A practical graphitic carbon nitride (g-C₃N₄) based fluorescence sensor for the competitive detection of trithiocyanuric acid and mercury ions

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Highlights

- Graphitic nitride displayed competitive fluorescence detection towards TCA and Hg²⁺.
- Theoretical calculations were used to evaluate the interactions and help describe the detection mechanism.
- Normalized 2D fluorescence contour plots have been used to understand the fluorescence phenomenon.

Abstract

A fluorescent sensor for the detection of trithiocyanuric acid (TCA) and Hg²⁺ was developed based on competitive interactions: non-covalent stacking between g-C₃N₄ and TCA *vs* coordinative interaction between TCA and Hg²⁺. Electrostatic simulations were used to evaluate the interactions and help describe the detection mechanism. Moreover, normalized 2D fluorescence contour plots have been used to understand the fluorescence phenomenon. When TCA was added into a g-C₃N₄ nanosheet solution free of Hg²⁺, TCA interacted with g-C₃N₄ nanosheets *via* hydrogen bonding and π - π interactions, resulting in fluorescence quenching of the g-C₃N₄ nanosheets. However, upon the addition of Hg²⁺, the fluorescence of the TCA-g-C₃N₄ nanosheet hybrid system was restored, due to coordination of Hg²⁺ with TCA through the S atoms, breaking the TCA-g-C₃N₄ stacking

interaction. Our results provide a new approach for the design of multifunctional nanosensors suitable for the detection of environmental pollutants.

1. Introduction

With rapid global industrialization, heavy metal ions have polluted the biosphere's water supplies mainly as a result of the disposal of industrial and agricultural waste [11, 12, 13]. As a result, organic and/or inorganic pollutants in freshwater systems have become an important environmental issue due to their adverse influence on human health and environmental stability [4, 5, 6, 7]. Trithiocyanuric acid (TCA), which is a widely used vulcanizing agent for rubber [8, 9, 10], is one of the many contaminants entering the environment. High concentrations of TCA can pose a serious threat to aquatic organisms and human health [11]. Currently, numerous analytical methods have been developed for the detection of TCA, including high-performance liquid chromatography (HPLC) [12], mass spectrometry [13] and electrochemistry. However, the implementation of these detection methods is practically limited by high operational costs, possible secondary contamination and maintenance difficulties. Among the various possible methods to detect TCA, methods using fluorescence have been demonstrated as an effective alternative due to the simpler equipment requirements, fast response times and lower operating costs [14, 15]. In addition, fluorescence based methods display high sensitivity and selectivity. Nanomaterial-based fluorescent sensors are extremely attractive owing to their intrinsic sensitivity and simplicity [16, 17]. To the best of our knowledge, this is the first report on the detection of TCA using a nanomaterial based fluorescent sensor.

Inorganic pollutants inevitably coexist with organic pollutants in aqueous solutions. Especially mercury ion (Hg^{2+}), one of the most toxic metal ions [18, 19, 20, 21], widely exists in the environment and can be converted into methylmercury, a strong neurotoxin that can accumulate in the human body through the food chain resulting in many brain related diseases [22, 23, 24]. Significant effort has been devoted to design nanomaterial-based fluorescent sensors for Hg^{2+} detection due to the many advantages including sensitivity, selectivity, versatility and device portability [25, 26, 27, 28, 29]. Nevertheless, their widespread implementation has been delayed by the remaining limitations, such as high cost, difficult synthesis and potential chemical toxicity [30]. Moreover, most nanosensors for Hg^{2+} detection work using a turn-off process, which can result in false signals caused by the existence of other quenchers in real world samples. Therefore, with this research we set out to fabricate a selective turn-on fluorescent sensor for practical applications.

Two-dimensional (2D) nanomaterial based fluorescent sensors are popular due to their low toxicity and excellent optical properties [31, 32]. Among them, graphitic carbon nitride is a chemically and thermally stable metal-free semiconductor [33, 34]. It is the most stable allotrope of various carbon nitrides under ambient conditions. The framework topology of the previously identified g- C_3N_4 is a defect-rich and N-bridged "poly(tri-s-triazine)" [35].

Our approach uses the coordinative interactions between TCA and Hg^{2+} and non-covalent stacking between g- C_3N_4 and TCA. The fluorescence of g- C_3N_4 nanosheets can be

quenched by TCA, due to supramolecular interactions between the aromatic TCA and g-C₃N₄ nanosheets. While, the fluorescence of g-C₃N₄ nanosheets is recovered by the addition of Hg²⁺ since the interaction between Hg²⁺ and TCA results in the removal of TCA from the surface of g-C₃N₄, as shown in [Scheme 1](#). The detection system proved to be selective for the detection of TCA and Hg²⁺. Furthermore, the detection mechanism was evaluated using theoretical calculations. Our results provide a new approach for the design of multifunctional nanosensors based on competitive interactions for the detection of environmental pollutants.

Scheme 1. Schematic representation of the sensing process of the g-C₃N₄ nanosheets as a fluorescent sensor for the detection of TCA and Hg²⁺.

2. Experimental

2.1. Materials

The reagents were obtained from standard commercial sources and were used as received: isopropyl alcohol (IPA, Tianjin Bei Chen Fang Zheng Reagent, AR, purity ≥ 99.7%), mercury acetate (Shanghai Huadong Reagent Co., Ltd. AR, Purity ≥ 98%), trithiocyanuric acid (Aladdin Reagent (Shanghai) Co., Ltd. ≥ 95%), potassium chloride (Tianjin Kermel Chemical Reagent Co., Ltd., AR, Purity ≥ 99.5%), zinc chloride (Tianjin Guangfu Fine Chemical Research Institute, AR, purity ≥ 98.0%), calcium chloride (Tianjin Tianda Chemical Experimental Plant, AR, purity ≥ 96.0%), cobaltous chloride hexahydrate (Tianjin Kermel Chemical Reagent, AR, purity ≥ 99.0%), iron chloride tetrahydrate (Tianjin Guangfu Fine Chemical Research Institute, AR, purity ≥ 99.7%), nickelous chloride (Tianjin Guangfu Fine Chemical Research Institute, AR, purity ≥ 99.0%), magnesium chloride hexahydrate (Tianjin Fuchen Chemical Reagent, AR, purity ≥ 98.0%), sodium hydroxide (Tianjin BeiChen Fang Zheng Reagent, AR, purity ≥ 96.0%), sodium chloride (Tianjin BeiChen Fang Zheng Reagent, AR, purity ≥ 99.5%), copper chloride (Tianjin Guangfu Fine Chemical Research Institute, AR, purity ≥ 99.0%), lead chloride (Tianjin Kermel Chemical Reagent, AR, purity ≥ 99.5%), iron nitrate nonahydrate (Aladdin Reagent (Shanghai) Co., Ltd. ≥ 98.5%), silver nitrate (Tianjin Kermel Chemical Reagent, AR, purity ≥ 99.8%), cobalt nitrate hexahydrate (Aladdin Reagent (Shanghai) Co., Ltd. ≥ 99%), lead nitrate (Tianjin Kermel Chemical Reagent, AR, purity ≥ 99.0%), cupric nitrate (Tianjin Fuchen Chemical Reagent, AR, purity ≥ 99.5%), calcium nitrate (Tianjin Fuchen Chemical Reagent, AR, purity ≥ 99.0%), 2-mercaptobenzothiazole (Shanghai Macklin Biochemical Co.,

Ltd. $\geq 98\%$), 4-mercaptobenzoic acid (Shanghai Macklin Biochemical Co., Ltd. $\geq 90\%$), toluene (Tianjin Kermel Chemical Reagent, AR, purity $\geq 99.5\%$), phenol (Tianjin Fuchen Chemical Reagent, AR).

2.2. Instruments

The morphology of the g-C₃N₄ nanosheets was observed using a HitachiS-4800 SEM at the magnification of 2500–100000 times. A JEM-2100 transmission electron microscope (TEM) was employed to observe the morphology and the structure of the sample at an acceleration voltage of 200 kV. The crystalline phases of the prepared samples were characterized *via* X-ray diffraction (XRD, Bruker D8 Advance) under wide-angle (10–900) scanning with a step size of 0.010°. X-ray photoelectron spectroscopy (XPS) was conducted using an ESCALAB 250Xi energy spectrometer with a resolution of 0.48 eV (Ag 3d5/2) and 0.68 eV (C 1s) to investigate the surface chemical composition and valence state of g-C₃N₄, respectively. The obtained UV–vis absorption spectrum was performed on the Beijing Puxi T6 New Century UV–Vis spectrophotometer. Fluorescence detection was performed using Shanghai Lengguang F97 pro fluorescence spectrophotometer.

2.3. Synthesis of g-C₃N₄ nanosheets

Bulk g-C₃N₄ was prepared by direct pyrolysis of melamine in a tube furnace. In detail, 3 g melamine was put in an agate mortar, then put into a ceramic boat, and heated at 550 °C for 4 h with a heating rate of 5 °C min^{−1} for both of the heating and cooling processes. The obtained yellow powder was the bulk g-C₃N₄. In the next step, ultrathin g-C₃N₄ nanosheets were synthesized by sonication, centrifugation and drying of the bulk g-C₃N₄. Briefly, 0.2 g of bulk g-C₃N₄ powder was dispersed in 200 mL solution with the 1: 1 ratio of water: IPA and the mixture was sonicated for 8 h. The dispersed solution was placed in a centrifuge tube, centrifuged at 5000 rpm for 5 min, and the supernatant liquid was freeze-dried for further use.

2.4. Fluorescence detection of TCA and Hg²⁺

The general detection procedure for TCA was as follows: 200 μL of g-C₃N₄ nanosheets stock solution (0.1 mg mL^{−1}) and different amounts of TCA were sequentially added into a series of 5 mL colorimetric tubes, and finally diluted to 2 mL with water: IPA = 1:1 solution before the fluorescence spectrum was measured.

For the detection of Hg²⁺, into a series of 5 mL colorimetric tubes, different concentrations of Hg²⁺ were mixed with TCA, then 100 μL of g-C₃N₄ nanosheets stock solution was added into the above solution. The mixture was diluted to 2 mL with water: IPA = 1:1 solution, shaken thoroughly and equilibrated. The reference solution was the same without any ions added.

All fluorescence measurements were performed at room temperature. The pH conditions of the g-C₃N₄ solution in fluorescence titrations were in IPA/phosphate buffer solution (pH = 5.0, 50/50, v/v). The fluorescence intensity was measured with an excitation wavelength of 310 nm.

3. Results and discussion

3.1. Characterization of g-C₃N₄

The morphology of g-C₃N₄ nanosheets was characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). From the SEM images (Fig. 1a), it can be seen that g-C₃N₄ is a relatively amorphous aggregation and the lamellae flake size is small. TEM images of the g-C₃N₄ (Fig. 1b) reveals a sheet-like monolayer structure. XRD patterns for bulk g-C₃N₄ and g-C₃N₄ nanosheets confirm the successful exfoliation of bulk g-C₃N₄ (Fig. 1c). Two peaks at 13° and 27.8° were observed for bulk g-C₃N₄. The peak at 13° derived from in-planar repeated tri-s-triazine units was indexed to the (100) plane of g-C₃N₄, while the peak centered at 27.8°, a characteristic inter-planar stacking peak of the layered aromatic system, was indexed to the (002) plane in g-C₃N₄. Compared with the bulk g-C₃N₄, the (100) peak in g-C₃N₄ nanosheets disappeared and the (002) peak in g-C₃N₄ nanosheets became weaker, suggesting the successful exfoliation of bulk g-C₃N₄. The binding states of C, N and O of g-C₃N₄ nanosheets were investigated by X-ray photoelectron spectroscopy (XPS) in Fig. 1d. The C1s spectrum (Fig. S1a) could be divided into three peaks. The peak located at 284.6 eV arises from C–C coordination of adventitious carbon. The peak at 288.1 eV corresponds to N–C=N coordination and the peak at 293.8 eV was ascribed to carbonate groups. The N1s spectrum (Fig. S1b) displayed three peaks at 398.5, 400.4 and 405.4 eV, which could be attributed to the C=N–C, C–N–H and charging effects, respectively. Fig. S1c shows the O1s spectrum with a binding energy of 531.8 eV, the low oxygen content probably originated from the adsorbed H₂O or CO₂ on to the surface of g-C₃N₄ nanosheets [25].

Fig. 1. a) SEM image of g-C₃N₄ nanosheets; b) TEM image of g-C₃N₄ nanosheets; c) The Typical XRD patterns of bulk g-C₃N₄ and g-C₃N₄ nanosheets; d) the survey spectrum of g-C₃N₄ nanosheets.

3.2. Theoretical calculations between g-C₃N₄ and TCA

Theoretical calculations were used to understand the non-covalent interactions between g-C₃N₄ and TCA and help explain the sensing mechanism. The interaction between the g-C₃N₄ fluorescent material and TCA was investigated using electrostatic simulations. First, the structures of both compounds were optimized using MMFF94s Force Field in Avogadro (v 1.2.0) [36]. Then, the electrostatic surface potentials were calculated in MarvinSpace (v 17.21.0), ChemAxon. Different π - π stacking between the fluorescent g-C₃N₄ and TCA were proposed using the Hunter and Sanders (HS) model and calculations of the electrostatic surface potentials (Fig. 2 and S2). From these results, it was confirmed that TCA can readily attach to the g-C₃N₄ surface by π - π stacking.

Fig. 2. a) Optimized structures of TCA and b) g-C₃N₄ (red denotes areas of relatively high electron density and blue denotes electron deficient areas); c) Proposed stacking arrangements. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

3.3. Spectral studies of g-C₃N₄ with TCA and Hg²⁺

UV–vis absorption spectra were used to probe the coordination interaction between Hg²⁺ and TCA. As illustrated in Fig. 3a, TCA-g-C₃N₄ had similar absorption bands with TCA pristine system, and for the mixture UV absorption peak, there were no obvious peak shift, which indicated that while the TCA was attached on the g-C₃N₄ nanosheet and the weak non-covalent π - π stacking between g-C₃N₄ nanosheets and TCA has no significant effect on TCA absorption behaviour. However, upon the addition of Hg²⁺ to the TCA-g-C₃N₄ system solution, the absorption band of TCA has a large blue shift, which proves that the Hg²⁺ ions form coordinative bonds with the sulfur atoms of TCA (Fig. 3b).

Fig. 3. a) UV–vis absorption spectrum of g-C₃N₄ nanosheets, g-C₃N₄ nanosheets + TCA, TCA, g-C₃N₄ nanosheets + TCA + Hg²⁺. The concentrations of g-C₃N₄ nanosheets and TCA and Hg²⁺ were 10 $\mu\text{g mL}^{-1}$, 45 μM and 60 μM , respectively. b) Schematic representation of possible coordination modes of Hg to TCA.

The fluorescence emission properties of g-C₃N₄ in the absence and presence of TCA were examined by 2D fluorescence spectra (Fig. 4a and b and Fig. S3a). The g-C₃N₄ alone exhibits a fluorescence emission when excited at 310 nm and no time dependant changes are observed indicating that the g-C₃N₄ nanosheet is stable. In the presence of TCA, the fluorescence intensity of g-C₃N₄ nanosheets at 436 nm gradually decreases, and the decrease is enhanced with increasing concentrations of TCA, due to formation of non-covalent π - π stacking interactions between the g-C₃N₄ nanosheet and TCA. The detection limit was calculated to be 9.6×10^{-8} M (Fig. S4). Subsequent addition of Hg²⁺ into the TCA-g-C₃N₄ solution, causes the emission at 436 nm to gradually recover (Fig. 4c and Fig. S3b). This reversible fluorescence emission results from the formation of coordination bonds between the Hg²⁺ and TCA, which can remove the TCA from the g-C₃N₄ surface. The effect of pH on the detection of TCA with g-C₃N₄ nanosheets was investigated and changes in pH had little effect on the fluorescence intensity (Fig. S5). Meanwhile, the fluorescence response of g-C₃N₄ nanosheets towards other aromatic compounds such as 2-mercaptobenzothiazole (2-MPT), 4-mercaptobenzoic acid (4-MBA), toluene, phenol was investigated (Fig. S6). It can be seen that only the addition of 2-MPT resulted in fluorescence quenching, suggesting the sensor has good selectivity for TCA detection.

Fig. 4. Normalized 2D fluorescence contour plots recorded for dispersions of: a) g-C₃N₄ solution (0.1 mg mL⁻¹); b) TCA-g-C₃N₄ system upon the addition of TCA (45 μM); c) TCA-g-C₃N₄-Hg system in the presence of Hg²⁺ (60 μM).

The capability of TCA-g-C₃N₄ nanosheet composites for the quantitative detection of Hg²⁺ were determined (Fig. 4c and Fig. S3b). The fluorescence intensity of the g-C₃N₄ nanosheets increases with the addition of Hg²⁺, suggesting TCA binds to Hg²⁺ and removes it from the g-C₃N₄ nanosheets. The fluorescence does not fully recover to the original intensity, which indicates that some TCA remains attached to the g-C₃N₄. Furthermore, the fluorescence intensity at 436 nm follows a linear relationship for Hg²⁺ concentrations from 0 to 60 μM, and the detection limit was evaluated to be 6.2×10^{-7} M, indicating that the hybrid is particularly sensitive for the detection of Hg²⁺ (Fig. S7). The pH dependency for TCA was investigated (Fig. S8a). It is clear that g-C₃N₄ nanosheets are stable towards TCA over a wide range of pH. Meanwhile, the effect of pH on Hg²⁺ detection was also evaluated (Fig. S8b). Since the precipitation of Hg(OH)₂ occurs at pH ≥ 6. Only acidic pH conditions were used for further studies. It was found that pH exerted little effect on the response of g-C₃N₄ nanosheets toward Hg²⁺, which indicates the potential application of this hybrid system over a wide range of pH.

To evaluate the selectivity of the developed TCA-g-C₃N₄ system for heavy metal ions, a selection of heavy metal ions were evaluated. As shown in Fig. 5a, only the addition of Hg²⁺ (60 μM) led to an obvious increase in fluorescence intensity of the g-C₃N₄ nanosheets, while negligible changes were observed in the presence of other metal ions (100 μM). The fluorescence titration of g-C₃N₄ nanosheets with different coexisting ions was measured to evaluate the interference of other ions in the detection of Hg²⁺ ions (Fig. 5b). It was found that these ions barely had any effect on the fluorescence recovery of the g-C₃N₄ nanosheets, which suggests that the sensor has a high selectivity towards Hg²⁺. The high selectivity was ascribed to the stronger affinity of thiol-containing ligand for Hg²⁺ compared to other metal ions. Meanwhile, the effect of the counter ion was determined. Therefore, we evaluated the metal ions with nitrate as the counter ion (Fig. S9). It can be seen that the counter ion has little effect on the sensing of Hg²⁺.

Fig. 5. a) The relative fluorescence intensity (I/I_0) at 436 nm upon the addition of different metal ions (chloride counter ion); b) The relative fluorescence intensity (I/I_0) at 436 nm after the addition of mixtures of different metal ions with Hg^{2+} . The concentrations of TCA and metal ions were 45 μM and 100 μM , except Hg^{2+} at 60 μM .

4. Conclusion

In summary, we have designed and fabricated a practical fluorescent sensor for the detection of TCA and Hg^{2+} using g- C_3N_4 nanosheets. Our design principle is promising for the development of nanosensors suitable for the detection of pollutants in wastewater since the fluorescence of the g- C_3N_4 nanosheets was sensitively quenched by TCA (9.6×10^{-8} M for TCA), while the addition of Hg^{2+} to the TCA-g- C_3N_4 nanosheets hybrid led to fluorescence recovery with low detection limits (6.2×10^{-7} M for Hg^{2+}). Furthermore, the detection mechanism was investigated using theoretical calculations to confirm our experimental results. The results reported here provide a new approach for the design of a multifunctional nanosensor for the detection of environmental pollutants. The simplicity of this method makes it suitable for real world applications.

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supporting this study are provided as supplementary information accompanying this paper. T.D.J. wishes to thank the Royal Society for a Wolfson Research Merit Award.

Appendix A. Supplementary data

The following is the Supplementary data to this article:

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Multimedia component 1.

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