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# An efficient method for assembling layered g-$C_3N_4$ nanosheets grow on 1D pore channels carbon fibers as a composite photocatalyst by ultrasound-assisted exfoliation and hydrothermal method

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## ABSTRACT

A composite catalyst that layered graphite carbon nitride (g-$C_3N_4$) nanosheets adhered on electrospun carbon fibers (CFs) carrier was prepared, and this catalyst occupied the efficient photocatalytic activity. The carbon fiber was obtained through electrospinning technology and high-temperature calcination process. The layered g-$C_3N_4$ nanosheets was derived through the direct heating and ultrasonic exfoliation. After that, the g-$C_3N_4$/CFs were successfully synthesized in the hydrothermal process. In the process of degradation, composites had the capacity of degradation to different organic dyes under the UV-light irradiation, meanwhile, catalyst had excellent capacity of adsorption and a certain recycling performance. Thus, g-$C_3N_4$/CFs catalyst has potential appliance value in the degradation of organic pollutants.

## 1. Introduction

As the environment pollution is more serious, photocatalysis technology plays a great role in the field of environmental purification. Semiconductor photocatalysis has been widely recognized as a potential material with great promise because of its outstanding properties, which solved the problems of environmental pollution [1–5]. In the past few decades, titanium dioxide ($TiO_2$) has been regarded as one of the most promising semiconductor materials for its superior characteristics such as high activity, physical and chemical stability, low cost and nontoxicity [6–8]. But the wide band gap of $TiO_2$ and the fast recombination of photogenerated charges hindered the practical application of $TiO_2$ [9].

Recently, a promising photocatalyst has attracted considerable attention. A novel semiconductor material graphitic carbon nitride (g-$C_3N_4$) with some remarkable properties such as metal-free, suitable bandgap (2.7 eV) and high activity under the light irradiation has been proposed to be utilized in environment purification including air purification and waste water remediation [10–12]. Wang and his co-workers [13] reported firstly that polymeric carbon nitride could produce hydrogen from water under visible-light irradiation in the presence of a sacrificial donor. However, the rapid expansion of pure bulk g-$C_3N_4$ prepared by direct high temperature thermopolymerization of appropriate precursors has been hindered by many disadvantageous factors including its low quantum efficiency, low surface area, and rapid recombination of the photogenerated charges [14,15]. To solve these existing problems, the various of methods for exfoliating g-$C_3N_4$ nanosheets [16–19] have been proposed. Niu and her co-workers [18] obtained g-$C_3N_4$ nanosheets with a thickness of around 2 nm easily by a simple top-down strategy that thermal oxidation etching of bulk g-$C_3N_4$ in air. Exfoliation of layer could enlarge the surface area and make it more evenly dispersed [21], so layered nanosheets acquired by ultrasonic-assisted exfoliating have been regarded as an excellent photocatalysis for their small thickness and high surface area [18,20].

In the era of vigorously promoting the concept of sustainable development, the recovery and reuse of energy and materials have become the focus of scholars' attention, and it has become one of the standards for evaluating the performance of catalysts. However, the existence form of pure g-$C_3N_4$ was powder so that recycling of g-$C_3N_4$ became an urgent problem to be solved. Herein, to separate g-$C_3N_4$ from solution phase, fixing g-$C_3N_4$ on a supporting material has been a popular means. Among a variety of novel materials, high surface area, high porous volume and fast adsorption rates of

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carbon fibers made them occupy a more significant position during a long period compared to those conventional supporting materials [22–24]. Electrospun carbonized fibers as one-dimensional carbon materials have following advantages. Firstly, electrospun carbon fibers have high surface area and they can be assembled into two-dimensional fiber membranes that are much easier to be recycled. Secondly, when electrospun carbon fibers as a carrier, it owned better adsorption ability to organic matter and it can be used to enrich the pollutant in the dispersion system [25–27].

In this paper, g-$C_3N_4$/CFs were fabricated by electrospinning technology, high temperature calcination technology, thermal polymerization, ultrasonic-assisted exfoliating and hydrothermal synthesis (Scheme 1). The design of this structure had combined the advantages of both the high adsorption and stability of CFs and the photocatalytic activity of g-$C_3N_4$, and efficient photocatalyst loading layered g-$C_3N_4$ nanosheets on carbon fibers will avoid the loss during use. In order to evaluate the photocatalytic activity, various of organic pollutants including methyl orange (MO), acid red 18 (AR 18), methylene blue (MB), sodium fluorescein (SF) and Ethylrhodamine B (ER B) were degraded as the aimed compounds.

## 2. Experimental section

### 2.1. Materials

Polyacrylonitrile (PAN, $M_w = 80{,}000$) was derived from Kunshan Hongyu Plastics Co., Ltd. *N*, *N*-dimethylformamide (DMF, 99.5%) was purchased from the Tianjin Guangfu Technology Development Co. Melamine ($C_3H_6N_6$, 99.5%) was bought from Tianjin Guangfu Fine Research Institute. Alcohol ($C_2H_5OH$, 99.7%) was purchased from Sinopharm Chemical Reagent Co., Ltd. All reagents were the analytical grade and not further purified before the experiment.

### 2.2. Preparation of photocatalysts

#### 2.2.1. Preparation of carbon fibers

The homogeneous solution of 8 wt % PAN/DMF was obtained by dissolving a certain amount of PAN in DMF with vigorous stirring for 12 h, and then poly styrene (PS) was added into the solution at a molar ratio of 10 of PAN and PS monomers, and the solution was continued to stir for 12 h.

The polymer fiber membrane was prepared by electrospinning technique. In the subsequent electrospinning process, the distance between the nozzle and the receiving device was 15 cm, and high voltage power supplied for 16 kV.

Carbon fibers (CFs) were prepared by the high-temperature calcination. First, the pre-oxidation of polymeric fiber membrane was completed at 250 °C for 2 h. Second, the temperature of the sample was raised to 800 °C at a heating rate of 5 °C $min^{-1}$ in nitrogen atmosphere and kept for 2 h.

#### 2.2.2. Preparation of bulk g-$C_3N_4$

Bulk g-$C_3N_4$ was prepared through direct heating method as the lecture has reported [28]. Melamine powder (5.0 g) was put into the quartz crucible with a cover, and the whole crucible was wrapped in aluminum foil, heated to 550 °C at a heating rate of 10 °C $min^{-1}$ in a muffle furnace and kept for 4 h. After cooled to room temperature, the yellow bulk g-$C_3N_4$ was acquired.

#### 2.2.3. Preparation of g-$C_3N_4$/CFs composites

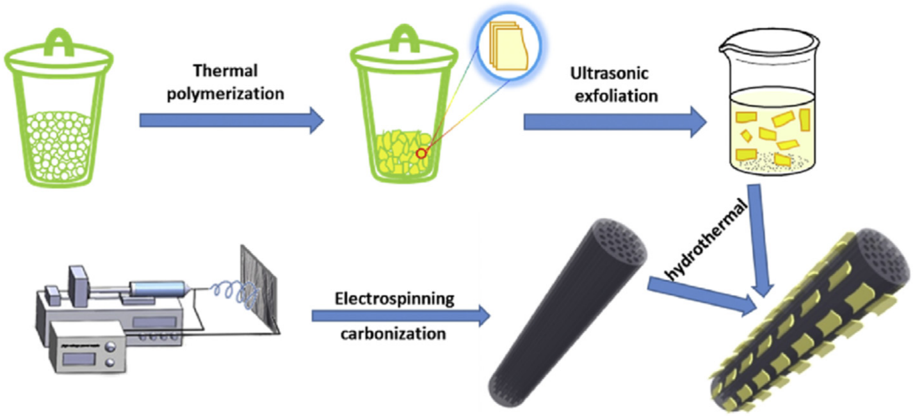
The g-$C_3N_4$ powder of 0.5 g was dispersed in 150 mL deionized water and exfoliation by ultrasonication for 10 h to gain the layered g-$C_3N_4$ nanosheets. Then, 0.15 g CFs were immersed in the above layered g-$C_3N_4$ nanosheets water system for 12 h. The mixed system was transferred into a Teflon-sealed autoclave and maintained in a drying oven at 150 °C for 12 h. The collected products were washed with deionized water and ethanol and then the samples were dried in a vacuum drying oven at 60 °C for 4 h.

### 2.3. Characterization

The morphology and structure of as-prepared composites was observed by a field emission scanning electron microscope (FE-SEM, Quanta 650 FEG, FEI) and transmission electron microscopy (TEM, Jeol, JEM-2010, Japan). The X-ray diffraction (XRD, Rigaku Ultima IV, Japan) was utilized to survey the samples in the range of $2\theta$ angles from 10° to 90°at a scanning rate of $2°min^{-1}$. Fourier transform infrared spectroscopy (FTIR, 670, Thermo Nicolet Corporation) was used to certify the functional groups of composites. Chemical binding valence states of elements of sample were tested by X-ray photoelectron spectroscopy (XPS, Escalab 250 xi, Thermo Fisher Scientific USA).

### 2.4. Evaluation of photocatalytic activity

In order to evaluate the photocatalytic activity, the photocatalytic reactions were carried out in an ultraviolet light catalytic reactor with a 500 W high pressure Hg lamp. Various of organic pollutants with a concentration of 5 mg $L^{-1}$, including methyl orange (MO), acid red 18 (AR 18), methylene blue (MB), sodium fluorescein (SF) and Ethylrhodamine B (ER B), were degraded as the aimed compounds. For instance, the as-prepared catalyst (0.05 g)



**Scheme 1.** Schematic illustration for the preparation of g-$C_3N_4$/CFs composites.