

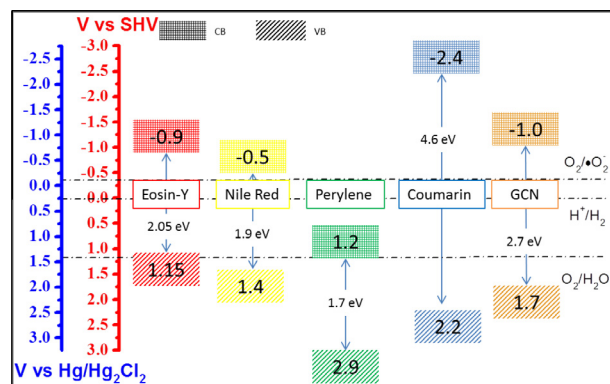
Integrated oxygen-doping and dye sensitization of graphitic carbon nitride for enhanced visible light photodegradation



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ABSTRACT

Graphitic carbon nitride (GCN) is a promising metal-free photocatalyst while suffering from low charge mobility induced inefficient photocatalysis. In this work, oxygen doping was employed to enhance the photodegradation of organic pollutants in water on graphitic carbon nitride (GCNO) under visible light. For further absorption extension, four organic dyes (Eosin-Y, Perylene, Nile-red and Coumarin) were adopted to dye-sensitize the GCNO photocatalyst. It was found that O-doping can promote dye sensitization, which was dependent on the type of dyes and influenced the photodegradation efficiencies of methylene blue (MB) and phenol. Nile-red sensitized GCNO presented the best activity in MB degradation under $\lambda > 480$ nm irradiations while Eosin-Y showed the best sensitization performance for phenol degradation under $\lambda > 420$ nm light source. However, dye sensitization was not effective for enhanced pollutant degradation on GCN without O-doping. UV-vis diffuse reflectance spectra (UV-vis DRS), photoluminescence (PL) spectra, and photocurrent analyses were applied to investigate the mechanism of carriers' transfer, which indicated that dye molecules could inject extra electrons into GCNO energy band and the energy dislocation could suppress electron/hole recombination, enhancing photocatalytic performances.

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1. Introduction

In the 21st century, it has been a big challenge to explore renewable energy to replace traditional fossil fuels because of the

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over-depletion and numerous environmental issues associated with fuel combustion. Since the discovery of hydrogen production by photoelectrochemical water splitting in 1972 [1], semiconductor-based photocatalysis has been widely devoted to the new energy innovation. However, until now there is no such a semiconductor ideally balancing the low cost, high activity, high sunlight harvest and satisfactory chemical stability [2–4]. Recently, graphitic carbon nitride (*g*-C₃N₄, GCN) has been considered as a metal-free, photosensitive semiconductor, which can be adopted in photoelectrochemical applications, because it is chemically stable, environmentally benign, and has suitable band gap energy for visible light absorption [5]. GCN-based materials have demonstrated great potential in hydrogen production from water splitting [6,7], photodegradation of gaseous or liquid pollutants [8–10], electrochemical fluorescence sensors [11,12], and electrode materials for fuel cells or batteries [13,14]. But GCN has a limited light absorption and low photocatalytic efficiency due to the high recombination rate of photo-excited electron/hole pairs, which becomes the main barricade to practical photocatalytic application [6,15,16]. Many methods have been developed for modification of GCN to overcome the limitation, such as improved textural porosity [17,18], heteroatom doping [19–21], semiconductor coupling [22,23], and activating [6,8]. Among the modifications, oxygen doping is able to enlarge the porosity, increase light absorption, and reduce the carrier recombination. Moreover, O-doped GCN could be easily prepared from mild hydrothermal treatment with H₂O₂, making the O-doped GCN a promising future in fabrication of solar energy devices [24–27]. But it still suffers from a high disparity of quantum yield compared to classical metal-based photocatalysts (such as TiO₂ and ZnO).

Today, dye sensitization technology is being widely utilized in fabrication of photovoltaic devices, namely low-cost but commercially feasible solar cells. Dye photosensitization can extend the light absorption range, enhance photon harvesting efficiency, provide extra excited electron pairs from a dye and accelerate charge transfer, leading to a high efficiency of photoelectric conversion [28]. TiO₂ semiconductor film was successfully grafted with a dye, RuL₂(μ – (CN)Ru(CN)L'₂) (where L represented 2,2'-bipyridine-4,4'-dicarboxylic and L' is 2,2'-bipyridine) and the derived photovoltaic system showed a higher proration solar energy harvesting (46%), and a high photo-generated electrical current (80% higher than TiO₂) [29]. Recent studies revealed that organic dye molecules with a porphyrin core and alternative π-system have a good ability in photosensitization [30–33]. In GCN studies, Eosin-Y sensitized, Pt doped mesoporous *g* – C₃N₄ showed a good activity in H₂ generation. Eosin-Y assistance not only extended the light absorption but also improved the apparent quantum efficiency at 19.4% [34]. Erythrosin B sensitized, Pt doped *g* – C₃N₄ nanosheets were reported to present 7.1 times higher activity in photocatalytic H₂ generation [35]. However, the photocatalytic activity highly depends on *g* – C₃N₄ textural properties and metal co-catalyst [36–38], and there are no reports on dye sensitized only with a high activity.

In this study, we present an investigation on the synergistic effect of oxygen doping and dye sensitization on GCN for photocatalysis. Oxygen doped GCN (GCNO) catalysts sensitized by several cooperative asymmetric organophotoredox organic dyes, Eosin-Y, Perylene, Nile Red and Coumarin, were prepared and found to exhibit high activities in methylene blue (MB) and phenol photodegradation under visible light irradiations. Nile-Red effectively enhanced the light harvesting of GCNO with the highest activity in MB degradation while Eosin-Y grafted GCNO demonstrated the best activity in phenol degradation. The photosensitization mechanism was studied by UV–vis diffuse reflectance spectra (DRS), photoluminescence (PL) spectra analysis, and photocurrent analysis.

2. Experimental section

2.1. Materials

All chemicals utilized in this study are of analytical grade. Melamine, Nafion, Eosin-Y, Perylene, Nile Red and Coumarin were supplied by Sigma-Aldrich. Hydrogen peroxide (30 wt%), methylene blue, acetone, sodium sulfate and phenol were obtained from Biolab, Australia.

2.2. Preparation of GCNO and dye sensitized GCNO

Oxygen doped graphitic carbon nitride (GCNO) was synthesized by a hydrothermal treatment of GCN with hydrogen peroxide (30 wt%). Firstly, 10 g melamine was put in a 20 mL alumina crucible with semi-covering. Then the precursor in the crucible was heated in a muffle furnace at 400 °C for 2 h and then heated at 520 °C for another 2 h with a heating rate of 1 °C/min. The well grinded yellow product was referred as GCN. Secondly, 1 g GCN was mixed with 50 mL hydrogen peroxide solution in a 120 mL Teflon-lined stainless steel autoclave with vigorously stirring for 30 min. After that, the autoclave was sealed and put into an oven for a hydrothermal treatment at 130 °C for 12 h. The product was named as GCNO. For dye sensitization, 0.5 g GCNO was mixed with 30 mL acetone and 2 mg dye (Eosin-Y, Perylene, Nile Red and Coumarin), and then the suspensions were vigorously stirred for 3 h and dried at 100 °C for 12 h. The Eosin-Y, Perylene, Nile Red and Coumarin grafted products were labelled as GCNO-E, GCNO-P, GCNO-N and GCNO-C, respectively. The structures of the dyes are presented in Fig. S1 (SD).

2.3. Preparation of working electrodes

An ITO conductive glass (Sigma-Aldrich) with 8 Ohm resistance was cut into 2 × 1 cm² dimension as a working electrode substrate. Before coating samples, the ITO surface was cleaned by ethanol, acetone, and isopropanol successively, and then dried by argon flush. One side of ITO slice (1 × 1 cm²) was covered with copper wire and heat conductive and electrical insulated adhesive, and the other side was coated with catalyst particle suspensions. The suspension was obtained from 40 mg particle sample, 5 mL Nafion, and 200 mL ethanol with 2 h sonication treatment. The slurry suspension was gradually dropped on the 1 cm² substrate and dried at 110 °C for 3 h.

2.4. Evaluation of photocatalytic performance

Photocatalytic performances of dye sensitized GCNO catalysts were evaluated by the photodegradation of MB and phenol solutions under λ > 480 and λ > 420 nm visible light irradiations, respectively. In a typical process, 10 mg/L, 200 mL MB solutions (or 10 mg/L, 200 mL phenol) and the photocatalysts (100 mg) were mixed in a 1 L double-jacket cylindrical reactor with water cycling at 25 °C, under a constant stirring of 350 rpm. Two light sources were applied in this study: λ > 420 nm (the photon intensity were 0.01, 9.24, 84.1 × 10³ μW/cm² in 220–280, 315–400, 400–1050 nm) and λ > 480 nm (the photon intensity were 0, 0.24, 60.5 × 10³ μW/cm² in 220–280, 315–400, 400–1050 nm), by light cut-off filters from a MSR 575/2 metal halide lamp (575 W, Philips). The light was positioned 30 cm away from the reactor. The reaction was initiated by switching on the lamp. At certain time intervals, the reaction solution was withdrawn by a 5 mL syringe. MB would be analyzed by a JASCO UV–vis spectrophotometer at a wavelength of 664 nm. Phenol solution was analyzed by an

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