



Facile modification of a graphitic carbon nitride catalyst to improve its photoreactivity under visible light irradiation

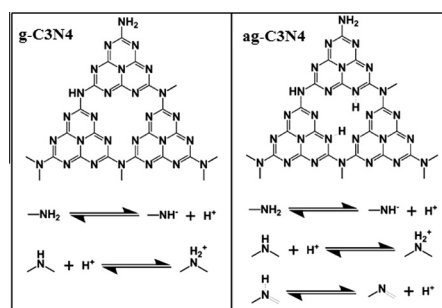
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HIGHLIGHTS

- Acidified g-C₃N₄ was prepared and exhibited enhanced photoreactivity toward rhB.
- Growth orientation of the self-polycondensed crystals changed on acidification.
- Acidified g-C₃N₄ was durable under acidic conditions during recycle tests.

GRAPHICAL ABSTRACT



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ABSTRACT

Graphitic carbon nitride (g-C₃N₄) has attracted much attention worldwide ever since the recent discovery of its photocatalytic activity and metal-free property. In the current study, one-step acidification of melamine, by an easy to operate and low-cost approach, is proposed to improve the photocatalytic activity of prepared ag-C₃N₄. Rhodamine B (rhB), a typical organic dye, was chosen as a model pollutant to verify improvement in the photocatalytic performance of acidified g-C₃N₄ (ag-C₃N₄). The results reveal that the apparent reactive rate constant (k_{app}) of ag-C₃N₄ increases approximately three-fold under visible light at pH 7.0 compared to that of g-C₃N₄. Based on a systematic analysis of properties of ag-C₃N₄ and g-C₃N₄, this substantial improvement in photoreactivity is mainly attributed to changes in the growth orientation of self-polycondensed sheets and surface properties by acidification treatment, which endows ag-C₃N₄ with a high photoreactivity.

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1. Introduction

Intensified environmental pollution associated with worldwide economic growth necessitates the development of efficient environmental remediation techniques. To this end, semiconductor photocatalysis has, in the last few decades, materialized as one of the most promising solutions to this issue. A number of researchers have reported the photocatalytic degradation of organic pollutants in water or air with the aid of semiconductors that possess a suit-

able bandgap [1–4]. Metal oxide semiconductor photocatalysts have attracted much attention owing to their strong oxidizing ability. However, most metal oxide semiconductors, such as TiO₂, can only absorb ultraviolet (UV) light (e.g., $\lambda < 385$ nm for the anatase form), which accounts for less than 5% of sunlight and limits material efficiency when utilizing solar energy. More importantly, some metal oxide photocatalysts, such as TiO₂ and ZnO, may increase environmental risk by the release of heavy metals into water during their application [5,6].

Graphitic carbon nitride (g-C₃N₄) has gained much attention from the scientific community since discovery of its photocatalytic activity [7–11]. Unlike conventional inorganic semiconductor

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photocatalysts, this metal-free polymer comprises only carbon, nitrogen, and a small amount of hydrogen, all of which are earth-abundant elements. This polymer has proven to be an indirect semiconductor with a moderate gap (ca. 2.70 eV for bulk $g\text{-C}_3\text{N}_4$) and can be readily used to split water for hydrogen or oxygen production, reduce CO_2 to CO, and degrade organic pollutants in water (e.g., dyes and phenolic compounds) under visible light [12–18]. However, the primary issue that needs to be addressed with respect to practical application of this environmentally benign catalyst is to notably improve its photoreactivity and stability.

Among many studies aimed at improving the photocatalytic activity of $g\text{-C}_3\text{N}_4$, modification of $g\text{-C}_3\text{N}_4$ is an interesting method [19]. Zhang et al. [20] first reported the modification of $g\text{-C}_3\text{N}_4$ through post-treatment with concentrated HCl and observed an accompanying increase in ionic conductivity. However, whether or not such post-treatment leads to enhanced photocatalytic or photoelectrochemical performance is ambiguous, considering the decrease in regularity of in-plane packing of the poly (tri-s-triazine) motifs brought about by protonation. Gao et al. [21] synthesized an interesting millimeter-long carbon nitride nanotube that exhibits intense photoluminescent emission using a nitric-acid-treated melamine as the precursor; however, the nanotube prepared at 350 °C had an absorption edge below 400 nm and exhibited no photocatalytic activity under visible light. Yan et al. [16] used H_2SO_4 -treated melamine as a precursor and fabricated $g\text{-C}_3\text{N}_4$ with a large specific surface area (SSA) and photocatalytic H_2 production rate under visible light, both of which were twofold higher than those of bulk $g\text{-C}_3\text{N}_4$. The observations of this research team also indicated that the photoreactivity per SSA of the functionalized $g\text{-C}_3\text{N}_4$ was virtually unimproved [22]. A previous study further showed that thermal condensation of an HCl-treated precursor results in $g\text{-C}_3\text{N}_4$ with much higher SSA and structural porosity but lower photocatalytic activity per SSA for either dye bleaching or CO_2 reduction. In a word, the different modification of synthesis method of $g\text{-C}_3\text{N}_4$ has not significantly improved its photoreactivity up to now.

In the current study, we prepared an acidified $g\text{-C}_3\text{N}_4$ photocatalyst ($ag\text{-C}_3\text{N}_4$) by a one-step, easy to operate method, i.e., the precursor melamine was deliberately treated by HCl and alcohol. The photoreactivity for the visible-light-driven photocatalytic degradation (PCD) of Rhodamine B (rhB) was investigated. To reveal the multifaceted effects of modification on the significant improvement of photoreactivity of $ag\text{-C}_3\text{N}_4$, the textural, surface, and band characteristics, and time-resolved fluorescence decay spectra were systematically analyzed. The stability of $ag\text{-C}_3\text{N}_4$ and its ability to mineralize rhB, which are important factors influencing the practical application of $ag\text{-C}_3\text{N}_4$, were also evaluated.

2. Materials and methods

2.1. Preparation of photocatalysts

$g\text{-C}_3\text{N}_4$ and $ag\text{-C}_3\text{N}_4$ were prepared following a facile method of thermal condensation of the organic precursors. $g\text{-C}_3\text{N}_4$ was prepared through thermal self-condensation of melamine ($\geq 99.0\%$, Sinopharm, Shanghai, China) in a covered porcelain crucible at 550 °C in a muffle furnace. A 4.0 g portion of melamine was added to a crucible in a typical run. The temperature was ramped from room temperature to 550 °C at a rate of 4.17 °C/min and maintained at 550 °C for 4 h.

The precursor for $ag\text{-C}_3\text{N}_4$ was HCl-treated melamine, which was obtained as follows: Melamine (4.0 g) was first dispersed in 30 mL of absolute alcohol for 30 min under vigorous stirring and then mixed with 3 mL of concentrated HCl (1:1, v/v). The suspension was vigorously stirred for another 30 min before being

transferred to an oven at 75 °C to vaporize the solvent and obtain the HCl-treated melamine. After thermal condensation at 550 °C for 4 h, the pale yellow-colored products were washed three times with copious amounts of absolute ethanol and deionized water to remove possible by-products. The catalysts were dried at 80 °C overnight and then collected and ground into powder using a pestle and mortar for further characterization and experimentation.

2.2. Characterization

Fourier Transform infrared (FTIR) spectra in the range of 4000–400 cm^{-1} were collected on a VERTEX 70 FT-IR spectrometer (Bruker Inc., Germany) by the KBr pellet method. Each spectrum represents the average of 64 scans at a spectral resolution of 4 cm^{-1} . Powder X-ray diffraction (XRD) patterns in the 2θ range of 10–70° were recorded on a rotating-target X-ray diffractometer (MXPAHF, Japan) that was operated at 30 kV and 150 mA with Cu-K α radiation ($\lambda = 1.54056 \text{ \AA}$). The morphologies of $g\text{-C}_3\text{N}_4$ and $ag\text{-C}_3\text{N}_4$ were observed on a JEOL-2100F transmission electron microscope (TEM) that was operated at a 200-kV accelerating voltage.

The pH values of the points of zero charge (pH_{PZC}) of $g\text{-C}_3\text{N}_4$ and $ag\text{-C}_3\text{N}_4$ were determined by the pH drift method [23,24]. Typically, a series of 50 mL of 0.01-M NaCl solutions were placed in 100 mL conical flasks, and their pH adjusted to successive initial values between 2 and 12 using a 1-M NaOH or HCl solution. A 0.15-g portion of $g\text{-C}_3\text{N}_4$ or $ag\text{-C}_3\text{N}_4$ catalyst was then added to each flask. After oscillation at 25 °C for 48 h, the equilibrium pH was measured and plotted against the initial pH. The pH_{PZC} of a given material lies at the pH where the initial pH equals the equilibrium pH.

UV–visible absorption spectra in the range of 240–800 nm were recorded on a SOLID 3700 UV–VIS–NIR spectrophotometer (Shimadzu Inc., Japan), which was equipped with an integrating sphere accessory with BaSO_4 as the reference. Data were transformed by the Kubelka–Munk equation to determine the bandgap energy (E_g) of the photocatalysts. Elemental analysis of prepared and recovered catalysts was carried out on a Vario EL III elemental analyzer (Elementar Inc., Germany). N_2 adsorption and desorption isotherms of $g\text{-C}_3\text{N}_4$ and $ag\text{-C}_3\text{N}_4$ were measured on a Micromeritics Tristar II 3020 surface area and porosimetry analyzer at $-196 \text{ }^\circ\text{C}$. Prior to measurement, samples were degassed at 200 °C in vacuum for 6 h.

Time-resolved fluorescence decay spectra of $g\text{-}$ and $ag\text{-C}_3\text{N}_4$ were obtained using a Tempro spectrofluorometer (Horiba Jobin Yvon Inc.) equipped with a time-correlated single photon counting (TCSPC) module. Samples were excited by monochromatic pulses (340 nm, <1 ns, 1-MHz repetition rate) from a nanosecond light-emitting diode and the fluorescence emissions were monitored at their respective maximum emission wavelengths. Measured decay curves were fitted with a two-exponential model using the non-linear least squares regression method. Intensity averaged lifetime, $\bar{\tau}$, was calculated with the Eq. (1)

$$\bar{\tau} = \sum_{i=1}^2 f_i \tau_i \quad (1)$$

where τ_i and f_i were the lifetime and the fractional contribution to the fluorescence intensity of component fluorophore i , respectively.

2.3. Photocatalysis experiments

The photocatalysis experiments were conducted in a 125 mL magnetically stirred and top-irradiated cylindrical reactor at room temperature (26 °C). The light source was a 350 W Xenon lamp (XD-300, Nanjing Yanan Special Lighting Co., Ltd). The UV radiation

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