



Surface hydroxylation of graphitic carbon nitride: Enhanced visible light photocatalytic activity

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ABSTRACT

To improve the photocatalytic activity of graphitic carbon nitride (g-C₃N₄), surface hydroxylation was employed as an efficient modification method. Characterizations were conducted to examine the formation of surface hydroxyl groups, including Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and diffuse-reflection spectroscopy (DRS). The improvement of photocatalytic activity brought by the surface hydroxylation modification was examined by measuring the degradation of *Rhodamine B* under visible light irradiation. Both theoretical and experimental explanations were given concerning the formation of photo-generated active radicals. This study sheds light on the benefits of surface hydroxylation modification, as well as on the differences in the roles of active radical species.

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1. Introduction

In recent years, environmental pollution as a result of uncontrolled usage of fossil fuel has become one of the major problems worldwide, and has in turn boosted the application of sustainable chemistry. The development of novel, environmentally-friendly chemical processes and catalysts are two factors that impact sustainable chemistry to a great extent [1–3]. Solid heterogeneous photocatalysts utilize light as the energy source, and may be conveniently recovered and recycled following usage, thus are good examples of the application of sustainable chemistry.

Owing to the lack of knowledge surrounding binary compounds consisted solely of carbon and nitrogen, carbon nitrides (CN_x), which are polymeric semiconductors, have drawn a considerable amount of attentions in recent years [4–8]. From the aspect of light absorption, nitrides should be better than the commonly studied oxide photocatalysts, due to smaller electronegativity of nitrogen and correspondingly smaller band gaps of nitrides [9,10]. In principle, all binary carbon-nitrogen compounds over a wide range of nitrogen-to-carbon atom ratios may be classified as carbon nitrides [8]. In this large system of compounds, carbon(IV) nitride, C₃N₄, stands out owing to the postulation that the β phase C₃N₄ (β-C₃N₄) has a bulk modulus close to that of diamond [11,12]. With

attractive properties such as a low compressibility [6,8], biocompatibility, and chemical as well as thermal endurance [13], C₃N₄ has become one of the most promising materials for energy conversion [14], hydrogen storage [15], and photocatalysis [3,7]. In all postulated C₃N₄ phases (e.g. α-, β-, cubic-, and graphitic- etc.), the graphitic-C₃N₄ (g-C₃N₄) structure based on heptazine (i.e. tri-*s*-triazine) units has lower energy than other phases [16]. The heptazine motif units have special electronic structures endowed by the hybridized nitrogen atom lone-pair states [17], and when the heptazine rings are connected via trigonal planar coordinated N atoms, π-conjugated planar layer structures can be formed [3,8,13]. The heptazine ring structure and the high degree of condensation endow g-C₃N₄ with an appealing electronic structure as well as both chemical and thermal endurance, along with a medium-valued band gap (~2.7 eV [7]), potentially making g-C₃N₄ a visible light responded photocatalyst.

The band position of g-C₃N₄ however, (with a valance band at ~1.58 V with respect to the standard hydrogen electrode (vs. SHE)) makes it incapable to generate highly oxidative holes as well as hydroxyl radicals, limiting its wide application in photocatalysis. There are a number of methods that could enhance the photocatalytic properties of g-C₃N₄, such as doping [18–23], constructing heterojunction [24–29] and modulating morphology [30–33].

In this work, attempt was made to enhance the visible light photocatalytic ability of g-C₃N₄ by means of simple surface hydroxylation modification without damaging the composite

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structure. In theory, surface hydroxyl groups can function as traps for photo-generated holes and in turn generate active surface bound hydroxyl radicals. Researches have previously been conducted concerning the enhancement of photocatalytic activity through surface hydroxylation method [34–38]. Generally, treatments with oxidizers will result in the generation of hydroxyl and carboxyl groups on the basal plane of carbon materials [39–42]. Considering that oxidants with too strong oxidability will destroy the special structure of $g\text{-C}_3\text{N}_4$ [43], a relatively mild oxidant, hydrogen peroxide, was used in this work. The photocatalytic activities of the surface-hydroxylated $g\text{-C}_3\text{N}_4$ (OH-g) were investigated through the degradation of Rhodamine B (RhB) as a target pollutant under visible light irradiation.

2. Experimental

2.1. Preparation of carbon nitride samples

Pristine $g\text{-C}_3\text{N}_4$ was synthesized by thermal decomposition (pyrolysis) of urea. Typically, 10 g of urea was placed in a 40 mL crucible with a cover (Fisherbrand, FB-965-F). The crucible was then placed in a muffle furnace (BF51748C-1, Thermo Electron Corporation) and heated to 550 °C for 2 h with a heating rate of 2 °C

per minute. The surface hydroxylation modification of $g\text{-C}_3\text{N}_4$ was performed by ultrasonically treating 0.2 g of the synthesized pristine $g\text{-C}_3\text{N}_4$ with 30 mL of hydrogen peroxide (H_2O_2) of different concentration (0, 10, 20 and 30 wt%) in an ultrasonic cleaner (FS20, Fisher Scientific) for 1 h. After the ultrasonic treatment, the sample was filtered and dried at 60 °C for 24 h. The samples were then labelled as $\text{OH}_0\text{-g}$, $\text{OH}_{10}\text{-g}$, $\text{OH}_{20}\text{-g}$, and $\text{OH}_{30}\text{-g}$, with the subscripted number referring to the concentration of H_2O_2 .

2.2. Characterization

The Fourier transform infrared (FTIR) transmission spectra were measured on an Agilent FTIR spectrometer (Cary 630, Agilent Technologies). The crystal structures of the pristine sample and surface-modified sample were characterized by X-ray power diffraction (XRD) with a $\text{Cu-K}\alpha$ radiation diffractometer at 40 kV and 44 mA recorded with 2θ scope ranging from 5 to 90°. The surface chemical states of the sample were analyzed by an XSAM-800 X-ray photoelectron spectrometer (XPS). Ultraviolet-visible (UV-vis) diffuse reflectance spectra (DRS) were measured on a UV-vis spectrophotometer (Thermo Evolution 300) equipped with

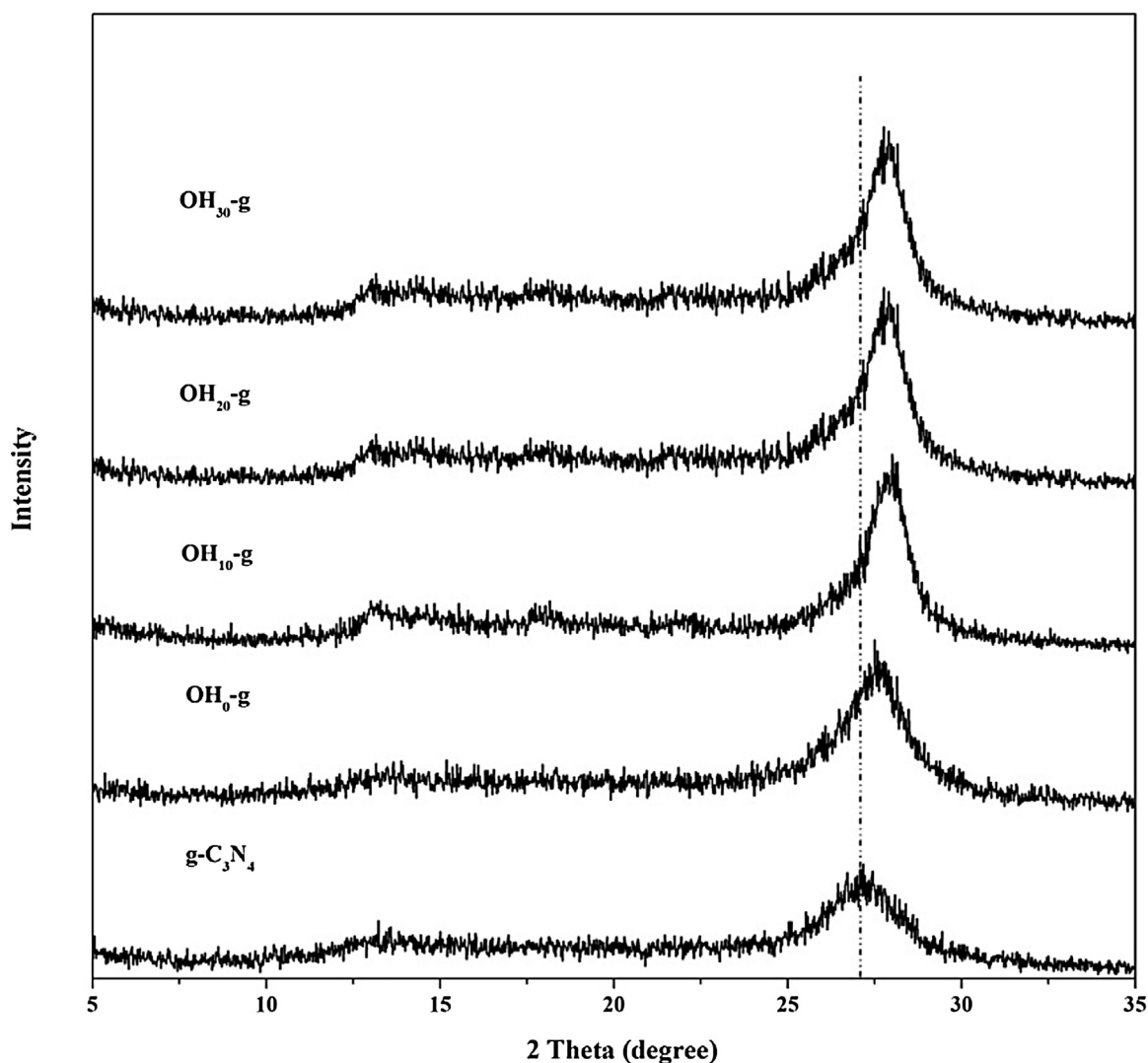


Fig. 1. XRD patterns of pristine $g\text{-C}_3\text{N}_4$ and OH-g samples.

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