



One-step synthesis of graphitic carbon nitride nanosheets with the help of melamine and its application for fluorescence detection of mercuric ions

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ABSTRACT

A facile, simple, and relatively environment-friendly hydrothermal approach was developed for one-step synthesis of graphitic carbon nitride nanosheets (GCNNs) using melamine and sodium citrate as the precursors. The prepared GCNNs emit strong fluorescence with a high quantum yield of 48.3%. The GCNNs were then characterized by various techniques including transmission electron microscopy, atomic force microscopy, X-ray diffraction, Fourier transform infrared spectroscopy, and UV–Vis absorption spectroscopy. In addition, the fluorescence quenching behavior of the GCNNs by mercuric ions (Hg^{2+}) was exploited to fabricate a label-free fluorescence quenching sensor for sensitive and selective detection of Hg^{2+} . The results showed that there existed a linear relationship between the fluorescence intensity and the concentration of Hg^{2+} from 0.001 to 1.0 μM with a detection limit of 0.3 nM. Finally, the sensor was successfully used to detection of Hg^{2+} in water and milk samples.

1. Introduction

Recently, melamine as a molecule of high nitrogen contents (66 mass%) has been frequently added to milk products and animal feed to artificially increase the measured protein content. The illegal addition of melamine may cause many diseases, such as urinary calculus, obstructive acute renal failure, cognitive deficits, and so on [1–3]. Therefore, it is appealing to finding a method for proper disposal of the hazardous substance.

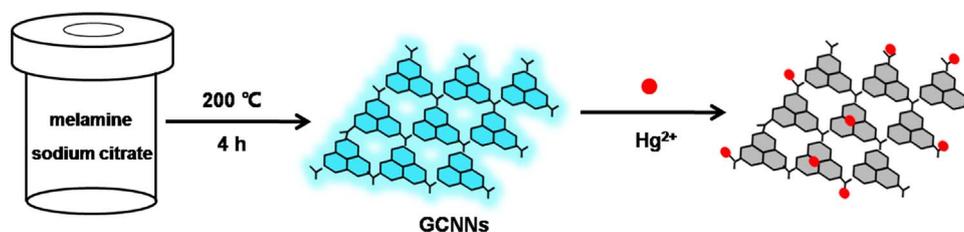
A promising method for disposal of melamine is to transform the hazardous substance to other non-toxic or low-toxic material. To this end, in the past few years, many researchers have exploited melamine as raw materials to synthesize various non-toxic or low-toxic materials, such as microporous organic polymers [4], urea-formaldehyde resin [5], and nitroheterocycles [6,7]. Recently, melamine has been also used to synthesize non-toxic two-dimensional graphitic carbon nitrides nanosheets (GCNNs) [8–13]. Lin et al. [8] and Tian et al. [9] prepared GCNNs by several steps: direct pyrolysis of melamine at 600 °C to form bulk carbon nitrides, chemical oxidization of bulk carbon nitrides, and ultrasonic exfoliation of bulk carbon nitrides. Gu et al. [10] proposed a two-step strategy to synthesize GCNNs: polymerization of melamine by ammonium persulfate into microstructures, and paralyzation of the microstructures under Ar. Cheng et al. [11] prepared GCNNs by pyrolyzing a melamine– KBH_4 mixture at 550 °C in Ar atmosphere.

Bian et al. [12] synthesized GCNNs by two-step strategy: direct pyrolysis of melamine at 550 °C to produce bulk carbon nitrides, and ultrasonic exfoliation of the product. Li et al. [13] synthesized nitrogen-doped mesoporous graphitic carbon using melamine and citric acid through 900 °C carbonization. Moreover, GCNNs have been recently demonstrated to possess many unique and outstanding physicochemical properties [14], and are widely applied in the field of biosensing [15,16], energy storage [17,18], and catalysis [19,20]. However, the aforementioned methods for transformation of melamine into GCNNs usually involve multistep routines, or harsh reaction conditions, which seriously limit the applications of the nanomaterials. Therefore, a facile, less complicated, and environment-friendly synthesis approach of GCNNs is highly desirable.

In the present work, a rapid, simple, and relatively environment-friendly hydrothermal method for one-step synthesis of highly fluorescent GCNNs was studied, which using sodium citrate and melamine as carbon and nitrogen sources, respectively. On the other hand, mercury is one of the most toxic heavy metals in the environment, which tends to be accumulated in human body and result in severe damages in central nervous system, kidney failure and various cognitive and movement disorders [21–23]. Herein, on the basis of the fluorescence quenching behavior of the as-synthesized GCNNs by Hg^{2+} , a label-free fluorescence quenching sensor for highly selective and sensitive detection of Hg^{2+} was constructed (Scheme 1).

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Scheme 1. Schematic illustration of fluorescence sensing of Hg^{2+} .

2. Experimental

2.1. Materials

Melamine and sodium citrate were purchased from Sigma Co. (USA). Quinine sulfate, trichloroacetic acid, lactose, fructose, glucose, vitamin C, vitamin B1, vitamin B9, amino acid, and the metal salts used were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Unless specified, all chemicals were of analytical reagent grade and were used without further purification. Deionized distilled water was used throughout the experiments.

2.2. Apparatus

Fluorescence spectra were recorded by a LS-55 photoluminescence spectrometer (Perkin Elmer Co., MA, USA) with a 1.0 cm quartz cuvette. UV–Vis spectra were collected with an Agilent 8453 UV–visible spectrophotometer (Agilent Technologies, Santa Clara, CA, USA) with a standard 1.0 cm cuvette. Transmission electron microscopy (TEM) images were performed by using a JEM-2010 microscope (JEOL Co., Japan) operated at an accelerating voltage of 200 kV. Atomic force microscope (AFM) measurements were made on an AJ–III Instrument (Shanghai Aijian Nanotechnology, China). Fourier transform infrared spectra (FT–IR) were observed using a Nicolet 380 FT–IR spectrometer (Thermo Nicolet Co., USA). X–ray diffraction (XRD) spectra were obtained with the use of a Bede D1 high–resolution X–ray diffractometer (Bede Co., UK).

2.3. Preparation of GCNNs

The fluorescent GCNNs were prepared through a simple one-step hydrothermal method. In brief, 0.075g of sodium citrate was added to 20 mL water, followed by adding 0.22g melamine. After a 5 min ultrasonication, the mixture was then transferred into a 50 mL Teflon-lined stainless autoclave and heated at 200 °C for 4 h. After cooling, the brown-yellow product was centrifuged for 30 min at 12000 rpm. The obtained product was then dialyzed against distilled water to remove the impurities using a cellulose dialysis membrane (MWCO =500) for 12 h.

2.4. Fluorescence detection of Hg^{2+}

For a typical detection, 15.0 μL GCNNs dispersion and 2.0 mL water were sequentially added into a 1.0 cm cuvette. Hg^{2+} solution was then added to give a series of samples with different concentrations ($c_{\text{Hg}^{2+}} = 0, 0.001, 0.0025, 0.005, 0.01, 0.025, 0.05, 0.1, \dots, 1.0, 1.25, \dots, 2.0, 2.5, 3.0 \mu\text{M}$, total 23 samples) and mixed thoroughly. Each sample was incubated for 5 min, and the fluorescence emission spectra of each resultant solution were recorded at an excitation wavelength of 340 nm. The selectivity for Hg^{2+} was confirmed by adding other metal ion instead of Hg^{2+} in a similar way at a concentration of 0.9 μM . All experiments were taken at room temperature.

2.5. Detection of Hg^{2+} ion in water and milk samples

The lake water and milk samples were respectively collected from Qingshan lake of Nanchang and local supermarket. The lake water samples were filtered through a 0.22 μm filtered membrane and then centrifuged at 12,000 rpm for 30 min. After that, the obtained samples were spiked with Hg^{2+} with different concentration levels, and analyzed by the proposed method. For milk samples, the milk powders were treated as follows: 1% (v/v) trichloroacetic acid was added and ultrasonicated for 20 min to remove protein; the milk sample was then centrifuged at 12,000 rpm for 10 min and filtered through a 0.22 μm membrane. The resultant milk samples were spiked with Hg^{2+} as the water samples.

3. Results and discussion

3.1. Characterization of the GCNNs

In the work, the GCNNs were prepared by a facile one-step hydrothermal synthetic method. The obtained GCNNs were further characterized by means of transmission electron microscopy (TEM), atomic force microscope (AFM), X–ray diffraction (XRD), Fourier transform infrared spectra (FT–IR), fluorescence spectroscopy, and UV–Vis absorption spectroscopy. As shown in Fig. 1A, the GCNNs were monodispersed and nearly spherical with an average diameter of $12.58 \pm 3.67 \text{ nm}$ (statistically estimated on the basis of more than 100 GCNNs in the TEM images). From the magnified image (inset, Fig. 1A) it could be found that the diffraction contrast was very low with no obvious lattice fringes, suggesting the amorphous nature of the GCNNs. The AFM image in Fig. 1B showed that the height of the GCNNs was approximately 2–3 nm, indicating that most of the GCNNs were existed as two- or three-layers. As can be seen in Fig. 2A, the XRD pattern of GCNNs displayed a broad (002) peak at 27.8° , which was assigned to a stacking peak of π -conjugated layers [11,23]. It was worth noting that the intensity of this peak was not strong, indicating the poor crystallinity of the GCNNs. This result given by XRD was in good agreement with that of TEM. As could be noticed in Fig. 2B, there appeared a characteristic peak at 810 cm^{-1} , which corresponded to the vibration of the triazine ring. The intense bands peaked at 1563 and 1417 cm^{-1} arose from aromatic C–N stretches, whereas the band peaked at 1645 cm^{-1} was ascribed to C=O stretching. The broad bands peaked at 3141 and 3442 cm^{-1} were attributed to N–H and O–H stretching. All these results suggested that the surface of GCNNs likely contained carboxyl, hydroxyl and amino groups.

From the UV–Vis absorption and fluorescence emission spectra of the GCNNs (Fig. 3A), it was clearly shown that GCNNs exhibited two characteristic absorption peaks at 220 nm and 340 nm. The peak at 220 nm could be assigned to the π - π^* transition of the aromatic C^{C} sp^2 domains [24,25]. Another peak at 340 nm may arise from the trapping of excited state energy of the surface states [24,25] or the $\text{n}-\pi^*$ transitions of the unsaturated groups with nitrogen atoms [11]. In addition, when excited at 340 nm, GCNNs emitted strong fluorescence peaked at 439 nm. The quantum yield (QY) of the GCNNs was calculated to be 48.3% against quinine sulfate as a reference, which was much higher than those reported previously [8,9,20]. The inset in

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