



One step synthesis of oxygen doped porous graphitic carbon nitride with remarkable improvement of photo-oxidation activity: Role of oxygen on visible light photocatalytic activity

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ABSTRACT

A novel metal-free oxygen doped porous graphitic carbon nitride (OA-g-C₃N₄) was synthesized by condensation of oxalic acid and urea. The 40% OA-g-C₃N₄ catalyst can degrade bisphenol A (15 mg L⁻¹) in 240 min with a mineralization rate as high as 56%. The markedly higher visible-light-driven oxidation activity of OA-g-C₃N₄ is attributed to the porous morphology and unique electrical structure. The porous structure of OA-g-C₃N₄ provides more active sites for adsorption and degradation of pollutants. Moreover, oxygen atoms in the tri-s-triazine units help to extend sufficient light absorption range up to 700 nm, improve the separation of charge-carriers and alter the position of valence band (VB) and conduction band (CB). The VB edge shifts from 1.95 eV to 2.46 eV due to the incorporation of O atoms, which leads to the change of active species in the photocatalytic reaction. Trapping experiment shows that superoxide radicals play the major role in the photocatalytic degradation of BPA on g-C₃N₄, while hydroxyl radical is the dominant active species in the photocatalytic degradation process over 40% OA-g-C₃N₄. This study presents a simple, economical and environment-friendly method to synthesized oxygen doped porous graphitic carbon nitride.

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1. Introduction

Water pollution has become a serious environmental problem in China with the rapid economic development and industrialization [1]. As an economical and environmentally friendly oxidation technology, photocatalysis has great potential in wastewater treatment [2]. The oxidation activity of photocatalyst is crucial for wastewater treatment, especially for organic compounds degradation. However, traditional photocatalysts, such as TiO₂, only response to ultraviolet light due to the wide band gap, and cannot take full advantage of the solar energy [3]. Thus, the research of novel visible-light-driven (VLD) photocatalyst with high oxidation activity has attracted much attention.

Graphitic carbon nitride (g-C₃N₄), a metal-free VLD photocatalyst with a narrow band gap of 2.7 eV, has become a hot research topic in photocatalysis. [4]. In addition, g-C₃N₄ is nontoxic, highly stable and can easily be synthesized via one-step polymerization of the cheap raw material. However, g-C₃N₄ suffers from several disadvantages, such as low specific surface area, limited visible light absorption capacity and high recombination rate of photoinduced charge carriers [5]. Currently, it has been reported that the more ideal the chemical structure g-C₃N₄ is, the weaker activity it behaves in some catalytic processes, for that the structure defects and surface terminations may play an important role on photocatalytic activity [6]. Non-metal (e.g., B, P, F, C and O [7–10]) doping is a conventional method to increase the structure defects of g-C₃N₄, in order to alter the position of conductive band (CB) and valence band (VB), improve the separation rate of charge carriers and create more active sites to elevate the catalytic activity. For example, C doped g-C₃N₄ showed extensive visible light absorption and enhanced electrical conductivity due to the change of intrinsic electronic and band structure. The photocatalytic activity of C

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doped $g\text{-C}_3\text{N}_4$ in degradation of rhodamine B, reduction of Cr(VI) and hydrogen production was significantly improved [11]. Li et al. [12] synthesized oxygen-doped $g\text{-C}_3\text{N}_4$ by a hydrothermal method using H_2O_2 , and the obtained catalyst performed enhanced photocatalytic activity under visible light irradiation. Recently, Huang et al. [13] reported a porous oxygen-doped $g\text{-C}_3\text{N}_4$ catalyst synthesized by condensation of melamine and H_2O_2 , which exhibited 7.8 times higher H_2 evolution activity than pristine $g\text{-C}_3\text{N}_4$. Clearly, it is still highly desirable to explore the modification of $g\text{-C}_3\text{N}_4$ to achieve large light adsorption range and low charge recombination rate with enhanced oxidation activity.

Changing morphology is another approach to promote the catalytic performance, since larger surface area can provide more active sites for reaction and the textural structure may have influence on the electronic structure of photocatalyst. For instance, porous structure can promote the light adsorption due to multiple-reflection effect and suppress the recombination of photogenerated electron-hole pairs on account of the shortened diffusion distance [14,15]. Porous $g\text{-C}_3\text{N}_4$ catalysts have been synthesized through various methods, such as hard-template method [16], soft-template method [17], acid protection [18] and gas bubbling in the calcination process [19]. Nevertheless, it remains a challenge to simultaneously modify the pore-structure and achieve the non-metal doping of $g\text{-C}_3\text{N}_4$ through a facile and environment-friendly strategy.

Herein, we present a simple, economical and environment-friendly method to synthesize oxygen doped porous $g\text{-C}_3\text{N}_4$ (OA- $g\text{-C}_3\text{N}_4$) by condensation of oxalic acid and urea for the first time. The synthesized OA- $g\text{-C}_3\text{N}_4$ not only possesses high surface area but also extends the sufficient light absorption range up to 700 nm, which significantly enhances the degradation efficiency of bisphenol A (BPA) under visible light irradiation. The oxygen atoms incorporate into the network of $g\text{-C}_3\text{N}_4$ by replacing the sp^2 N atoms, which markedly influences the electrical structure of $g\text{-C}_3\text{N}_4$. The results show that 40% OA- $g\text{-C}_3\text{N}_4$ can degrade BPA with initial concentration of 15 mg L^{-1} in 240 min under visible light. Cycling tests showed that OA- $g\text{-C}_3\text{N}_4$ is still highly efficient after 5 rounds. Trapping experiments are conducted to explore the degradation mechanism. This research provides a brand new approach to achieve the oxygen doping in the polymeric $g\text{-C}_3\text{N}_4$ with superior photocatalytic activity.

2. Experimental section

2.1. Synthesis of photocatalyst

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

The $g\text{-C}_3\text{N}_4$ was synthesized by the polymerization of urea [20]. 20 g of urea was placed in a porcelain crucible with a cover and calcined at 550°C for 5 h with a heating rate of 3°C min^{-1} .

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

The porous oxygen-doped graphitic carbon nitride samples were synthesized by condensation of oxalic acid and urea under high temperature for the first time. In detail, 20 g of urea was mixed with a certain amount of oxalic acid by grinding in a mortar. The resultant powders were placed in a porcelain crucible with a cover and calcined at 550°C for 5 h with a heating rate of 3°C min^{-1} . The obtained samples were designated as x OA- $g\text{-C}_3\text{N}_4$ (where x is the weight ratio of oxalic acid to urea, x = 10%, 20%, 30%, 40%, 50%, respectively). The condensation of dicyandiamide and oxalic acid was carried out in the same process.

2.1.3. Synthesis of mesoporous graphitic carbon nitride (mpg- C_3N_4)

20 g of urea was dissolved in 50 mL of solution at 60°C . Then, 2 g of silica particles (Aladdin, China) with diameter of 15 nm was added into the solution and the mixture was stirred for 8 h at 60°C . The resulting powder was calcined at 550°C with a rate of 3°C min^{-1} in the air. The product was stirred in 4 mol L^{-1} NH_4HF for 24 h to remove the silica template. At last, the obtained product was washed with distilled water and ethanol, and dried at 70°C overnight.

2.2. Characterization

Transmission electron microscopy (TEM) image was observed on a JEOL JEM2100 microscopy at an acceleration voltage of 200 kV. The specific surface area was measured by N_2 adsorption-desorption on Micromeritics ASAP 2000. Before each measurement, the samples were out-gassed at 260°C for 6 h under vacuum. Powder X-ray diffraction (XRD) patterns were acquired from a Bruker D8 Advanced diffraction-meter with $\text{Cu K}\alpha$ radiation with a scanning angle ranging from 10° to 80° . The distribution of the elements (C, N and O) in the sample was analyzed using energy dispersive X-ray spectroscopy (EDX) equipped with the TEM (Titan G2 60–300). The content of C, N, O and H was measured by the elemental analyzer (CHN-O-Rapid, Heraeus). X-ray photoelectron spectrum (XPS) and valence band X-ray photoelectron spectra (VBXPS) were obtained on a PHI-5000C VersaProbe system (UIVAC-PHI) with $\text{Al K}\alpha$ radiation. The Fourier transform infrared (FT-IR) experiment was acquired on a Nexus 870 spectrometer. ^{13}C cross-polarisation magic angle spinning nuclear magnetic resonance spectrum (^{13}C NMR) was recorded by a Bruker Avance 400 spectrometer at room temperature with a 4 mm triple resonance Bruker MAS probe spinning at 14 kHz. Electron paramagnetic resonance (EPR) spectrum was acquired using a JOEL JES-FA200 spectrometer. UV-vis diffuse reflectance spectrum (DRS) was taken on a Hitachi U-3010 UV-vis spectrometer. Dielectric constant was measured on an N5244A PNA-X microwave network analyzer. The Schottky curve was obtained on CHI 660E electrochemical workstation equipped with a standard three-electrode system (a platinum foil electrode as the counter electrode and an Ag/AgCl electrode as the reference electrode.). Time-resolved fluorescence decay spectrum was performed on an Edinburgh FLS920 spectrofluorometer with the excitation wavelength at 340 nm. Photoluminescence spectrum (PL) was measured on a jobinYvon SPEX Fluorolog-3-P spectroscopy. Photocurrent transient response was carried out on a CHI 660B electrochemical workstation in a standard three-electrode system under illumination using a 300 W Xe lamp.

2.3. Photocatalytic degradation of BPA

The photocatalytic activities of the samples were conducted by degradation of bisphenol A (BPA) under visible light irradiation. In a typical run, 0.02 g catalyst was added into 50 mL of 15 mg L^{-1} BPA solution in a quartz tube reactor at 25°C . The mixture was kept stirring in dark for 60 min to reach adsorption-desorption equilibrium before a 500 W Xe lamp was turned on. At given time intervals of irradiation, 2 mL of suspension was withdrawn and then filtered. The concentration of BPA was determined by high performance liquid chromatography (e2685, Waters) equipped with a UV-vis detector (2489, Waters).

2.4. Adsorption of BPA

20 mg of photocatalyst was added into 50 mL of BPA solution with initial concentration of 15 mg L^{-1} and kept stirring at 25°C

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