

# An alkali treating strategy for the colloidalization of graphitic carbon nitride and its excellent photocatalytic performance



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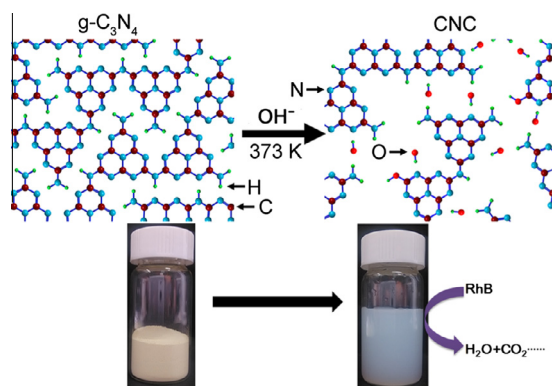
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## GRAPHICAL ABSTRACT

The graphitic carbon nitride was firstly colloidalized by a mild alkali treating route. The resulted g-C<sub>3</sub>N<sub>4</sub> colloid shows an enhanced photocatalytic performance for decomposition of RhB dye under visible light irradiation.



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## ABSTRACT

The colloid of graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) was of great importance for practical application. Herein we introduced an alkali treatment route to efficiently colloidalize g-C<sub>3</sub>N<sub>4</sub> under mild conditions by destroying the hydrogen bonds between linearly polymeric melon chains and hydrolyzing partial C–NH–C bonds linked two tri-s-triazine units. The obtained colloidal suspension was extremely stable due to its negative charges on surface, and the particle size of several hundred nanometers and the nanobelt-like morphology were revealed by electron microscopy and dynamic light scattering technologies. The structural, optical and functional group analysis demonstrated that the structure of CN heterocycles was preserved after the alkali treatment, and the produced colloidal g-C<sub>3</sub>N<sub>4</sub> can be re-assembled by an electrostatic interaction. Moreover, contributing to the reduced electron–hole recombination, the photocatalytic performance of restacked carbon nitride colloids had more enhanced photocatalytic performance than bulk g-C<sub>3</sub>N<sub>4</sub>.

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## 1. Introduction

Recently, a graphite-like analogue, graphitic-phase carbon nitride ( $g\text{-C}_3\text{N}_4$ ), has been regarded as a novel metal-free photocatalyst for photocatalytic  $\text{H}_2\text{O}$  splitting for  $\text{H}_2$  production, photo-reduction of  $\text{CO}_2$  to fuels and photodegradation of organic pollutants [1–5]. This organic polymeric carbon nitride was first discovered by Berzelius, and the yellow production was named in 1834 by Liebig as “melon”, which is constructed from tri-*s*-triazine units connected by planar amino group [6]. In recent study, many similar “melon” structures were detailedly discussed. Lotsch et al. clearly clarified the structure of a highly defined melon polymer, which is composed of layers made up from infinite 1D chains of NH-bridged melem ( $\text{C}_6\text{N}_7(\text{NH}_2)_3$ ) monomers [7]. Schnick et al. have thoroughly analyzed the crystal structure of an intermediate, 2,5,8-triaminotri-*s*-triazine, or melem ( $\text{C}_6\text{N}_{10}\text{H}_6$ ) [8]. More recently, McMillan and his group successfully prepared graphitic layered compound  $\text{C}_6\text{N}_9\text{H}_3\text{-HCl}$  by reaction between melamine and cyanuric chloride under high pressure–high temperature conditions [9]. However, this novel semiconductor was earliest discovered for the application in photocatalyst that could only date back to 2009 [1]. Being a new member of photocatalyst family, unlike the ordinary sulfide and oxynitride semiconductor catalysts,  $g\text{-C}_3\text{N}_4$  possesses superior thermal stability, chemical stability and outstanding electrical properties owing to its tri-*s*-triazine ring structure and the high degree of condensation [10,11]. All these excellent properties of  $g\text{-C}_3\text{N}_4$  imply it should be an ideal photocatalytic material, however, the high recombination of photo-induced electron–hole pairs still greatly restricts the photocatalytic performance of  $g\text{-C}_3\text{N}_4$  [12–14]. Continuous attempts have been carried out to improve the quantum efficiency of  $g\text{-C}_3\text{N}_4$ , including molecular design/copolymerization [15,16], element doping [17–20], texture/morphology engineering [21–25] and surface heterojunction design [26–28]. Although the photo-activity of  $g\text{-C}_3\text{N}_4$  has been greatly improved, its solid nature still does not meet the demand in some practical fields, for instance the fabrication of thin film for transparent self-cleaning glasses and photoelectrochemical devices. Because of the extremely high stability,  $g\text{-C}_3\text{N}_4$  cannot be dissolved in most solvents, resists the etching of acid and base, and even exhibits a high thermo-stability in air atmosphere up to 873 K [29,30]. Accordingly, realization of the solation or solution of  $g\text{-C}_3\text{N}_4$  is desirable for the viewpoint science or technology.

For the similar layered structure with graphite, a colloidal  $g\text{-C}_3\text{N}_4$  suspension was first obtained by destroying the interlayer Van der Waals force under a violently ultrasonic treatment [31,32]. The enhanced activity has been achieved by  $g\text{-C}_3\text{N}_4$  colloids for photocatalytic  $\text{H}_2$  production, whereas the low exfoliation efficiency and long treating period hinder the further application. The perfect structure of  $g\text{-C}_3\text{N}_4$  sheet (Fig. S1a) is composed of tri-*s*-triazine units connected with other three units by bridging nitrogen atoms. However, experimental results have identified the presence of amino groups in  $g\text{-C}_3\text{N}_4$  structure [1,33]. Therefore the most accepted structure is a “polymeric melon model” proposed by Lotsch et al. (Fig. S1b), where the two-dimensional (2D) sheet is formed with linearly  $\text{-NH-}$  linked tri-*s*-triazine units during the hydrogen bond connection [7]. By destroying the intralayer hydrogen bond via a heat etching route, the macroscopic  $g\text{-C}_3\text{N}_4$  is delaminated into nanosheets with extremely thin thickness [22,34–36]. In the meantime, wet-chemical methods are also explored to realize the colloidalization of carbon nitride [37–39]. Taking advantage of the similar Hummers method for preparation of graphene from layered graphite, the colloidal  $g\text{-C}_3\text{N}_4$  is obtained by breaking hydrogen bonds [34]. It has been demonstrated that after accepting proton from Brønsted acids, the amino groups in  $g\text{-C}_3\text{N}_4$  are transformed to ammonium ions [40]. However, the HCl acid treatment only realizes the surface functionalization.

Alternating with strongly oxidative acids, the solation of  $g\text{-C}_3\text{N}_4$  can be achieved [41–43]. With  $\text{H}_2\text{SO}_4$  refluxing,  $g\text{-C}_3\text{N}_4$  is even dissolved in water [44]. Very recently, we have successfully prepared a stable  $g\text{-C}_3\text{N}_4$  colloid by  $\text{H}_2\text{SO}_4$  treating and revealed its amphoteric surface property [42].

While the successful colloidalization was achieved by strongly acidic oxidants, the planar structure was destroyed and the colloidal color changed to white that means the low utilization of solar light. In recent years, many efforts have been endeavored to develop effective strategies to modify  $g\text{-C}_3\text{N}_4$  by alkaline treatment. For instance, Sano et al. reported an alkaline hydrothermal treatment method to activate graphitic carbon nitride through increasing the specific surface area [45]. Ye et al. developed an in situ method to graft hydroxyl groups over the  $g\text{-C}_3\text{N}_4$  photocatalyst by introducing KCl and  $\text{NH}_4\text{Cl}$  during the polymerization of melamine [46]. Kroke et al. found that the treatment of melon in a refluxed KOH solution would hydrolyze melon into oligomeric structures and even monomeric units of cyameluric acid with the prolonging of reaction time [47]. Unfortunately, the colloidalization of  $g\text{-C}_3\text{N}_4$  by the alkaline treatment has not been reported up to now. Herein, we attempt to adopt an alkali medium to realize the solation of  $g\text{-C}_3\text{N}_4$  and meanwhile maintain the high visible-light harvesting. Due to a bigger electronegativity of oxygen element, theoretically  $\text{OH}^-$  ions can substitute amino group in  $\text{N}\cdots\text{H-N}$  and  $\text{C-NH-C}$  units to form much more stable hydrogen bonds ( $\text{N}\cdots\text{H-O}$ ) and  $\text{C-OH}$  groups. Therefore, we firstly report the preparation of  $g\text{-C}_3\text{N}_4$  colloid (CNC) by an alkali treating strategy in current work. The possible mechanism, structure, morphology and optical properties, as well as the photocatalytic activity for degradation of organic pollutants are investigated.

## 2. Materials and methods

### 2.1. Preparation of $g\text{-C}_3\text{N}_4$ colloids

All reagents used in this study were analytical purity without further purification. The  $g\text{-C}_3\text{N}_4$  was obtained by thermal polycondensation of melamine, which was reported in our previous literatures [11]. Typically, 10 g of melamine was put into a semiclosed alumina crucible with a cover and heated at 520 °C for 4 h in a muffle furnace with a ramping rate of 10 °C  $\text{min}^{-1}$ . The obtained yellow solid was ground into a powder for further use.

The colloidal suspension was obtained by a simple alkali treatment at a reflux condition. In detail, 1 g  $g\text{-C}_3\text{N}_4$  powders were dispersed into a 50 mL NaOH aqueous solution (0.2 mol  $\text{L}^{-1}$ ), which was further heated to 100 °C and maintained for 12 h. After pouring off the clear supernatant, the sediments were re-dispersed into 50 mL deionized water. The mixture was centrifuged at 10,000 rpm for 5 min to remove precipitation, and then we obtained  $g\text{-C}_3\text{N}_4$  colloidal suspension, denoted as CNC (carbon nitride colloids). Moreover, the solid residue could be dispersed into deionized water during the further water washing. Finally, all of solids could be dispersed to form CNC suspension.

### 2.2. Characterizations

The phase identification of prepared samples was characterized by X-ray diffraction (XRD) on a DX-2700 diffractometer (Dandong Haoyuan Instrument Co. Ltd, China) using Cu K $\alpha$  radiation ( $\lambda = 0.15418$  nm). The morphology of materials was observed on a Hitachi S-4800 Field emission scanning electron microscope (SEM). Transmission electron microscope (TEM) images were taken on a JEOL-2100 electron microscope operating at an accelerating voltage of 200 kV. The Zeta potential and the Dynamic light scattering of  $g\text{-C}_3\text{N}_4$  colloid at different pH values were obtained by

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