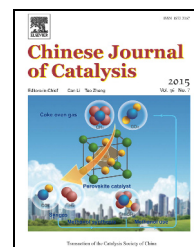


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## Article

# Simple synthesis of g-C<sub>3</sub>N<sub>4</sub>/rGO hybrid catalyst for the photocatalytic degradation of rhodamine B

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## ABSTRACT

A hybrid catalyst of g-C<sub>3</sub>N<sub>4</sub> (graphitic carbon nitride)/rGO (reduced graphene oxide) was prepared by directly heating a mixture of melamine and GO in air. g-C<sub>3</sub>N<sub>4</sub> in the hybrid retained the structure of pristine g-C<sub>3</sub>N<sub>4</sub>, and the heterojunction between g-C<sub>3</sub>N<sub>4</sub> and rGO was formed by  $\pi$ - $\pi$  interaction. The highest photocatalytic efficiency for the degradation of rhodamine B (RhB) was with the melamine/GO mass ratio of 800/1, with a first order rate constant 2.6 times that of pristine g-C<sub>3</sub>N<sub>4</sub>. The enhanced photocatalytic activity was assigned to the rGO-promoted separation of photo-generated electron (e<sup>-</sup>)-hole (h<sup>+</sup>) pairs. In addition, the photocatalytic activity of g-C<sub>3</sub>N<sub>4</sub>/rGO was pH sensitive with a much increased photodegrading rate at low pH values. The first order rate constant was 8.6 times that of pristine g-C<sub>3</sub>N<sub>4</sub> at pH = 1.98. The pH sensitive behavior resulted from the promoted oxidation of h<sup>+</sup> with RhB by the consumption of e<sup>-</sup> with the reaction of proton (H<sup>+</sup>) in which rGO acted as a good platform for transferring e<sup>-</sup> through its atomic sheets.

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## 1. Introduction

Graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>), a non-metal semiconductor consisting of only carbon and nitrogen, has attracted interest in the photocatalysis field [1–6]. Its band gap is 2.7 eV, which is much smaller than that of TiO<sub>2</sub> (3.2 eV) [7]. So, compared to TiO<sub>2</sub>, g-C<sub>3</sub>N<sub>4</sub> can absorb visible light, and its electrons can be excited from the valence band (VB) to the conduction band (CB) under visible light irradiation. Apart from its excellent sunlight harvesting ability, g-C<sub>3</sub>N<sub>4</sub> is very stable under irradiation even in acid and base solutions, which makes it a good photocatalyst in various hazardous environments [3–6].

However, the high recombination rate of the photo-generated e<sup>-</sup>-h<sup>+</sup> pairs limits its practical applications. Many modifica-

tion methods have been tried to improve its photocatalytic activity, such as physical coupling [8,9], chemical doping [10,11], microstructural shaping [12–15] and surface modification [16]. Among these methods, physical coupling is very effective and easy to perform. Due to the different potential levels of the CB and VB in the two different coupling materials, the photo-generated e<sup>-</sup> and h<sup>+</sup> of g-C<sub>3</sub>N<sub>4</sub> can be separated efficiently at the heterojunction, giving rise to enhanced photocatalytic activity. The materials chosen for the counterparts can be divided into four classes: metal sulfide or oxide (e.g., CdS [17] and TiO<sub>2</sub> [18]), noble metals (e.g., Au [19]), polymers (e.g., P3HT [20] and PANI [9]), and graphene-based materials (e.g., reduced graphene oxide (rGO) [8,21–25], GO [26] and carbon nanotubes [27]).

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Graphene or rGO is a very good candidate for the coupling because g-C<sub>3</sub>N<sub>4</sub> and graphene are both 2D materials, and the atomic sheets of graphene can facilitate electron transfer. g-C<sub>3</sub>N<sub>4</sub>/rGO has been synthesized from the molecular-level mixture of urea/GO [8], cyanamide/GO [21,22], dicyandiamide/GO [23], and melamine/GO [24,25]. The heterojunction between g-C<sub>3</sub>N<sub>4</sub> and rGO is formed by N bridging [8,23], O bridging [21], or van der Waals  $\pi$ - $\pi$  stacking [25]. The introduction of rGO has led to increased photocatalytic activity [21–25]. However, all these coupling processes use a non-oxygen environment to make the hybrid, such as N<sub>2</sub> [22,25], Ar [8,21,23], H<sub>2</sub> [24] or hydrazine hydrate environment [25]. This is because GO can be reduced to rGO at high temperature in an inert or reductive atmosphere [28], which generally needs a complicated fabrication process.

GO itself is effective in modifying the photocatalysis of g-C<sub>3</sub>N<sub>4</sub> when overlaid on the surface of g-C<sub>3</sub>N<sub>4</sub> as a GO/g-C<sub>3</sub>N<sub>4</sub> hybrid [26], even though the mechanism is not very clear. So, it may not be necessary to use a non-oxygen environment to fabricate the hybrid. That is, a g-C<sub>3</sub>N<sub>4</sub>/rGO hybrid can be prepared with the existence of oxygen, e.g., in air. On the one hand, g-C<sub>3</sub>N<sub>4</sub> has been polymerized in air and it showed increased photocatalytic activity due to the increased specific surface area [29]. On the other hand, GO can be reduced in air in some mixtures, as reported in our previous experiments [30]. During the heat treatment in air, GO is oxidized and splits into smaller unit, some down to the quantum dot level. The high temperature makes the major contributions to the removal of the epoxy, carbonyl and carboxyl groups, leading to a partially or fully reduced GO, *i.e.*, rGO. Local reductive gases, such as the released NH<sub>3</sub>, also contribute to the reduction [30].

In this work, we carried out a simple method to fabricate a g-C<sub>3</sub>N<sub>4</sub>/rGO hybrid by directly heating a mixture of melamine/GO in air. The chemical microstructure of the hybrid, photocatalytic performance for the degradation of rhodamine B (RhB), pH-response behavior, and the photocatalytic mechanism were studied. The hybrid showed much increased photocatalytic performance in acidic conditions under visible light irradiation.

## 2. Experimental

### 2.1. Preparation of the hybrid catalysts

GO dispersion was performed according to the modified Hummers method [27,29]. One gram of graphite and 6 g of KMnO<sub>4</sub> were put into a solution composed of concentrated H<sub>2</sub>SO<sub>4</sub> (120 mL) and H<sub>3</sub>PO<sub>4</sub> (13.3 mL). After 18 h under vigorous stirring at 50 °C, the mixture was cooled to room temperature. This was followed by adding some H<sub>2</sub>O<sub>2</sub> to react with the residual KMnO<sub>4</sub>. After filtration and washing, most of the acid and ions were removed. The GO was re-dispersed in water and dialyzed by dialysis bags of 8000–14000 D<sub>a</sub> to remove acid and ions completely.

Four grams of melamine and an amount of GO dispersion were mixed and put into deionised water. After vigorous stirring and oven drying, a grey melamine/GO mixture was ob-

tained. The mixture was put into a crucible and heated to 550 °C for 1 h in air. The g-C<sub>3</sub>N<sub>4</sub>/rGO hybrid was obtained after grinding and denoted as g-C<sub>3</sub>N<sub>4</sub>/rGO-*x*, where *x* means the mass ratio of melamine/GO. Pristine g-C<sub>3</sub>N<sub>4</sub> was prepared in a similar procedure using only melamine. rGO was prepared by heating GO under the same heating conditions.

### 2.2. Characterization of the hybrid catalysts

Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on a Bruker TENSOR-27 Fourier transform infrared spectrophotometer. The crystalline structure was investigated by X-ray diffraction (XRD) on a D8 ADVANCE instrument using Cu K $\alpha$  radiation. The scanning electron micrographs (SEM) were obtained on a JSM-6700F microscope. Transmission electron microscopy (TEM) images were obtained by a JEM-2100F electron microscope at an acceleration voltage of 200 kV with a CCD camera. X-ray photoelectron spectroscopy (XPS) was performed using a K $\alpha$  1063 instrument with focused monochromatized Al K $\alpha$  radiation. UV-Vis diffuse reflectance spectra (DRS) were obtained on a HITACHI U4100 spectrophotometer using BaSO<sub>4</sub> as the reference. The BET specific surface area ( $A_{\text{BET}}$ ) was determined by N<sub>2</sub> adsorption isotherm measurement at -196 °C on a Micromeritics ASAP 2010 system. Photoluminescence (PL) spectra in reflectance mode were recorded using an FL-3 transient fluorescence spectrometer. The dried sample was pressed into a solid state powder film with a relatively uniform thickness more than 1.0 mm.

### 2.3. Photocatalytic activity measurement

The photocatalytic activity of the as-synthesized samples was evaluated by the degradation of RhB under a 350 W Xe Lamp (XD350W-I, Changzhou Siyu Environmental Sci-Tech Co., Ltd.) with a 400 nm cut off filter. A photocatalyst sample (100 mg) was added into a 100 mL aqueous solution of RhB (10 mg/L). Prior to irradiation, the suspension was treated using ultrasound in the dark for 30 min to achieve adsorption-desorption equilibrium. A 350 W Xe Lamp was used as the visible light source to perform the photocatalytic experiment. During the degradation of RhB, 5 mL samples were taken out and centrifuged to remove the solid particles for analysis. The concentration of aqueous RhB was determined using a UV-vis spectrophotometer (SHIMADZU UVmin-1240) at 552.0 nm by measuring its absorbance. The RhB concentration was calculated by the Lambert-Beer equation. The photodegradation of RhB under visible light irradiation in the absence of the photocatalyst was also evaluated.

## 3. Results and discussion

### 3.1. Chemical and microstructural analysis

The chemical and crystalline structures of as-synthesized rGO, g-C<sub>3</sub>N<sub>4</sub>/rGO and g-C<sub>3</sub>N<sub>4</sub> were studied first. The FT-IR spectra and XRD patterns are shown in Fig. 1. In the FT-IR spectrum of rGO shown in Fig. 1(a), there are no obvious absorption

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