogenerated electrons and holes which could enhance the activity of photocatalyst. For example, $\text{CeO}_2/g\text{-C}_3\text{N}_4$ [36], $\text{CoSe}_2/g\text{-C}_3\text{N}_4$ [37], $\text{BiOX}/g\text{-C}_3\text{N}_4$ [38], $\text{TiO}_2/g\text{-C}_3\text{N}_4$ [39], $\text{ZnO}/g\text{-C}_3\text{N}_4$ [40] have been developed for construct heterojunction which could facilitate the photogenerated charge carrier separation resulting in enhanced photocatalytic activity. However, facile fabrication of high activity photocatalyst based on $g\text{-C}_3\text{N}_4$ heterojunction is crucial for practical applications in the fields of air purification, organic degradation and hydrogen evolution.

A number of studies have indicated that when the heating temperature and heating time is increased, the crystallinity and specific surface area of $g\text{-C}_3\text{N}_4$ increases simultaneously, accompanying with improved photocatalytic performance [16,35]. Therefore, more investigations are focused on higher condensed $g\text{-C}_3\text{N}_4$ which are always synthesized under temperature higher than 550 °C from dicyandiamide and melamine leading to little study about the performance of carbon nitride prepared under lower temperature or less pyrolysis time [16,47].

Unexpectedly, we discovered that the intermediates melem prepared under lower temperature play a crucial role in the determination of NO removal efficiency of carbon nitride. We have investigated the influence of intermediates on the morphology and photocatalytic performance of carbon nitride synthesized from dicyandiamide under different temperatures especially under treating temperatures lower than 550 °C. It is surprised to find that the $g\text{-C}_3\text{N}_4$ combined with melem (prepared with dicyandiamide) could greatly enhance the NO removal efficiency compared to carbon nitride, which could be compared to that of carbon nitride pyrolyzed from urea and thiourea, and at the same time the yield is much higher than carbon nitride synthesized from urea and thiourea. According to the results, the enhanced NO removal activity could be ascribed to the efficient charge transportation across the heterojunction interface. In addition, further studies about the ratio of intermediates were demonstrated through synthesizing $g\text{-C}_3\text{N}_4$ within different heating periods. The process of the carbon nitrides heterojunction preparation is simple and allows mass production with high visible-light catalytic activity. This work will provide us a new direction to apply this potential photocatalyst into practical application.

2. Material and methods

2.1. Sample synthesis

The samples for experiment were synthesized according to the steps in the literatures. In a typical preparing process, we put 10 g dicyandiamide into a semi-closed alumina crucible with a cover and heated to temperature between 450 °C and 600 °C at a heating rate of 15 °C/min in a muffle furnace, where it was kept for 4 h. The obtained yellow powder was collected for further experiment [41]. For investigating effect of reaction temperature, we remain other

reaction conditions unchanged, just change the temperature for treating dicyandiamide. The carbon nitride prepared from dicyandiamide pyrolyzed under 450 °C, 500 °C, 550 °C, and 600 °C for 240 min are labeled as CN-450, CN-500, CN-550 and CN-600, respectively. The heat preservation periods were also studied through variation of treating time. The carbon nitrides prepared from dicyandiamide pyrolyzed under 500 °C for 30 min, 120 min, 240 min, 360 min, 480 min and 600 min are labeled as CN-30 min, CN-120 min, CN-240 min, CN-360 min, CN-480 min, and CN-600 min, respectively.

2.2. Characterization

Thermalgravimetric analysis (TG) and differential scanning calorimetry (DSC) were carried out on Mettler TGA/DSC 1 SF/1382 instrument. The crystal structures of the prepared samples were recorded by an X-ray diffraction with Cu-K α radiation (XRD, PANalytical X'pert Powder). Transmission electron microscopy (TEM, Tecnai G2 F20 S-TWIN) and scan electron microscope (SEM, S-4800) were carried out to analyze the micro structure of samples. Fourier Transform infrared spectroscopy was analyzed by a Nicolet IS10 spectrometer with prepared samples and KBr hybrid tablet. The UV–vis diffuse reflection spectra was obtained using a Shimadzu spectrophotometer (UV–vis DRS: UV-2700, Shimadzu, Japan) equipped with an integrating sphere assembly and using BaSO_4 as the blank reflectance. The surface areas of the synthesis were achieved on a Micromeritic ASAP 2020 with all samples degassed at 180 °C for 12 h through obtaining a Nitrogen-absorption-desorption isotherms. X-ray photoelectron spectroscopy (XPS) spectra were recorded on a Thermo Scientific Escalab 250Xi. The in-situ FTIR was carried on Bruker Tensor II equipped with a 300 W tungsten halogen lamp irradiation during testing process.

2.3. Evaluation of visible light photocatalytic performance

For evaluating the prepared samples photocatalytic performance of removing NO, the experiment was processed in a continuous flow reactor at ambient temperature as shown in Scheme 1. The reactor's volume is 4.5 L (30 cm \times 15 cm \times 10 cm). In the experiment, a commercial 150 W tungsten halogen lamp was taken as the visible light source. The prepared samples (0.2 g) were coated onto a diameter 9 cm evaporating dish. NO flow from a compressed gas cylinder with 100 ppm concentration (N_2 balance) was the testing gas source. For controlling the initial NO concentration in the reactor, we diluted the 100 ppm NO with air stream to about 1000 ppb. The humidity of the gas was controlled at 50% by passing the zero air streams through a humidification chamber. We controlled the gas flow rate at 2.25 L/min by gas flow meter. The tungsten halogen lamp was vertically placed outside the reactor 10 cm above the sample dish. Until the system is stable, the concentration of NO could be continuously measured by a NO analyzer (Thermo Environment Instruments Inc., 42i-HL), which monitors NO, NO_2 , and NO_x (NO_x represents NO and NO_2) with a sampling rate of 1 L/min. The removal efficiency was represented by C/C_0 (%), where C_0 is the initial concentration (1000 ppb) of NO and C is the remaining concentration of NO after visible-light over photocatalyst treatments, respectively.

3. Result and discussion

The XRD patterns of CN-450, CN-500, CN-550 and CN-600 are presented in Fig. 1a. As shown in Fig. 1a, the XRD patterns of samples synthesized at 550 °C and 600 °C possessing two major peaks which are located at around 12.6° and 27.3°. The weak and broad

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