Supporting Information

Polymer Nanodots of Graphitic Carbon Nitride as Effective Fluorescent Probes for the Detection of Fe³⁺ and Cu²⁺ ions

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Experimental sections

Preparation of bulk g-C₃N₄

The bulk $g-C_3N_4$ was prepared by polymerization of melamine under high temperature. In detail, urea was heated at 600 °C for 4 h under air condition with a ramp rate of ~5 °C/min for both of the heating and cooling processes. The light yellow product was obtained as the bulk $g-C_3N_4$.

Preparation of ultrafine F-g-C₃N₄ dots

The ultrafine F-g-C₃N₄ dots were obtained by hydrothermal cutting of bulk g-C₃N₄ in water. In detail, 100 mg of bulk g-C₃N₄ was dispersed in 100 mL water, which was transferred into a Teflon-sealed autoclave and maintained at 180 °C for 10 h. The initial formed suspension was then centrifuged to remove weight precipitate and agglomerated particles, and then the products were dispersed in water for further characterization and use. The final yield of the F-g-C₃N₄ dots was calculated to be approximate 26.4%.

Characterizations

The samples were characterized by X-ray powder diffraction (XRD) with a Japan Rigaku Dmax X-ray diffractometer equipped with graphite monochromatized high-intensity Cu-K α radiation (λ =1.54178 Å). The transmission electron microscopy (TEM) images were carried out on a JEM-2100F field emission electron microscope at an acceleration voltage of 200 kV. The X-ray photoelectron spectra (XPS) were acquired on an ESCALAB MKII with Mg K α (*hv*=1253.6 eV) as the excitation source. Room-temperature UV-vis diffuse reflectance spectroscopy (DRS) were recorded on a Perkin Elmer Lambda 950 UV-vis-NIR spectrophotometer. The Fourier transform infrared (FTIR) experiment was carried out on a Magna-IR750 FTIR spectrometer in a KBr pellet, scanning from 4000 to 400 cm⁻¹ at room temperature. The PL and PL quantum yields were performed by FLUOROLOG-3-TAU fluorescence spectrometer equipped integrating sphere.

Fluorescence detection of Fe^{3+} and Cu^{2+}

 50μ L of the as-synthesized F-g-C₃N₄ dots were injected into 2.0 mL of Tris-HCl (pH 7.4, 10 mM) solution in a spectrophotometer quartz cuvette. Then, Fe³⁺ or Cu²⁺ were added into the probe solution. The PL spectra were recorded after reaction for 10 min at room temperature.

Selectivity measurements

To investigate the possible interference of other cations, the following nitrate salts were used: Ag^+ , Pb^{2+} , Ca^{2+} , Al^{3+} , Hg^{2+} , Mg^{2+} , Zn^{2+} , Na^+ , K^+ , Cd^{2+} , Ni^{2+} , Mn^{2+} and Co^{2+} , F-g-C₃N₄ dots were mixed with the salts solution with appropriate concentration. Then the spectral measurements were taken after the above solution was equilibrated for 10 min.

Detection of Fe^{3+} and Cu^{2+} in lake water

The lake water sample was obtained from a local lake and filtered five using the filter paper to remove the solid suspensions and then filtered through a 0.22 μ m membrane and then centrifuged at 12000 rpm for 20 min several times. The resultant water samples were add with Fe³⁺ and Cu²⁺ and then analyzed with the proposed method.

Results

The FTIR spectra of the bulk $g-C_3N_4$ and $F-g-C_3N_4$ dots were shown in Figure 2B, both of which exhibited typical IR peaks for graphite carbon nitride. The peaks found within the region from 1200 to 1800 cm⁻¹ corresponded to the characteristic stretching

modes of CN heterocycles.^[1] As reported by Larkin, C-C, C-O, and C-N single bonds have very similar force constants,^[2] which resulted in strong coupled C-C, C-O and C-N stretching vibrational peaks. Liao et al.^[3] also reported that the peaks around 1410 and 1060 cm⁻¹ were ascribed to the C-O vibrations in C-OH and C-O-C functional groups, respectively. Thus, the peaks of oxygen-containing species in F-g-C₃N₄ dots should locate in the same region to trigonal C-N(-C)-C (full condensation), amino functional groups (C-NH₂) or bridging C-NH-C species. Besides, due to the low compositions of oxygen atoms in the composites, it is difficult to specifically distinguish C-O species in the F-g-C₃N₄ dots by FTIR spectra. However, minor distinguishment could also be observed at 1234 and 1405 cm⁻¹, which were shifted by 8 and 7 cm^{-1} toward high frequencies after the hydrothermal treatment. The former could be attributed to the $=C(sp^2)$ bending vibration, while the latter should be ascribed to the out-of-phase stretching vibration of N-C(sp³) bond.^[2] The shifts might be caused by the electrophilic effect of the substitutional O atoms adjacent to C-N, resulting in the enhanced strength of C-N covalent bonds and the higher frequencies.

Two models of graphitic carbon nitride structures have been proposed. Model A is the sheet structure of "perfect g-C₃N₄", where each tri-s-triazine unit is connected to three tri-s-triazine units with bridging nitrogen atoms (ternary amine) without any primary amino groups (-NH₂) or secondary amino groups (-NH-). Model B is the sheet structure proposed by Lotsch and Niu.^[13b, 4] The graphitic carbon nitride is composed

of 1-dimensional chains of NH-bridged tri-s-triazine units with both primary and secondary amino groups. The chains adopt "zigzag-type" geometry to reduce the repulsion between the neighboring tri-s-triazine units, and are tightly linked by hydrogen bonds to form a 2-dimensional planar array. In the XPS spectra (Figure 2D), the presence of the tri-s-triazine unit and the -NH₂ group were confirmed.^[5] One of the structural periods in the carbon-nitride layer was 0.68 nm, which was observed in the XRD pattern of Figure 1A. Additionally, the interlayer spacing reported in the literature (0.319 nm) was close to the value for the prepared bulk g-C₃N₄ (0.326 nm). These observations suggested that the structure of the prepared g-C₃N₄ belonged to model B.

The bulk g-C₃N₄, belonged to model B, was unstable and decomposed into F-g-C₃N₄ dots under hydrothermal condition, which meant that the bulk g-C₃N₄ grains contained both stable and unstable carbon nitride domains, as illustrated in Figure S1A (left). The presence of these unstable domains made the bulk g-C₃N₄ fragile and be readily attacked. Some small pieces surrounded by the mixed unstable domains and/or stable domain may further break up during the hydrothermal process, replaced by either primary amino groups (-NH₂) or secondary amino groups (C-NH-C). Meanwhile, other unstable domains preferentially decomposed to form fragments of relatively stable domains, forming the F-g-C₃N₄ dots eventually (Figure S1A, right). This explanation is corroborated by the decreased gallery distance in XRD pattern of F-g-C₃N₄ dots, which means that the F-g-C₃N₄ dots are denser than the bulk g-C₃N₄. The hydrothermal process of the bulk g-C₃N₄ would also release NH₃ gas, which was also confirmed by XPS results of the disappeared peak of amino functional groups at 401.0 eV, as well as the decreased intensity ratio of $N(sp^2)/N(sp^3)$ from 2.81 to 2.32. A combination of the XRD and XPS analyses indicated that the bulk g-C₃N₄ was partially decomposed, that is, the amino functional groups and some sp²-hybridized nitrogen atoms in the bulk g-C₃N₄ nucleus were decomposed to oxygen-containing groups (-OH or C-O-C), as shown in Figure S1B.



Figure S1. (A) Schematic model of formation of F-g- C_3N_4 dots by hydrothermal treatment and (B) reaction scheme of decomposed bulk g- C_3N_4 .



Figure S2. The dependence of I/I₀ on the concentrations of Fe³⁺ (A) and Cu²⁺ (B) ions within the range of 0-50 μ M.



Figure S3. Time-dependent PL spectra of F-g-C₃N₄-Fe³⁺ (A, B) and F-g-C₃N₄-Cu²⁺ (C,

D) aqueous suspension at room temperature.

The selectivity was investigated in the presence of several metal ions, as shown in Figure S4. It is clear that PL intensity had no obviously decrease after several metal ions were added. However, further addition of Fe^{3+} or Cu^{2+} into the system caused a sharp decrease in PL intensity, which indicated that the detection of Fe^{3+} or Cu^{2+} was not interrupted by other metals.



Figure S4. Selective relative PL intensities of F-g-C₃N₄ dots in the presence of several metal ions.(#:Ag⁺, Pb²⁺, Ca²⁺, Al³⁺, Hg²⁺, Mg²⁺, Zn²⁺, Na⁺, K⁺, Cd²⁺, Ni²⁺, Mn²⁺, Co²⁺)

The Fe³⁺ or Cu²⁺ probe was also applied to a natural system by analyzing the water samples obtained from the Dongpu Lake of Hefei, Anhui province, China. After pretreatment, the resulting water samples were concentrated with Fe³⁺ or Cu²⁺ ion at different concentration levels, which were then analyzed by the above method. It can be seen that the water samples in the presence of different concentrations of Fe³⁺ or Cu²⁺ ions led to a significant decrease of the PL intensity. In spite of the interference from numerous minerals and organics existing in lake water, this sensing platform can still distinguish the fresh lake water from water that spiked with 0.5µM Cu²⁺ and 0.6µM Fe³⁺, satisfying the sensitivity requirement of Cu²⁺ and Fe³⁺ ion detection for drinking water (20µM and 5µM) defined by EPA. These results implied that the Fe³⁺ or Cu²⁺ fluorescent probe had potential application in real water samples.



Figure S5. PL intensities change of F-g-C₃N₄ dots in the presence of different Cu²⁺ and Fe³⁺ concentrations in natural water sample from Dongpu Lake of Hefei, Anhui province, China.

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