



Highly porous carbon nitride by supramolecular preassembly of monomers for photocatalytic removal of sulfamethazine under visible light driven

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ABSTRACT

Many organic and inorganic compounds have been developed as visible light driven photocatalysts for environment and energy application. In this work, a metal-free carbon doping-carbon nitride (BCM-C₃N₄) nanocomposite was synthesized by introducing barbituric acid and cyanuric acid during the polymerization of melamine. The BCM-C₃N₄ was characterized by structure, porosity, optical performance, and photoelectrochemical properties. Results demonstrated that BCM-C₃N₄ sample exhibited higher surface area, lower fluorescence intensity, better photocurrent signals and more efficient charge transfer in comparison to pure C₃N₄. The BCM-C₃N₄ exhibits excellent photocatalytic degradation ability of sulfamethazine (SMZ) under visible light irradiation. Much superior photocatalytic activity and high pollutant mineralization rate was achieved by BCM-C₃N₄, where it was 5 times than that of pristine C₃N₄. The effect of initial SMZ concentrations on photocatalyst was also investigated. Additionally, the trapping experiments and electron spin resonance tests demonstrated that the main active species, such as $\cdot\text{O}_2^-$ and h^+ , could be produced under light irradiation. This work might provide an effective approach to the design of low-cost and highly efficient photocatalysis degradation systems for water treatment.

1. Introduction

Water contaminated by antibiotics is becoming a worldwide environmental issue [1–6]. Potentially negative concerns of these antibiotics active compounds contain abnormal physiological processes, reproductive damage, increased cancer incidences, and enhanced toxicity of chemical mixtures [7,8]. The contaminants are in low concentration at present, but tend to be accumulated in long periods of time. Sulfonamide antibiotics have been detected at concentrations up to 900 mg kg⁻¹ in manure, which can be transported to surface water, groundwater and soils. Sulfamethazine (SMZ 4-amino-N-[4,6-dimethyl-2-pyrimidinyl] benzenesulfonamide), which belongs to the sulfonamide group of antibiotics, is commonly used in veterinary industry [9]. Traditional methods, including physical adsorption [10–14], chemical reactions [15,16], and biological degradation [17–20], may be effective for remediation. However, pollutants just transfer from water phase to another phase with these methods, and may cause the secondary pollution if there is no suitable further treatment [21–23].

Semiconductor photocatalysis technique has aroused widespread concern and has been successfully employed to solve the environmental

problems [24–28]. Also, it is an economic and environmental technology [29]. The solar photocatalysis process including three steps: (i) light harvest, (ii) photocarrier separation or transport, and (iii) surface reaction [30]. Unfortunately, photocarriers are easy to recombine via the long-distance transportation. To solve the problem and enhance the solar conversion efficiency, the photocarrier transfer kinetics should be accelerated to reach fast separation of the photoexcited electron-hole pairs with novel material or new structural design. Among the numerous photocatalysts, graphitic carbon nitride (g-C₃N₄) has gained much interest as an innovative material with desirable visible-light response and medium band gap of 2.7 eV [31,32]. As an earth-abundant, low-cost, biocompatible, and chemically stable photocatalyst, g-C₃N₄ can easily be fabricated from melamine, urea, etc. [33]. It has been developed as a metal-free visible-light sensitive photocatalyst in 2009 and applied in all kinds of photocatalytic branches, such as H₂/O₂ evolution from water splitting [34,35], contaminant degradation [36], CO₂ reduction [37], and so on. However, g-C₃N₄ has a low efficiency under visible light due to the high recombination of photo-generated electron (e^-)-hole (h^+) pairs. Thus, different techniques have been employed to improve the efficiency of g-C₃N₄. One strategy for

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improving the charge carrier separation and photocatalytic efficiency is to dope carbon nitride with heteroatoms [38] or heterojunction [39–41] or metal nanoparticles [42–44].

To date, researchers have reported that nonmetal element doping $g\text{-C}_3\text{N}_4$ enhanced visible-light photocatalytic activity, such as doping with P, B, C, Cl, and S [45–48]. For example, Deng et al. prepared P-doped $g\text{-C}_3\text{N}_4$ and presented improved photocatalytic activity for the simultaneous removal of Cr(VI) and 2,4-DCP under visible light irradiation [49]. Recently, triazine derivatives doped with melamine through hydrogen bonding led to carbon nitride structures attracted widespread attention owing to its outstanding catalytic and photocatalytic activity. $g\text{-C}_3\text{N}_4$ can be easily modified by standard organic protocols such as barbituric acid, which was proposed by Wang et al. [50]. Thomas et al. using dimethyl sulfoxide as a solvent to synthesize C_3N_4 based on the cyanuric acid-melamine (CM) complex, which can exhibited superior photocatalytic activity when compared with the bulk material [51]. Shalom et al. presented hollow carbon nitride structures for degradation of rhodamine B dye, using a CM complex in different solvents as a starting product [52]. Also, Zheng et al. prepared optimized carbon-doped $g\text{-C}_3\text{N}_4$ and enhanced the reaction rate for the degradation of phenol and persistent organic pollutants when compared with conventional $g\text{-C}_3\text{N}_4$ [53]. Mesoporous carbon nitride was synthesized using different nonionic surfactants by Peer et al. [54]. These results indicated that carbon doped $g\text{-C}_3\text{N}_4$ could act as a good catalyst for environment management. However, the weak efficiency of carbon doped $g\text{-C}_3\text{N}_4$ may due to the limited surface area ($40\text{--}60\text{ m}^2\text{ g}^{-1}$) [55,56]. Furthermore, a few studies are concerning the degradation system of the typical organic micropollutants in water such as SMZ via carbon doped $g\text{-C}_3\text{N}_4$.

In this work, we report a high-surface area, high-porosity carbon nitrides by a facile one-step approach. This technique using the ethanol as the solvent, taking advantage of both melamine-cyanuric acid and the barbituric acid as monomers to form supramolecular carbon nitride (BCM- C_3N_4) via electrostatic interactions or hydrogen bond. The BET surface area of BCM- C_3N_4 was up to $179\text{ m}^2\text{ g}^{-1}$. With the high surface area and porosity, the synthesized carbon nitrides presented desirable optical properties, and their wide band gap improved visible light absorption, which made them more suitable for photocatalytic applications. The photocatalytic activity was tested by measuring the degradation of SMZ under visible light illumination with the presence of photocatalyst. The chemical structure, morphology, and optical properties of the resulting carbon nitrides were characterized. The performance including degradation efficiency and photocatalytic stability of the photocatalyst under visible light was observed. The effects of initial concentration and the removal rate of total organic carbon were also discussed. The predominant radicals in the photodegradation system were discussed by radicals trapping experiment and electron spin-resonance spectroscopy (ESR) analysis. Meanwhile, a possible degradation pathway of SMZ was proposed. It is anticipated that this metal-free photocatalyst can be a promising candidate for other degradation systems.

2. Experimental

2.1. Materials

Melamine (> 99%), cyanuric acid (> 98%), barbituric acid (> 99%), and Sulfamethazine (> 99%) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). All the reagents and materials were of analytical grade and used as received without additional purification or treatment. De-ionized water ($18.25\text{ M}\Omega\cdot\text{cm}$) was used in the whole experiment.

2.2. Characterization

The specific surface area, pore volume and pore size of $g\text{-C}_3\text{N}_4$,

BCM- C_3N_4 were measured by the Brunauer-Emmett-Teller (BET) adsorption method (Micromeritics Instrument Corporation, TRI-STAR3020, USA). The photoluminescence (PL) spectra were recorded with Hitachi F-7000 fluorescence spectrophotometer at an excitation wavelength of 365 nm. The UV-vis diffuse reflectance spectra (DRS) were performed on a UV-vis spectrophotometer (Cary 300, USA) with an integrating sphere. The crystal phase of the samples was determined by a D/max-2500 X-ray diffractometer (XRD; Rigaku, Japan) using $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406\text{ nm}$) in the region of 2θ from 10° to 80° . X-ray photoelectron spectrum (XPS) of the samples was obtained by using an ESCALAB 250Xi spectrometer (Thermo Fisher, USA) with Al $K\alpha$ radiation ($h\nu = 1486.6\text{ eV}$). Their morphology was examined by transmission electron microscope (TEM, JEOL JEM-2100F). The light irradiation source was a 300 W Xe arc lamp (CEL-HXF300, Beijing). The visible light used in this study was obtained by cutting UV light ($\lambda < 420\text{ nm}$) with a filter (Beijing China Education Au-light Co., Ltd). The total organic carbon (TOC) was applied to analyze the mineralization degree of organic contaminants on Analytik Jena AG (Multi N/C 2100).

2.3. Preparation of samples

2.3.1. Synthesis of $g\text{-C}_3\text{N}_4$

In a typical synthesis process, 10 g of melamine was placed into a ceramic crucible with a cover and then loaded into the central region of a muffle furnace. The crucible was firstly heated to 550°C with a heating rate of $2.3^\circ\text{C min}^{-1}$ and maintained at 550°C for 4 h, and then cooled down naturally. After cooling to ambient temperature, the obtained yellow agglomerate ($g\text{-C}_3\text{N}_4$) was ground into powder.

2.3.2. Synthesis of BCM- C_3N_4

The BCM- C_3N_4 was prepared from melamine, cyanuric acid, and barbituric acid by modified method [57,58]. 5.0 g of melamine, 5.0 g of cyanuric acid, and 0.5 g of barbituric acid were first dispersed in 100 mL of ethanol to form suspension. The suspension was next stirred at ambient temperature for 2 h, followed by sonication at room temperature for an additional 1 h. The suspension was then dried on a hot plate at 90°C until no obvious liquid found. The calcination procedure was exhibited in the part of 2.3.1. For comparison, CM- C_3N_4 sample was obtained without barbituric acid.

2.4. Photodegradation evaluation

The photodegradation activities of obtained samples were investigated via the degradation of SMZ in aqueous solution under a 300W Xe lamp in an aqueous solution under visible light ($> 420\text{ nm}$). In photocatalytic degradation experiment, 50 mg of powder photocatalyst was dispersed into 50 mL of SMZ (10 mg L^{-1}) solution. Before illumination, the suspensions were stirred in dark for 1 h to reach the adsorption-desorption equilibrium. After that, the mixture solutions were illuminated under visible light. At a given time interval of irradiation, aliquots were separated from the suspension. The SMZ concentration was determined using an HPLC Series 1100 (Agilent, Waldbronn, Germany) equipped with a UV-vis detector. The Column was C-18 column ($4.6 \times 250\text{ mm}$) at the temperature of 30°C . The mobile phase was water-acetonitrile (80:20, v/v) with 0.1% acetic acid at the flow rate of 1 mL min^{-1} . The sample volumes for injection were all $20\ \mu\text{L}$ and the wavelength of detector was 270 nm .

2.4.1. Photoelectrochemical measurement

Photoelectrochemical tests were carried out on a CHI 660D workstation in a three-electrode model, utilizing a Pt electrode ($40 \times 0.55\text{ mm}$, 99%) as the counter electrode and an Ag/AgCl electrode as the reference electrode. A 300 W Xe lamp was used as a light source. Typically, the working electrodes were prepared as follows: 10 mg of the photocatalyst was suspended in 1 mL of 0.5% nafion

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