In situ fabrication of reduced graphene oxide/mesoporous g-C$_3$N$_4$ nanosheets with excellent visible light activity

Ying Yang*, Harui Zhao, Hongfei Yang, Ping Qiu**, Biao Zhou, Na Zhang

State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Changping, Beijing 102249, China

ARTICLE INFO

ABSTRACT

Severe energy shortage and environmental pollution prompt researchers to develop metal-free semiconductors as high-performance photocatalysts for wastewater treatment. Herein, highly efficient visible light-driven photocatalysts, reduced graphene oxide/mesoporous g-C$_3$N$_4$ (rGO/mpg-C$_3$N$_4$) nanosheets are *in situ* fabricated by surfactant-directed assembly of graphene oxide and melamine *via* an evaporation-induced self-assembly approach before a solid-state transformation. The mass ratio of rGO to mpg-C$_3$N$_4$ in final nanosheets is tailored in a wide range of 1–76%. All rGO/mpg-C$_3$N$_4$ nanosheets are covalently linked, highly porous, display improved separation of electron-hole pairs, narrowed bandgap and modulated band structure. And they are superior to Degussa's P25 and g-C$_3$N$_4$ in the degradation of methylene blue under visible light irradiation. The elaborately fabricated rGO/mpg-C$_3$N$_4$-15% gives the highest specific rate constant ($1.005\,min^{-1}\,g^{-1}$) of any g-C$_3$N$_4$ composite catalyst. Mechanism study reveals that the best performance is originated from the increased h$^+$ and $\cdot^-$O$_2$ species, linking to the strong interaction between rGO and mpg-C$_3$N$_4$. Mesostructure and proper rGO ratio, and their ensemble effect, are also responsible for the best activity, since merits including superior mass transfer, improved charge carrier separation and excellent visible light utilization are integrated.

1. Introduction

In recent years, energy shortage and environmental pollution have stimulated the study of photocatalytic technology through semiconductors for the degradation of organic pollutants in wastewaters [1]. A polymeric organic semiconductor, graphitic carbon nitride (g-C$_3$N$_4$), has been widely used as the photocatalyst in water splitting, pollutant degradation and selective oxidation, and also used for fuel cell and solar fuel production [2]. Unlike metal oxide-based photocatalysts that need expensive metal salts for synthesis [3], cheap nitrogen-rich precursors are involved in the synthesis of g-C$_3$N$_4$ *via* a simple polymerization process. The resulting metal-free photocatalyst holds high thermal and chemical stability, and has a small bandgap for visible light response. However, the activity of pure g-C$_3$N$_4$ is rather low owing to the severe recombination of electron-hole pairs, low efficiency of visible light utilization, and small surface area and porosity, and thus its further application is restricted.

In this regard, strategies including heteroatom-doping [4], morphology-tailoring [5] and heterostructure-constructing [6] have been employed to improve the charge carrier separation, adjust the bandgap, and modulate the electronic structure of g-C$_3$N$_4$. In particular, there is a growing interest in combining g-C$_3$N$_4$ with carbonaceous materials because the charge mobility can be largely enhanced in the presence of graphite, carbon nanotube, graphene or C$_{60}$ [7–16]. Besides superior electronic property, graphene oxide (GO) and partially reduced GO (rGO) provide additional oxygen-containing groups, which make them hydrophilic and sensitive under visible light irradiation, and render them the most compatible materials for building hybrids with g-C$_3$N$_4$. Ye and coworkers pioneered this research by thermal conversion of mixture of GO and dicyandiamide to give rGO/g-C$_3$N$_4$ layered intercalation, which shows the enhanced photocurrent [17]. By combining GO with g-C$_3$N$_4$ *via* a sonochemical approach, the GO/g-C$_3$N$_4$ nanosheet was fabricated and displays the enhanced photocatalytic capability in the degradation of rhodamine B [18]. However, the bandgap and valence band edge of GO/g-C$_3$N$_4$ changed little owing to the noncovalent interaction between GO and g-C$_3$N$_4$. Alternatively, the crosslinked g-C$_3$N$_4$/rGO nanosheet was constructed by conversion of mixture of GO and cyanamide. By varying the dosage of GO, the bandgap and band structure were tailored, and the catalytic performance was improved towards photocatalytic degradation of RhB and 4-nitrophenol under visible light irradiation [19]. Nevertheless, it is noteworthy that the porosity and surface area of the resultant composites are extremely

low by combining GO (rGO) with g-C$_3$N$_4$. Even if the large surface graphene ($\sim$2600 m^2 g^{-1}) was introduced, the porosity and surface area of the resultant graphene/g-C$_3$N$_4$ composite are no more than 25% and 30 m^2 g^{-1}, respectively [20]. The textual porosity of g-C$_3$N$_4$ hybrids can hardly be improved since the GO, rGO and graphene are inclined to aggregate irreversibly, making most pores and surfaces inaccessible. Despite of this, there is growing interest to fabricate highly porous, covalent-linked rGO/g-C$_3$N$_4$ composite, which could facilitate the mass transfer, and thus improve the photocatalytic activity. However, construction of highly efficient visible-light-driven rGO/g-C$_3$N$_4$ photocatalyst with high porosity and tailored structure remains challenging.

It is considered that the porous nature could enhance the photocatalytic capability of g-C$_3$N$_4$ by providing more photogenerated holes and active sites [21]. Porous g-C$_3$N$_4$ with a high surface area of 201–209 m^2 g^{-1} shows a ten times enhanced activity for methyl orange degradation under visible light irradiation [22], whereas, the role of pore arrays remains unclear. Even so, feature-ordered and morphology controlled g-C$_3$N$_4$ has been widely fabricated by a templating strategy. In comparison with the tedious and expensive nanocasting synthesis [23–25], a soft-templating approach is characterized by producing mesoporous g-C$_3$N$_4$ (mpg-C$_3$N$_4$) through one-pot conversion of N-rich precursor-surfactant supramolecular aggregates owing to their difference in chemical and thermal stability [26–28]. Inspired by this, one-pot transformation of N-rich precursor-surfactant-GO aggregates would be the solution to fabricate highly porous, covalent-linked rGO/g-C$_3$N$_4$ composite.

Herein, we report a series of highly efficient visible light-driven rGO/mpg-C$_3$N$_4$ nanosheets *in situ* fabricated by evaporation-induced self-assembly (EISA) of melamine, cetyltrimethyl ammonium bromide (CTAB) and GO before pyrolysis at 550 °C. Specifically, mesostructured melamine-CTAB-GO aggregates were constructed first, induced by the hydrogen bond between GO and melamine, as well as their electrostatic interaction with CTA$^+$. The following pyrolysis a unique "one stone, three birds" strategy to carbonize melamine, remove CTAB and reduce GO in a single step, yielding highly porous, covalently linked rGO/mpg-C$_3$N$_4$ nanosheets (Scheme 1). The mass ratio of rGO to mpg-C$_3$N$_4$ in the final nanosheets is tailored in a wide range of 1 ~ 76%. All rGO/mpg-C$_3$N$_4$ nanosheets are covalently linked, highly porous, display improved separation of electron-hole pairs, narrowed bandgap and modulated band structure. And they are superior to Degussa's P25 and g-C$_3$N$_4$ in the degradation of methylene blue under visible light irradiation. The elaborately fabricated rGO/mpg-C$_3$N$_4$-15% gives the highest specific rate constant (1.005 min^{-1} g^{-1}) of any g-C$_3$N$_4$ composite catalyst.

2. Experimental

2.1. Preparation of rGO/mpg-C$_3$N$_4$ nanosheets

The rGO/mpg-C$_3$N$_4$ nanosheets were synthesized using CTAB as the surfactant, melamine as the nitrogen-rich precursor, and graphene oxide (Supporting information) as the reduced form precursor. The

molar ratio of the precursor gels used in the preferred preparation is: 0.12 CTAB: 8.0 NH$_3$ (25 wt%): 114 H$_2$O: 10 EtOH: 0.28 melamine: x GO, where x represents the GO molar proportion in the synthetic mixture, and was set to be 0, 0.01, 0.02, 0.07, 0.18 and 0.36. Typically, 0.5 g of CTAB was dissolved in 31.8 mL aqueous solution containing 18.0 mL of deionized water, 6.8 mL of ammonia and 7 mL of ethanol. Under a constant agitation, 0.4 g of melamine combined with certain amount of GO aqueous solution (1 mg mL^{-1}) was introduced and the resulting mixture was stirred at room temperature for 0.5 h. And then the mixture was heated at 60 °C until completed removal of liquid, yielding gray supramolecular aggregates with different amount of GO. Then the dried products were heated to 350 °C with a rate of 2 °C min^{-1} in N$_2$ flow and kept for 0.5 h, and then were heated up to 550 °C with a rate of 5 °C min^{-1} and kept for 4 h, yielding a series of nanosheets denoted as rGO/mpg-C$_3$N$_4$-n. Here n was defined as the weight ratio of rGO to mpg-C$_3$N$_4$, which was estimated based on the product yield by assuming that the rGO weight in the composite equals to the initial GO amount. The value of n is 0, 1, 3, 15, 36 and 76%, corresponding to 0, 1.2, 3.0. 10.0, 25.0, 50.0 mg of GO used in the synthetic mixture, respectively. g-C$_3$N$_4$ and rGO/mpg-C$_3$N$_4$-15%-p are also prepared for compasion (Supporting information).

2.2. Synthesis of g-C$_3$N$_4$

A 3 g portion of melamine was transfer into a crucible with the cover and heated directly in N$_2$ flow as the procedure mentioned above, yielding g-C$_3$N$_4$.

2.3. Photocatalytic reactions

The photocatalytic activity was evaluated by the decomposition of methyl blue (MB) under visible light irradiation (> 420 nm). Visible irradiation was obtained from a 500 W Xe lamp (Perfect Light, PLS-SXE300C) with a 420 nm cut-off filter, and the average visible light intensity was 180 mW cm^{-2}. 20 mg of photocatalyst was dispersed in an aqueous solution of MB (100 mL, 10 mg L^{-1}) in Pyrex double-jacket reactor. Prior to irradiation, the suspension was magnetically stirred in dark for 30 min to get absorption-desorption equilibrium between the photocatalyst and MB. And then the light was on, of which distance from the surface of solution was set to be 10 cm, and the temperature was mentained at 25 °C. At certain time intervals, 4 mL of aliquots was sampled and centrifuged to remove the particles. The concentration of MB was analyzed by recording the absorbance at the characteristic band of 665 nm using a UV–vis spectrophotometer (PC-745). The photocatalytic degradation efficiency (E) of MB was obtained from the following formula:

$$E = (1 - C/C_0) \times 100\% = (1 - A/A_0) \times 100\%$$

and calculated from C_t/C_0, measured from the relative intensity of absorbance (A_t/A_0) at 665 nm, where C_0 and C_t are the MB concentration at time t and 0, respectively. After the reaction was completed, the spent photocatalyst was washed and dried before next run.
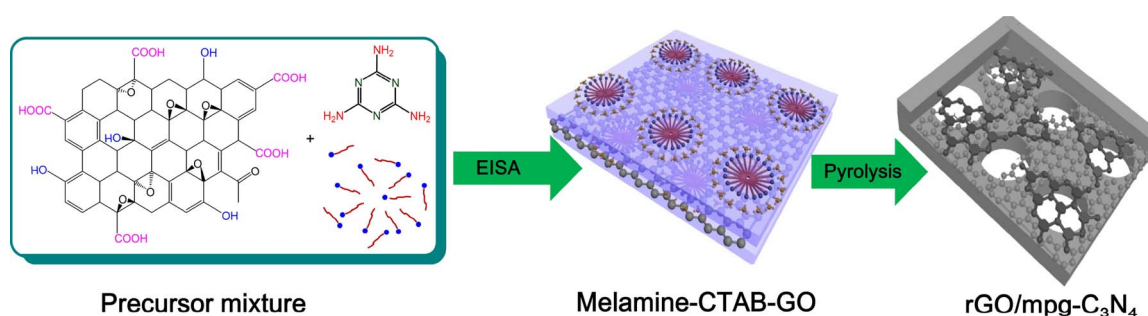
Scheme 1. The overall sketch for preparing rGO/mpg-C$_3$N$_4$ nanosheets by a self-assembly approach before pyrolysis.