



## Full Length Article

# Efficient synthesis of monolayer carbon nitride 2D nanosheet with tunable concentration and enhanced visible-light photocatalytic activities



Qiuyan Lin<sup>a</sup>, Li Li<sup>a</sup>, Shijing Liang<sup>a,b,\*</sup>, Minghua Liu<sup>a</sup>, Jinhong Bi<sup>a,b</sup>, Ling Wu<sup>b</sup>

<sup>a</sup> Department of Environmental Science and Engineering, Fuzhou University, Minhou, Fujian, 350108, PR China

<sup>b</sup> State Key Laboratory of Photocatalysis on Energy and Environment, Fuzhou University, Fuzhou 350002, PR China

## ARTICLE INFO

## Article history:

Received 19 May 2014

Received in revised form 21 July 2014

Accepted 25 July 2014

Available online 4 August 2014

## Keywords:

C<sub>3</sub>N<sub>4</sub> nanosheet

Monolayer

Mixed solvents

Tunable concentration

Photocatalytic activity

## ABSTRACT

A versatile and scalable mixed solvent strategy was developed to prepare monolayer C<sub>3</sub>N<sub>4</sub> nanosheets with tunable concentration for the first time. This approach could also be used to prepare other 2D nanosheets from their layered materials (such as MoS<sub>2</sub>, BN, WS<sub>2</sub> etc.). The structural features and intrinsic semiconductor properties of the as-prepared C<sub>3</sub>N<sub>4</sub> nanosheets have been investigated in detailed. The photocatalytic activities were evaluated by photocatalytic oxidation of both benzyl alcohol and rhodamine B (RhB) under visible light irradiation. Results showed that the as-prepared monolayer C<sub>3</sub>N<sub>4</sub> nanosheets with thickness of 0.4 nm still retained the structural features of g-C<sub>3</sub>N<sub>4</sub> layer. The functionalities of C<sub>3</sub>N<sub>4</sub> nanosheets well inherited from the layered parent counterpart. Furthermore, due to the exceptionally high 2D anisotropy, C<sub>3</sub>N<sub>4</sub> nanosheets showed the distinctive physicochemical properties and unique electronic structures, such as high surface area, lower surface defects, stronger reduction ability of the photogenerated electrons, increased photoelectric response, and promoted the charge-carrier migration and separation. All of these favorable factors co-contributed to the greatly improved photocatalytic activities over C<sub>3</sub>N<sub>4</sub> nanosheets compared with those of its bulk counterpart.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

Two-dimensional (2D) nanosheets with molecular thickness have attracted tremendous attention in heterogeneous catalysis [1–3], electronics [4–6], sensors [7], and energy storage [8,9]. Generally, they are prepared by the exfoliation of layered materials [10–12], resulting in that their functionalities could inherit from the layered parent compounds. Furthermore, these 2D nanosheets also exhibit novel electronic structures and distinctive physicochemical properties owing to the exceptionally high 2D anisotropy [13,14]. For example, very recently, we have designed a coupled HNb<sub>3</sub>O<sub>8</sub> 2D nanosheet and benzylic alcohols system for visible-light-induced aerobic oxidation of alcohols to corresponding aldehydes with high selectivity [3]. Due to the molecular thickness, large surface area, low surface defects, high photoexcited charge carriers separation rate, abundant Lewis acid sites, strong Brønsted acidity, and a high concentration of surface complexes, the monolayer nanosheet exhibited an amazingly improved photocatalytic activity versus its

layered parent HNb<sub>3</sub>O<sub>8</sub>. However, our knowledge regarding on how to efficiently synthesize the 2D nanosheets and how to adequately harness the unique performances of the 2D nanosheets is far from satisfactory.

Graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>), a typical graphite-like layered material, is regarded as a kind of promising photocatalyst for the water splitting and degradation of organic pollutants under sunlight irradiation [15–17]. However, it is worth noting that bulk g-C<sub>3</sub>N<sub>4</sub> photocatalyst shows a low photocatalytic activity by far. This may be ascribed to the fact that bulk g-C<sub>3</sub>N<sub>4</sub> was typically synthesized by high-temperature and high-pressure routes using melamine and cyanamide as precursor [18,19]. As a result, a vast grain boundary defects would be formed and subsequently the photoexcited charge carriers would recombine at a relatively high rate. Although many strategies have been used to improve the photoactivity [20–25], it is to be said that at present the quantum efficiency is still rather low.

Encouraged by the reported 2D nanosheet photocatalysts, if layered g-C<sub>3</sub>N<sub>4</sub> was prepared into the mono- or few-layer C<sub>3</sub>N<sub>4</sub> sheets, it could be expected that the photocatalytic activity of carbon nitride would be greatly improved. For example, Liu and co-workers have developed a post-thermal treatment method to

\* Corresponding author. Tel./fax: +86 591 22866070.  
E-mail address: [sjliang2011@gmail.com](mailto:sjliang2011@gmail.com) (S. Liang).



Fig. 1. Schematic illustration of mixed solvent exfoliation process from layered  $g\text{-C}_3\text{N}_4$  powders to  $\text{C}_3\text{N}_4$  nanosheets with molecular thickness.

reduce the dimension of  $g\text{-C}_3\text{N}_4$  [26]. As a result, the as-prepared  $\text{C}_3\text{N}_4$  showed much superior photocatalytic activities than the bulk parent  $g\text{-C}_3\text{N}_4$  under visible light irradiation. Notably, this method still has some disadvantages, such as the formation of the interface defects during the calcination process, the reduction of the photoabsorption ability, the relatively thick nanosheet, and the poor yield (< 6%). These are not conducive to the photocatalytic reactions. Although the exfoliation of high quality  $\text{C}_3\text{N}_4$  2D nanosheet with low defects could also be achieved mechanically on a small scale, a simple liquid exfoliation method would allow the formation of 2D nanosheets in large quantities. Some researchers have developed some liquid exfoliation methods inspired by the preparation of graphene to fabricate few-layered  $\text{C}_3\text{N}_4$  nanosheets [27–33]. Unfortunately, the concentration of the as-prepared  $\text{C}_3\text{N}_4$  nanosheets suspension is very low (below 0.3 mg/mL) [27] and the monolayered  $\text{C}_3\text{N}_4$  nanosheet is limited [32]. What is worse, the planar atomic structure may also be seriously destroyed in the exfoliation process [26]. These may be caused by the fact that the  $\text{C}_3\text{N}_4$  nanosheet layer was cohered by covalent bonding and hydrogen bonding [34], which is definitely different from the planar pure covalent bonding cohesion of the graphene. Therefore, it is necessary to develop a novel, facile, and rapid route to fabricate the  $\text{C}_3\text{N}_4$  nanosheets with molecular thickness in a high concentration because a number of applications exist where nanosheets will be required in large quantities.

Herein, we have developed a versatile and scalable mixed solvent strategy for liquid exfoliation of bulk  $g\text{-C}_3\text{N}_4$  to produce monolayered  $\text{C}_3\text{N}_4$  nanosheets for the first time (as shown in Fig. 1). By simply changing the volume ratio of solvents, the concentration of the  $\text{C}_3\text{N}_4$  nanosheets would be tunable (0.1–3 mg/mL). More importantly, the exfoliated nanosheets could be stabilized against reaggregation for more than half year. The physicochemical properties of the products were characterized in detail. The photocatalytic activities of the as-prepared  $\text{C}_3\text{N}_4$  nanosheet were evaluated by the selective oxidation of benzyl alcohol and the degradation of RhB under visible light irradiation compared with the layered counterpart. The origin of the improved photocatalytic activity of  $\text{C}_3\text{N}_4$  nanosheet was also discussed.

## 2. Experimental

### 2.1. Synthesis of photocatalysts

All chemical reagents were of analytical grade agents and purchased from Sinopharm Chemical Reagent Co. Ltd. without further purification. Bulk  $g\text{-C}_3\text{N}_4$  powder was synthesized following the previous paper [16]. In a typical procedure, 10 g melamine was heated at 550 °C for 4 h in static air with a heating rate of 2.3 °C/min. After cooling naturally, the resultant yellow agglomerates were milled into powder in an agate mortar for further use.

The graphene-like  $\text{C}_3\text{N}_4$  2D nanosheets were prepared by a mixed-solvent exfoliation method. In detail, 500 mg of bulk  $g\text{-C}_3\text{N}_4$  powders were added into 150 mL solvents which were composed of ethanol (isopropanol (IPA), dimethyl formamide (DMF)) and

water with different volume ratios. After that, the suspension was sonicated for 10 h. The resultant suspension was centrifuged at 3000 rpm for 10 min to remove the residual layered  $g\text{-C}_3\text{N}_4$  nanoparticles. Finally, the as-prepared  $\text{C}_3\text{N}_4$  2D nanosheets were collected by centrifuging at 10,000 rpm for 5 min and dried at 60 °C in a vacuum oven.

### 2.2. Characterizations

The as-prepared samples were characterized by powder X-ray diffraction (XRD) on a Bruker D8 Advance X-ray diffractometer operated at 40 kV and 40 mA with Ni-filtered  $\text{Cu K}\alpha$  irradiation ( $\lambda = 1.5406 \text{ \AA}$ ). The Fourier transform infrared (FTIR) spectra of products were obtained on a Nicolet Nexus 670 Fourier transform infrared spectrometer at a resolution of  $4 \text{ cm}^{-1}$ . A total of 64 scans were performed to obtain each spectrum. UV–vis diffuse reflectance spectra (UV–vis DRS) were obtained by using a UV–vis spectrophotometer (Varian Cary 500) and the data were converted to Kubelka–Munk (KM) functions. Barium sulfate was used as a reference. The photoluminescence (PL) spectra were surveyed by an Edinburgh FL/FS900 spectrophotometer with an excitation wavelength at 400 nm. The time-resolved fluorescence decay spectra were surveyed by an Edinburgh FLS980 spectrophotometer with an excitation wavelength at 377 nm and an emission wavelength at 460 nm. The Brunauer–Emmett–Teller (BET) surface area was measured with an ASAP2020 M apparatus (Micromeritics Instrument Corp.). The morphologies of the products were examined by scanning electron microscopy (SEM, FEI Nova NANO-SEM 230 spectrophotometer). Transmission electron microscopy (TEM) images were recorded using a JEOL model JEM 2010 EX microscope at an accelerating voltage of 200 kV. A tapping-mode atomic force microscopy (AFM, Nanoscope Multimode IIIa, Veeco Instruments) with Si-tip cantilever was used to evaluate the morphology of the obtained nanosheets on the mica substrate.

### 2.3. Electrochemistry measurement

The working electrode was prepared on fluorine-doped tin oxide (FTO) glass, which was cleaned by sonication in chloroform, acetone and ethanol for 30 min. The glass was then rinsed with pure water ( $18 \text{ M}\Omega \text{ cm}$ ) and dried in air. The FTO slide was dip coated with  $10 \mu\text{L}$  of slurry, which was obtained from mixture of 5 mg powder and 0.5 mL dimethylformamide under sonication for 2 h, to get thin film of the samples coated on the FTO slide. After air drying naturally, a copper wire was connected to the side part of the FTO glass using a conductive tape. The uncoated parts of the electrode were isolated with an epoxy resin, and the exposed area of the electrode was  $0.25 \text{ cm}^2$ . The electrochemical measurements were performed in a conventional three electrode cell, using a Pt plate and a saturated Ag/AgCl electrode as counter electrode and reference electrode, respectively. The working electrodes were immersed in a 0.2 M  $\text{Na}_2\text{SO}_4$  aqueous solution without any additive for 30 s before measurement. The photocurrent measurements were conducted with a CHI650E electrochemical workstation (Chenhua

Download English Version:

<https://daneshyari.com/en/article/44864>

Download Persian Version:

<https://daneshyari.com/article/44864>

[Daneshyari.com](https://daneshyari.com)