



Carboxyl-rich g-C₃N₄ nanoparticles: Synthesis, characterization and their application for selective fluorescence sensing of Hg²⁺ and Fe³⁺ in aqueous media



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ABSTRACT

A new method has been introduced for synthesizing of carboxyl-rich g-C₃N₄ nanoparticles through a facile procedure from g-C₃N₄ nanosheets prepared by one-pot thermal polymerization of dicyandiamide under nitrogen atmosphere. The formation of these nanosheets was confirmed by the AFM, XRD, FESEM and FTIR analyses. These nanosheets subsequently were transformed to carboxyl-rich nano structures through hydrothermal oxidation and were characterized by XRD, AFM, DRS, FESEM, Zeta-potential and FTIR. AFM studies revealed that the thickness and lateral size of these nano structures were 6 and 35–50 nm, respectively. In the present work, carboxyl-rich g-C₃N₄ was used as a selective sensor for detection of Hg²⁺ and Fe³⁺ which showed 12 and 190 nM detection limits, respectively. In addition, CN⁻ was added as a discriminative agent to the aqueous media of these ions that enhanced and quenched PL intensities of Hg²⁺ and Fe³⁺, respectively.

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1. Introduction

Graphitic carbon nitride (g-C₃N₄) recently has been introduced as a new class of semiconductors that have structural similarity to graphite [1–4]. g-C₃N₄ exhibits the typical absorption pattern with a band gap at about 2.7 eV which can increased up to 5 eV [5]. In addition, g-C₃N₄ shows the photoluminescence (PL) property with a peak maximum between 366 and 472 nm depending on the degree of condensation and electronic coupling between the carbon nitride sheets [6,7]. Due to their optical and electronic properties; these materials have gained a lot of attentions to be applied in chemical sensing [8–11], photocatalytic processes [12–15] and solar cells [16,17]. In general, tri-azine and tri-s-triazine rings are the main building block of g-C₃N₄ [2]. The size of one tris-s-triazine unit is ca. 0.73 nm appearing around of ~13° in the XRD pattern

of melon-based g-C₃N₄ [18]. Moreover, due to nitrogen groups (such as primary and secondary aromatic amines) in their structural skeletons, g-C₃N₄ structures have the potential applications in absorption [19,20] and modification processes [21–23].

Despite excellent properties of bulk carbon nitride, low surface area leads to low active sites in these structures. Therefore, a lot of efforts have been devoted to the synthesis of g-C₃N₄ with higher surface area. Consequently, many forms of g-C₃N₄ have been developed such as nanotube [24], nanofiber [25,26], mesoporous [27,28] and nanosheet [29–31]. In comparison with bulk structures, g-C₃N₄ nanosheet has higher surface area (active sites), high fluorescence quantum yield and superb water dispersity. Thereby, carbon nitride nanosheets have been applied in a wide variety of applications.

Several strategies have been used for preparation of g-C₃N₄ nanosheets. Liquid phase exfoliation [31–33] and thermal etching [34–36] are the most widely used methods for synthesis of g-C₃N₄ nanosheets. In these methods, nanosheets are synthesized from bulk structures through two-step processes. Bulk carbon nitride is prepared through thermal polymerization followed by transformation to nanosheets using exfoliation and etching. Thus, these

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methods are time-consuming processes and have low final yield. Therefore, it is desirable to develop a new synthetic method to prepare nanosheet carbon nitride using a facile direct method. There are only few number reports on the one-pot synthesis of carbon nitride nanosheets [37–39].

As mentioned above, $g\text{-C}_3\text{N}_4$ nanosheets contain many available active sites (NH and NH_2) in which all nitrogen lone-pair electrons are available to react with other species [40]. These groups enable nanosheets to be modified with other compounds. For example, $g\text{-C}_3\text{N}_4$ was modified with phenyl [41], zinc phthalocyanine [42], ferrocene [43], cobaloxime complexes [22] and oxygen [44]. In addition, the aforementioned coordination sites can be replaced with hydroxyl or carboxyl groups [45–47]. Due to the optical properties of the pristine and modified $g\text{-C}_3\text{N}_4$, the use of $g\text{-C}_3\text{N}_4$ for preparation of fluorescence sensors has been increased rapidly [10,25,48]. For example, $g\text{-C}_3\text{N}_4$ has been used as a fluorescent sensor to detect various species such as squamous cell carcinoma antigen [45], xanthine [49], Cu^{2+} [50,51], glutathione [52], Cr (IV) [53], Fe^{3+} [25,54] and Hg^{2+} [55–57]. To the best of our knowledge, the application of carboxylated- $g\text{-C}_3\text{N}_4$ as a fluorescence sensor for detection of metal ions has not been investigated. Therefore, it is desirable to study the PL properties of these nanoparticles as fluorescence sensor of metal ions.

In this study, we developed a new one-pot process for preparing $g\text{-C}_3\text{N}_4$ nanosheet through thermal polymerization of dicyandiamide under inert atmosphere. Then, the carboxylated carbon nitride nanoparticles were prepared via chemical oxidation of these nanosheets. The prepared carboxyl-rich nanoparticles (carboxylated- $g\text{-C}_3\text{N}_4$) were used as an effective fluorescence sensor for detection of Hg^{2+} and Fe^{3+} in aqueous media. In addition, when CN^- is added to the solution containing Hg^{2+} and Fe^{3+} , the PL intensities were enhanced and quenched, respectively. Therefore, CN^- was introduced as discriminator for detection of these ions. Hg^{2+} and Fe^{3+} ions were also successfully detected in real water samples.

2. Results and discussion

2.1. Materials characterization

2.1.1. Characterization of $g\text{-C}_3\text{N}_4$ nanosheets

Graphitic carbon nitride nanosheets (GCNN) were prepared in the three different thermal conditions. The precursor was poured into an open crucible in tubular furnace under nitrogen atmosphere followed by heating to 550°C at three different ramp rates (5, 10 and 20°Cmin^{-1}) to prepare carbon nitride nanosheets labeled GCNN-5, GCNN-10 and GCNN-20, respectively. (More details are in Supplementary information). The obtained particles were characterized by FTIR, XRD, FESEM AFM and UV–vis techniques.

The XRD analysis was used to study the changes in structural properties of the obtained nanosheets. According to the XRD patterns (Fig. 1), it was concluded that the structure of nanosheets were based on the heptazine motifs ($\text{C}_6\text{N}_7\text{H}_3$) since they have the reflection peak at 13.2° (indexed as (100)), stemmed from the lattice planes parallel to the c-axis, representing in-planar order of the tri-s-triazine unit cell [18,58]. In addition, the second peak at 27.5° corresponds to inter layer order of $g\text{-C}_3\text{N}_4$ sheets (002) [2]. Therefore, it was proposed that the peak intensities at 13.2° and 27.5° were the representative parameters of thickness and lateral size, respectively. By comparing the peak intensities at 13.2° and 27.5° ($\alpha = \text{intensity at } 13.2^\circ / \text{intensity at } 27.5^\circ = I_{13.2^\circ} / I_{27.5^\circ}$), it was found that GCNN-20 has the highest α value shown in the inset of (Fig. 1). Thus, it was suggested that the in-planar order of GCNN-20 was stronger than GCNN-10 and GCNN-5. Based on these results,

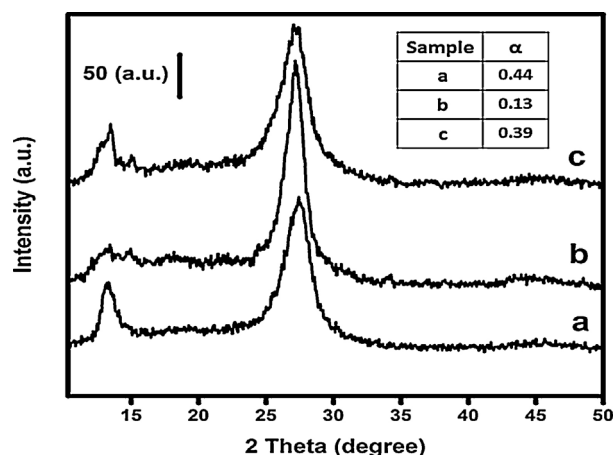


Fig. 1. The XRD patterns of as-prepared nanosheets: (a) GCNN-20, (b) GCNN-10 and (c) GCNN-5, inset is the table of intensities ratio of peaks at 13.2° and 27.5° ($\alpha = I_{13.2^\circ} / I_{27.5^\circ}$).

GCNN-20 was chosen as a suitable candidate for the preparation of carboxylated-heptazine- $g\text{-C}_3\text{N}_4$ nanoparticles.

To gain the insight into the topology and size of the as-synthesized $g\text{-C}_3\text{N}_4$, atomic force microscopy (AFM) was used. According to the published reports, $g\text{-C}_3\text{N}_4$ nanosheets have planar structure and the thickness (z) of these particles are negligible in comparison with lateral size (x, y) [29,59,60]. As shown in Fig. 2, all three synthesized nanosheets had at least one dimension (there is thickness, z) below 100 nm. Therefore, it can be concluded that nanosheets of carbon nitride were formed in all experimental conditions. The changes in lateral size and thickness of these nanosheets are shown in Table 2. The AFM findings were supported the XRD discussion about the changes in particles size of as-prepared nanosheets.

The FTIR spectra of carbon nitride nanosheets showed characteristic peaks for graphitic type of carbon nitride (Fig. S1). Furthermore, UV–vis spectra of these structures represented a maximum absorption in 320 nm (Fig. S2) that were similar to other reports for graphitic carbon nitride [61,62]. According to the obtained results, $g\text{-C}_3\text{N}_4$ nanosheets were obtained in all thermal conditions. Moreover, among the synthesized nanosheets, GCNN-20 had the smallest lateral size and the highest heptazine order. Therefore, GCNN-20 was used for preparing carboxylated- $g\text{-C}_3\text{N}_4$ nanoparticles.

2.1.2. Characterization of carboxylated- $g\text{-C}_3\text{N}_4$ nanoparticles (CGCNP)

In the present work, the synthesized nanosheet (GCNN-20) was used to produce carboxylated- $g\text{-C}_3\text{N}_4$ through hydrothermal oxidation method (More details of experiments are available in Supporting information). The obtained CGCNP was characterized by different techniques such as XRD, AFM, FESEM, FTIR, DRS, Zeta potential and UV–vis spectroscopy.

In the earlier reported work, dichromate/sulfuric acid were used as an oxidizing agent [63] to produce the porous structures from bulk- $g\text{-C}_3\text{N}_4$. But, the purpose of the present research was production of carboxyl-rich nanoparticles from $g\text{-C}_3\text{N}_4$ nanosheets. Therefore, herein, a reagent was needed that the oxidizing and cutting processes of these nanosheets were carried out at the same times. On the other hand, this reagent must oxidize and cut the large particle of nanosheets to the small particles containing COOH and OH groups. In a reported work, nitric acid was proposed as a scissor for cutting $g\text{-C}_3\text{N}_4$ [64]. Therefore, HNO_3 was used to produce the small size and carboxyl-rich nanoparticles.

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