Enhanced fluorescent effect of graphitic C₃N₄@ZIF-8 nanocomposite contribute to its improved sensing capabilities†

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A novel graphitic carbon nitride (g-C₃N₄)@ZIF-8 nanocomposite was synthesized by a facile approach and applied as a fluorescent sensor. The fluorescent quenching and enhancing effect of g-C₃N₄@ZIF-8 nanocomposite was explored for potential applications in sensing metal ions and solvents based on photoluminescence (PL) measurements. Compared with g-C₃N₄ nanosheets alone, the combined g-C₃N₄@ZIF-8 nanostructure greatly improved the sensitivity for the detection of metal ions due to the special fluorescent quenching effect. In particular, the sensitivities of the detection of Cu²⁺ and Ag⁺ improve from 29.1 to 11.2 ppm and from 40 to 16.5 ppm, respectively, which were significantly improved compared to that of g-C₃N₄ nanosheets alone. The sensitivity could increase about 100% and 250% for Cu²⁺ and Ag⁺ by the g-C₃N₄@ZIF-8. The limit of detection (LOD) for Cu²⁺ and Ag⁺ by g-C₃N₄@ZIF-8 was 11.2 ppm and 13.2 ppm, respectively. Both g-C₃N₄ nanosheets and g-C₃N₄@ZIF-8 nanocomposite can be used for distinguishing Fe²⁺ and Fe³⁺ in solutions. The LOD of Fe²⁺ by g-C₃N₄@ZIF-8 was as low as 65.4 ppm. On the other hand, the relative increased luminescence of g-C₃N₄@ZIF-8 to the g-C₃N₄ in tetrahydrofuran (THF) was selective, which was successfully applied for detecting this specific solvent. An excellent linear relationship (0–1.0 v/v of THF/water) between the THF fraction and PL intensities was obtained. These results demonstrate that the g-C₃N₄@ZIF-8 nanocomposite provide a convenient and novel approach for the enhance fluorescence detection of metal ions and distinguishing of specific solvents.

1 Introduction

Heavy metal ions and their derivatives are of great current interest owing to their severe adverse impact on the environment and human health.¹ For example, copper is an essential trace element for the living organisms, but an excessive copper ion is toxic when it accumulated in living organism.² Similar to copper ion, silver ion can accumulate in the living organism and cause severe physiological problem.³ Through various absorption channels such as soil, reservoir water, food, these heavy metal ions can gather in developing brains, or binding to protein/peptide, leading to debilitating diseases.⁴ As a result, a variety of methods have been developed for detecting the harmful heavy metal ions, for example, coupled plasma mass spectroscopy,⁵ atomic absorption spectroscopy,⁶ Raman spectroscopy,⁷ electrochemical method,⁸ and fluorescent methods.¹ Among these methods, fluorescent method is facial and highly sensitive.⁹ Organic dyes and semiconductor quantum dots are the most commonly used fluorescent probes.⁴ However, these materials suffer from some intrinsic detects such as easy oxidation, photobleaching, high toxicity and cost, which hampered their practical applications greatly.¹⁰ Therefore, it is highly desirable to develop novel materials to address these issues, which are suitable to be used as sensitive elements for the detection of metal ions.

Metal–organic frameworks (MOFs), self-assembled by the coordination of metal ion/cluster with organic linkers, is a new porous material.¹¹ The structural rigidity, high porosity, and turntable component support its potential applications in a variety of fields, such as gas separation and storage,¹² catalysis,¹³ sensing,¹⁴ and biomedical applications.¹⁵ ZIF-8 is often composited by a zinc ion center and 2-methylimidazole (Hmim) ligand, which belongs to the superfamily of MOFs and possess a sodalite (SOD)-type structure.¹⁶ Pyridyl nitrogen sites have been reported to be able to selectively bind to metal ions and used as metal ion sensor.¹⁷ With similar structure, imidazole-based conjugated polymer has also been reported to be used as a metal ion sensor.¹⁸ Since the imidazole nitrogen has specific affinity to metal ions, ZIF-8 can be used for detecting the metal ions.¹⁹ However, the fluorescence of ZIF-8 is low and thus limits its selectivity and detection sensitivity. Thus, ZIF-8 encapsulated AlQ₃ (tris(8-hydroxyquinoline)-aluminium), FITC
(fluorescein isothiocyanate) and Eu(n)-complex-functionalized Fe2O3 and Zn2GeO4:Mn2+ nanorods were reported as a luminescent ions sensor.20–22

Recently, graphitic carbon nitride (g-C3N4) has attracted much attention due to its decisive advantages such as easy preparation, high thermal stability, high visible photocatalysis activity, and high water splitting activity.23–25 Fluorescent g-C3N4 quantum dots used for detecting heavy metal ions have been reported very recently.26–28 The selectivity and sensitivity of g-C3N4 for detecting copper ions are reasonable because the photoinduced electron transfer (PET) between the CB of g-C3N4 to the complexed Cu2+ leading to the fluorescent quenching.26 Additionally, g-C3N4 decorated ball-like Co3O4 composite exhibited 1.6 times higher sensitivity than that of pure Co3O4.29 The g-C3N4/Bi2MoO6 composite which displayed nearly 3-fold and 6-fold enhanced photocurrent intensity than pure g-C3N4 and Bi2MoO6, could be applied in copper ion sensor with a linear range from 3 nM to 40 μM by a photoelectrochemical method.23 The C3N4–tyrosinase hybrid was a sensitive fluorescent probe for the detection of dopamine with detection limit as low as 3 × 10–8 mol L–1.22 Many carbon nitride nanohybrid, including C3N4/metal oxide nanoparticles, metal nanoparticles, metal–organic frameworks, graphene have been applied in the sensor application.23–28

It is thus tempted to combine the advantages of g-C3N4 and ZIF-8 to develop novel materials that are suitable for sensing metal ions. Herein, a facile method was developed for the preparation of g-C3N4@ZIF-8 nanocomposite that is suitable to be used as sensitive elements for the detection of metal ions and solvents. The morphology and structure of g-C3N4@ZIF-8 nanocomposite was characterized. Photoluminescence (PL) measurements were carried out to test the performance of g-C3N4@ZIF-8 nanocomposite for sensing metal ions. The fluorescent quenching effect can not only be found during sensing copper and silver ions, but also be observed during sensing Fe3+. On the contrary, the Fe3+ has little fluorescent quenching effect. The comparative phenomenon on Fe2+ and Fe3+ fluorescent quenching effect could be used for distinguishing the Fe2+ and Fe3+. In addition, compare to other solvents, tetrahydrofuran (THF) has the most enhanced fluorescence for g-C3N4@ZIF-8, which could be potentially applied for distinguishing this THF from other solvents.

2 Materials and methods

2.1 Materials

Melamine, Zn(NO3)2·6H2O, HgCl2, CaCl2, NaCl, FeCl3, FeCl2, KCl, MnCl2·4H2O, Li(CH2COO)2, SnCl2, CoCl2·6H2O, AgNO3, CuCl2, Ni(NO3)2·6H2O were ordered from Sinopharm Chemical Reagent Co., Ltd. Tetrahydrofuran (THF), 2-methylimidazole (Hmim), dimethylformamide (DMF), ethanol, methanol, and acetone were purchased from Sigma Aldrich. All the other chemicals were analytical pure grade or better quality. Deionized water (18.2 MΩ cm–1) produced by a Milli-Q system (Bedford, MA) was used throughout.

2.2 Synthesis of the g-C3N4 nanosheet

The g-C3N4 nanosheet was synthesized according to previous report.29 For the first, bulk C3N4 was firstly synthesized by pyrolysis of melamine. Typically, 5 g melamine was heated to 550 °C with a ramp rate of 3 °C min–1 and maintained at the final temperature for 4 h in the air environment. For the next, the resultant yellow powder was milled for thermal treatment. The thermal treatment was conducted in an open ceramic container with a heating rate of 5 °C min–1 to 500 °C and maintained for 2 h. Through the process, the yellow powder turned into a light-yellow product.

2.3 Synthesis of the g-C3N4@ZIF-8

Graphitic C3N4@ZIF-8 was synthesis by an in situ method. Briefly, 10 mg of g-C3N4 was firstly dissolved into a 5 mL of 75 mM Hmim methanol solution and stirred for 10 min. Then, 5 mL of 150 mM Zn(NO3)2·6H2O methanol solution was added. For the next, the solution was left undisturbed for 2 h. The finally product was collected by the centrifugation method and washed with methanol for 3 times.

2.4 PL measurements

For sensing various metal ions, 0.2 mL of 1 mM g-C3N4@ZIF-8 DMF solution was added to 6 mL of DMF to form a homogeneous solution. Certain volumes of 1 mM DMF solution with metal ions were added to the g-C3N4@ZIF-8 solution. The excitation wavelength was 330 nm and the emission peak were 450 nm. Since silver ions can be reduced by DMF,29 silver ion test was conducted in aqueous solution.

For sensing properties with respect to various solvents, 0.2 mL g-C3N4@ZIF-8 solution was added to 6 mL solvent (DMF, distilled water, acetone, methanol, ethanol, THF). After shaking 2 min, 3 mL of the solution was used for PL measurements.

2.5 Characterization

X-ray diffraction (XRD) patterns of the samples were recorded on a D2 PHASER (BRUKER) diffractometer with Cu Kα irradiation, 30 kV, 10 mA. The structure and morphology of the samples were determined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) performed on PHILIPS XL30 and PHILIPS Tecnai 12, respectively. Fourier transform infrared spectroscopy (Spectrum 100, PerkinElmer) spectrum of samples were recorded using a KBr disk in the range of 4000 to 400 cm–1. Nitrogen physisorption isotherms were measured at 77 K on automatic Nova Station A. The UV-visible spectrum was performed on Agilent Cary 4000. The PL spectroscopy of the samples was carried on Hitachi F 4600.

3 Results and discussion

3.1 Characterization of g-C3N4@ZIF-8

Enable to test the PL spectrum, the stability of the nanoparticles is of great importance. Therefore, the dispersion of g-
C₃N₄@ZIF-8 nanocomposite and g-C₃N₄ nanosheet in DMF solution was investigated at different times. The result indicates that the g-C₃N₄@ZIF-8 nanocomposite solution was more homogeneous and stable than that of bulk g-C₃N₄ solution (Fig. 1), which indicating the PL intensity change was only induced by the metal ions but not the nanoparticles sedimentation. This suggested a good stability of g-C₃N₄@ZIF-8 nanocomposite was suitable for PL spectrum measurements.

The morphologies of g-C₃N₄ nanosheet and g-C₃N₄@ZIF-8 were observed by SEM and TEM, respectively. As shown in Fig. 2, the results indicate the g-C₃N₄ dispersed well and was the analogue of wrinkled graphene. After in situ decorated with ZIF-8, small nanoparticles assembled on the g-C₃N₄ nanosheet, leaving fewer margins. This ensured that the metal ions or solvents must cross the pores of ZIF-8 to interact with g-C₃N₄.

The high resolution TEM images indicated that all nanoparticles assembled on the nanosheet with average diameter of 50 nm. In addition, N₂ absorption and desorption isotherms of the g-C₃N₄@ZIF-8 (Fig. S1†) further confirm its surface area and the pore structure.

The structure of the nanocomposite was confirmed by XRD pattern. As shown in Fig. 3a, a peak of 7.0° was the characteristic of ZIF-8. The sharp peak at 27.7° corresponded to the nanosheet of g-C₃N₄. The further FTIR spectrum confirmed the component (Fig. 3b). The sharp peak at around 810 cm⁻¹ was originated from heptazine ring system. The peaks range from 900 to 1800 cm⁻¹ were associated to C–N–C or C–NH–C units. The peak at 421 cm⁻¹ was attributed to Zn–N stretching. And peaks 1350–1500 cm⁻¹ were attributed to the entire ring stretching of imidazole. The UV-visible spectra results indicated that after decorated with ZIF-8, the absorption edge and peak of g-C₃N₄ did not shift (Fig. 3c). The strong peak at 319 nm was the characteristic peak of g-C₃N₄. Besides this peak, g-C₃N₄ also had two peaks at 370 nm and 380 nm, respectively. When excited at 320 nm, the emission peak appeared at 450 nm, which indicated the nanocomposite was fluorescent. To check whether the g-C₃N₄@ZIF-8 was an excitation-independent PL material, different excitation wavelength was applied. As showed in the Fig. 3d, when the excitation wavelength changed from 310 nm to 370 nm, the PL spectra did not shift, and a peak around 450 nm was invariable.

### 3.2 Detection of metal ions

Screening experiments with different metal ions (66 ppm) were carried out by investigating the changes in PL intensity of the g-C₃N₄@ZIF-8. As showed in Fig. 4, the PL intensities of g-C₃N₄@ZIF-8 were greatly decreased by Fe²⁺, Cu²⁺ and Ag⁺, while the other ions presented less or no effect. This indicated that g-C₃N₄@ZIF-8 was sensitive to the specific ions and can be used as sensitive elements for the fluorescent detection of metal ions. The sensitivity of g-C₃N₄@ZIF-8 for Fe²⁺, Cu²⁺ and Ag⁺ may be due to the higher binding affinity of these ions to N of the ZIF-8 and g-C₃N₄. Due to the high porosity of ZIF-8, a large

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**Fig. 1** Dispersion of g-C₃N₄@ZIF-8 nanostructure (left) and bulk g-C₃N₄ (right) in DMF solution at different times: (a) 0 min, (b) 10 min.

**Fig. 2** (a) SEM image and (b) TEM image of g-C₃N₄ nanosheets; (c) SEM image and (d) and (e) TEM images of g-C₃N₄@ZIF-8 nanostructures.

**Fig. 3** (a) XRD patterns and (b) FTIR spectra of g-C₃N₄ and g-C₃N₄@ZIF-8; (c) UV-visible spectra of g-C₃N₄ and g-C₃N₄@ZIF-8; (d) PL spectra of g-C₃N₄@ZIF-8 with excitation of different wavelengths.

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number of metal ions can interact with g-C3N4. Therefore, g-
C3N4@ZIF-8 had a higher sensitivity than g-C3N4, especially for
Ag+ and Cu2+. Additionally, using DMF replacing water could
limit the hydrolysis of transition metal ions.

To evaluate the g-C3N4@ZIF-8 and g-C3N4’s sensitivities
ward different concentrations of Cu2+, Ag+ and Fe2+, PL
intensities were monitored by the titration method. The
enhanced selectivity was observed for Cu2+ and Ag+. Therefore,
these two ions were tested by g-C3N4@ZIF-8 and g-C3N4, indi-
vidually. It can be seen from Fig. 5a and b that the PL intensity
of g-C3N4@ZIF-8 and g-C3N4 decreased gradually with
increasing of Cu2+ concentrations. The limit of detection (LOD)
for sensing Cu2+ by g-C3N4@ZIF-8 was about 11.2 ppm because
less Cu2+ did not influence the PL intensity. A linear relation-
ship between Cu2+ concentration and PL intensity in the range
of 5 ppm to 11 ppm was obtained (Fig. 5g). The LOD of Cu2+ was
lower than the maximum allowable level of Cu2+ (~20 μM) in
the drinking water regulated by US Environmental Protection
Agency (EPA). While for the g-C3N4, the LOD for sensing Cu2+
was about 22.8 ppm. It indicated that the using of g-C3N4@ZIF-8
for sensing Cu2+ was able to increase the LOD by about 100%.

Organic dyes were the most commonly used sensing mate-
rial to distinguish Fe2+ and Fe3+ due to its convenient and
selectively. However, organic dyes are only specific to one kind
of metal ions, which can’t be used for the detection of several
kinds of metal ions. In this work, g-C3N4 nanosheet and g-
C3N4@ZIF-8 can be easily prepared, which show the capability
of sensing Fe2+ with high selectivity (Fig. 5e and f). It indicated
that the LOD of Fe2+ by g-C3N4@ZIF-8 was about 65.4 ppm with
a linear range of 0–30 ppm.

3.3 Detection of specific solvents
Changes in the PL intensities of g-C3N4@ZIF-8 and g-C3N4 in
different solvents were also investigated. Various solvents were
tested as a comparison to the PL intensity of g-C3N4@ZIF-8 and g-
C3N4 in DMF. The PL intensity of H2O was same to the DMF,
indicating the replace of DMF to H2O for the further solvent
sensor. As shown in Fig. 6a, the relative PL intensities of g-
C3N4@ZIF-8 to g-C3N4 was 13.2 ppm and 33.8 ppm, respec-
tively. The LOD for sensing Ag+ by g-C3N4@ZIF-8 was enhanced
by about 250%. A linear response was also obtained for sensing
Ag+ by g-C3N4@ZIF-8 (Fig. 5h).

Fig. 5 (a) and (b) PL intensity evolution of (a) g-C3N4@ZIF-8 and (b) g-
C3N4 in the presence of different concentrations of Cu2+; (c) and (d) PL
intensities of (c) g-C3N4@ZIF-8 and (d) g-C3N4 in the presence of
different concentrations of Ag+; (e) and (f) PL intensity evolution of
(c) g-C3N4@ZIF-8 and (d) g-C3N4 in the presence of different
concentrations of Fe2+; linear regression line of PL intensities of g-
C3N4@ZIF-8 for sensing (g) Cu2+, (h) Ag+ and (i) Fe2+. I and I0 are PL
intensities of in the presence and absence of metal ions, respectively.
4 Conclusions

In summary, g-C₃N₄@ZIF-8 nanocomposite was facile prepared, characterized and applied for the enhanced fluorescent detection of metal ions and solvents based on the PL measurement. The enhanced selectivity of g-C₃N₄@ZIF-8 to g-C₃N₄ was obvious in detecting Cu²⁺ and Ag⁺. The sensitivities for the detection of metal ions and solvents.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant No. 31470956, 31661143030, 31700859, 51861145307), the Doctoral Fund of Education Ministry of China (Grant No. 2016M602832), and the Fundamental Research Funds for the Central Universities.

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Conflicts of interest

There are no conflicts to declare.
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