

Ozone treatment of graphitic carbon nitride with enhanced photocatalytic activity under visible light irradiation

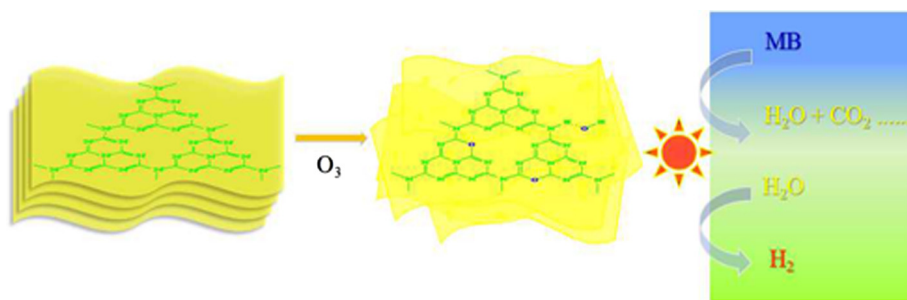


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GRAPHICAL ABSTRACT



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ABSTRACT

An efficient and stable catalyst with fragment-exfoliating structure was prepared by directly ozone treatment of bulk graphitic carbon nitride (g-C₃N₄). The photocatalytic performances of the as-prepared catalysts were evaluated by degradation of methylene blue (MB) and photocatalytic hydrogen evolution reaction under visible light irradiation. Compared with untreated g-C₃N₄, the ozone-treated g-C₃N₄ (OCN) exhibited almost 5 times higher photodegradation activity and 2 times H₂ evolution rate. The enhanced photocatalysis capability could be assigned to a narrowed band gap (2.62 eV), the increased defects and active sites, and the reduced recombination efficiency of photoinduced carriers in OCN. Furthermore, the photocatalytic mechanism in degradation process of MB was discussed and the hydroxyl radical and superoxide radical have proven to be the predominant active species. It is reasonable to believe that chemical modifying of catalysts through ozone treatment could efficiently regulate its catalytic activity.

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1. Introduction

With the increasing of environmental pollution issues and global energy demand, semiconductor-based photocatalysis has garnered widespread attention and become a hot topic [1–4]. It is considered to be a green, clean and promising technology which

relies on the inexhaustible sunlight and suitable photocatalysts. In order to take full advantage of the abundant visible light energy, much efforts have been made to develop visible-light-driven photocatalysts. Graphitic carbon nitride (g-C₃N₄), a new type metal-free layered semiconductor, has attracted intensive research interest and been extensively reported in the field of visible light photocatalysis in recent years [5–7]. Unlike metal-containing catalysts, g-C₃N₄ is mainly composed of carbon and nitrogen atoms which are low-cost and earth-abundant elements. It can be simply prepared via thermal condensation of appropriate nitrogen-rich

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precursors, such as melamine, urea, thiourea, cyanamide, guanidine hydrochloride and other s-triazine heterocyclic compounds [8]. Especially, due to intriguing electronic property, superior light trapping capability, as well as good thermal stability, g-C₃N₄ as an efficient visible light photocatalyst has been applied to the environmental contaminant removal [9–12], photocatalytic hydrogen evolution from water [13–15] and carbon dioxide (CO₂) photochemical reduction [16,17]. With the progressively serious water pollution issues, the photocatalysis utilizing visible light to degrade the toxic organic contaminant from wastewater was expected as a green and cleaning way for environmental remediation [18]. Similarly, the development of sustainable hydrogen energy also depends on effective photocatalysts.

Nevertheless, the high recombination rate of photogenerated electron-hole pairs in pristine g-C₃N₄ restricts its efficient utilization of visible light, thus attracting researchers make efforts to promote the photocatalytic performance of g-C₃N₄. Currently, various strategies have been developed, including nanostructure regulation [19,20], metal or nonmetal heteroatoms doping [10,17,21–23], coupling with other materials [24,25]. Among these approaches, chemical modification by oxidant is quite an effective method to modulate the photochemistry property of g-C₃N₄. Different oxidants such as H₂O₂ [26], H₂O [27], KMnO₄ + H₂SO₄ like Hummers method [28], and the mixtures of HNO₃ with H₂SO₄ [29] have been employed to oxidize, exfoliate, or cut the g-C₃N₄. The chemical modification process can regulate the electronic structure of g-C₃N₄, enlarge its surface area, and extend the visible light response [29–31]. More importantly, the fast separation rate of charge carriers could be achieved in catalyst after modification by oxidant, thereby resulting in the enhanced visible-light photocatalytic ability. Meanwhile, the chemical modification of g-C₃N₄ with different oxidant have a great impact on its composition and structure. The HNO₃ or H₂O₂ or KMnO₄ + H₂SO₄ mixture is liquid oxidant, while ozone is gaseous at room temperature with a better diffusivity. As one of the commonly used green oxidants, it has been customarily applied to various advanced oxidation technologies and photocatalysis coupling systems for wastewater treatment [32]. Ozone not only has a rather powerful oxidizability itself, but also produce oxidative species after decomposition. However, hitherto, using ozone as oxidizing agent to directly modify the photocatalytic behavior of g-C₃N₄ has not been reported to the best of our knowledge.

Herein, we developed a facile method to modulate the band gap and improve the photocatalytic performance of g-C₃N₄ via ozone treatment. The photocatalytic activity and photochemical stability of as-prepared catalysts were studied by decomposition of Methylene blue (MB) and photocatalytic hydrogen production under visible light illumination. It is worth noting that the ozone treatment exerted significant influence on the photocatalytic activity of g-C₃N₄. Consequently, OCN catalyst with enhanced photoactivity was obtained by ozone treatment for 1 h, showing a considerably fast degradation efficiency of MB and increased hydrogen production rate compared with untreated g-C₃N₄. And compared with some previously reported works, the active OCN catalyst also have a comparable photocatalytic capability. The enhancement of photocatalytic activity could be mainly ascribed to the narrowed band gap energy, adequate surface defects and slow recombination rate of carriers in catalyst. Moreover, the reactive species and degradation mechanism in the photocatalytic reaction were explored in detail.

2. Experimental

2.1. Materials and reagents

Melamine, Methylene blue (MB), Ethylenediaminetetraacetic acid disodium salt (EDTA-2Na) and Potassium iodide (KI) were

purchased from Chengdu Kelong Chemical Co. (Chengdu, China). *Tert*-butanol (tBA) and Triethanolamine (TEOA) were obtained from Tianjin Meilin trade limited Co. (Tianjin, China). All chemicals were of analytical grade and used as received without further purification. Deionized (DI) water produced by a DI water system (SZ-93, Shanghai Yarong Co. China) was used for all of the experiments.

2.2. Sample preparation

2.2.1. Synthesis of g-C₃N₄

The g-C₃N₄ was obtained by a polycondensation calcining method according to the literature [25]. In detail, 10 g melamine powder, which was put into an alumina crucible with a cover, was heated to 550 °C in a muffle furnace with a rising rate of 15 °C min⁻¹ and maintained for 4 h. Then the resultant products of pale yellow color were formed and collected after nature cooling to room temperature, denoted as g-C₃N₄.

2.2.2. Synthesis of OCNs

The OCNs (treated by ozone) were synthesized through a facile method by bubbling the gaseous ozone in g-C₃N₄ suspension solutions with ice-bath (Fig. S1). Meanwhile, the ozone was generated by an OZ-7G Ozone Generator and its remnant tail gas was absorbed by 2 wt.% KI solution to prevent air pollution. In a typical procedure, 0.2 g of as-prepared g-C₃N₄ was added in 80 mL DI water and ultrasonically dispersed for 2 h. The resulting suspension was subsequently transferred into an ice-bath with 80 vol.% ozone continuously bubble, and stirred for 0.5 h, 1 h, 2 h, 4 h and 6 h, respectively. Finally, the obtained samples were vacuum dried overnight at 80 °C and labeled as OCN-0.5 h, OCN-1 h, OCN-2 h, OCN-4 h and OCN-6 h on the basis of the ozone treatment time, respectively. For convenience, one of the best samples was renamed as OCN for the following characterization.

2.3. Characterization

X-ray powder diffraction (XRD) measurements were obtained by a XRD-6100 X-ray diffractometer (Shimadzu, Japan) equipped with Cu K α irradiation as source ($\lambda = 0.154$ nm). The morphology and microstructure of samples were performed by a high-resolution FEI Tecnai G20 transmission electron microscopy (TEM) operated at an accelerating voltage 200 kV and a NoVaTM Nano SEM 250 field emission scanning electron microscopy (SEM). UV-vis diffuse reflection spectra (UV-vis DRS) was taken on a Hitachi U-4100 UV/Vis/NIR spectrophotometer using BaSO₄ as the reference. X-ray photoelectron spectroscopy (XPS) was collected on a Thermo ESCALAB 250 XI instrument with Al K α radiation. Photoluminescence (PL) spectra were measured by a Hitachi F-7000 spectrophotometer with excitation wavelength of 365 nm, using a pulsed Xe arc lamp as illumination source. Elemental analysis (EA) and thermogravimetry (TG) were gained by a Flash EA 1112 elemental analyzer and a Shimadzu DTG-60H thermal analyzer, respectively. Fourier Transform Infrared spectroscopy (FTIR) was determined between 400–4000 cm⁻¹ by embedding samples in KBr pellets using a NEXUS 6700 spectrometer. The absorbance values of MB solutions during degradation process were tested by a Hitachi U-2900 UV-visible absorption spectrophotometer. The photocurrent and electrochemical impedance spectroscopy (EIS) experiments were carried out on a PGSTAT128N electrochemical workstation (Metrohm Autolab, China) with a standard three-electrode cell. Electron spin resonance (ESR) spectra technology was exploited to identify the type of active radicals. Signals of radical spin-trapped by 5,5'-dimethyl-1-pyrroline-*N*-oxide (DMPO) were examined with a Bruker mode ER200-SRC electron spin resonance spectrometer when the

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