Luminescent AIZS-GO nanocomposites as fluorescent probe for detecting copper (II) ion

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Abstract
A selective copper (II) sensor based on graphene oxide (GO) modified Ag-In-Zn-S (AIZS) quantum dots (QDs) was proposed. The fluorescence of the water-soluble AIZS QDs was quenched after addition of Cu²⁺ ion, which was triggered by the aggregation of the QDs in the form of R-COO-(Cu²⁺)-OOC-R, as verified by the TEM and FTIR. The fluorescence probe can be applied to detect Cu²⁺ ion in a wide concentration range of 0-850 μM based on the degree of fluorescence quenching, with its limitation of detection (LOD) and R² of 0.18μM and 0.99, respectively. Moreover, the nanosensor can distinguish Cu²⁺ ion from other ions, offering great potentials in copper (II) determination in drinking water.

1. Introduction
Copper element is one of crucial transition metallic elements to human health and many living tissues. It is physiologically essential in various aspects such as bone formation, cellular respiration, and connective tissue development and serves as the significant catalytic cofactor for hemoglobin, elastin, and collagen [1, 2]. In the recent decades, quantum dots (QDs), zero-dimensional nanomaterials, are ever-increasingly attractive to scientists, and have already become a hot issue [3-5]. Compared with traditional organic dyes and lanthanide probes, such materials possess broad absorption spectra, tunable wavelength, big Stokes shift, fueled by the quantum confinement, and provide a new method to the quantification of heavy metals [6-9]. Up to now, several types of functionalized QDs have been used for selective ion recognition such as silver, copper, cadmium, and mercury [10-16]. Phase transfer by thiol-derivative molecules into water-soluble QDs always renders low quantum yield (QY) (~1%), which exerts detrimental influence on the sensitivity of these developments [17]. In addition, the time response of theses sensors is relatively long, which is unfavorable in practical applications.

In the work, water-soluble AIZS QDs transferred by GO were synthesized and used as fluorescent probe for copper (II) detection. The AIZS-GO nanocomposites have a QY as high as (~25%), which is much higher than the thiol-derivative modified water-soluble QDs mentioned above. Its pH value effect and selectivity toward copper were discussed, and quenching mechanism was experimentally verified by the Fourier transform infrared (FTIR) spectra and TEM images. The fluorescence probe has a wide detection span of 0 - 850μM, detection of limitation of 0.18μM, and the fast time response of one minute, which is superior to that of the probes mentioned above. This offers great potentials in copper (II) detection in drinking water.

2. Experimental

2.1. Copper (II) studies
The quenching effect of Cu$^{2+}$ ion on the fluorescence of GO AIZS QDs was performed as following procedures. Stock solution of copper (II) (50 mM) was prepared by the dissolution of copper sulfate in deionized water. 2 mL as-prepared water-soluble AIZS was added to a 10 mL volumetric flask with the following addition of some Tris-HCl buffer solution to adjust the solution pH value at 7.4, and then 3 μL stock solution. The mixture was finally diluted to 5.0 mL by deionized water and the final concentration of Cu$^{2+}$ ion and AIZS QDs are 30 μM and 0.5 mg/mL, respectively. The fluorescence intensity was measured under the excitation wavelength of 365 nm at the room temperature at different response time using a fluorescence spectrophotometer with an accelerating voltage of 200 kV. The slit widths of excitation and emission are 10 nm and 10 nm, respectively.

2 mL as-prepared water-soluble AIZS QDs, Tris-HCl buffer solution and different amount of Stock solution of copper (II) were sequentially added into a 10 mL volumetric flask. After thoroughly shaking for one minute, the fluorescence was recorded by a fluorescence spectrophotometer in the same operation conditions as the above.

3. Results and discussion

3.1. Characteristics and optical properties of AIZS-GO QDs

The absorption and fluorescence spectra were shown in Fig.1 (A). We can see that the absorption spectra of AIZS (black curve) and AIZS-GO (red curve) QDs are almost identical in shape. The PL spectrum of AIZS-GO QDs (purple curve) keeps nearly the same as AIZS QDs (blue curve) after phase transfer, and there is no wavelength shift in PL spectrum but only a small difference is PL intensity, which is mainly due to the fact that the surface traps were exposed to the aqueous solution and the existence of blackish GO. The full width at half maximum (FWHM) fluorescence spectra of AIZS and AIZS-GO QDs were both about 100nm and symmetric, indicating that they were homogeneous. Therefore, we can draw a conclusion that phase transfer by GO did not affect its optical properties. The size and morphology of AIZS-GO QDs were evaluated by TEM as shown in Fig.1 (B). From Fig.1 (B) and (D), we can clearly observe that the average diameter is about 5.2 nm and the QDs are monodisperse. All the characterizations indicate that AIZS-GO QDs were successfully synthesized.

![Fig.1. (A) Absorbance and PL spectrum of AIZS and AIZS-GO QDs; (B) TEM image of AIZS-GO QDs.](image)

3.2. Copper (II) studies

Time response of the AIZS-GO QDs in 10 μM Cu$^{2+}$ ion was studied (data not shown). It is clear that the PL keeps stable after one minute of the addition of copper (II), which indicates that the AIZS-GO QDs can be used as a fast time response sensor. Time response (1 minute) is much faster than reported in [18] (~10 minutes) and [19] (~20 minutes). Therefore, the PL in the following experiments was recorded at...
one minute after the addition of copper (II).

The PL dependence on Cu$^{2+}$ ion was analyzed by adding different Cu$^{2+}$ ion concentration into probe solution, as shown in Fig.2 (A). We can observe that the PL intensity decreased after addition of copper (II) with an obvious red shift triggered by increasing the size scale of QDs, and when copper (II) concentration was larger than 850 $\mu$M, there was no significant quenching anymore in the PL intensity in that binding rate between carboxyl groups and Cu$^{2+}$ ion decreased with the increase of copper (II) concentration, and gradually saturated.

Upon the addition of Cu$^{2+}$ ion into the solution, the Cu$^{2+}$ ion was drawn to the QDs physically due to the negatively charged carboxyl groups on GO, and then chemical reaction occurred between carboxyl groups and the added Cu$^{2+}$ ion. As a result, the carboxylate copper complex in the form of R-COO-(Cu$^{2+}$)-OOC-R was formed, aggregating the QDs, and the size scale of AIZS-GO QDs ion became larger, an indication of the quenching of fluorescence [20]. This quenching mechanism was experimentally proved by the TEM image as shown in Fig. 2. It can be seen that the average diameter of AIZS-GO QDs in the presence of 850 $\mu$M Cu$^{2+}$ ion was 21.7 nm, which is larger than that in solutions without Cu$^{2+}$ ion, verifying the quenching mechanism.

**Fig. 2** TEM image of the QDs in the presence of 850$\mu$M Cu$^{2+}$.

**Fig. 3** (A) The fluorescence spectra of the QDs after one minute of the addition of different Cu$^{2+}$ concentrations. The Cu$^{2+}$ concentrations from 1 to 16 were 0, 10, 30, 60, 100, 150, 200, 250, 300, 350, 400, 500, 550, 650, 750, 850 $\mu$M, respectively; (B) the calibration curve for the PL intensity of the QDs with the function of Cu$^{2+}$ ion, extracted from peak PL intensity in Fig. 3 (A).
The relationship between $I_0/I$ and Cu$^{2+}$ ion concentration is shown in Fig. 3 (A). The PL dependence on Cu$^{2+}$ ion concentration can be best expressed by the following Stern-Volmer equation:

$$I_0/I = 1 + K_{SV}[Q]$$

Where $I_0$ and $I$ are the fluorescence intensity of quantum dots in solution without and with a given concentration of copper(II) respectively. Herein, $K_{SV}$ is the Stern-Volmer constant (slope), $4.041 \times 10^3$ /M in this study. As shown in Fig. 3 (B), a good linear relationship between $I_0/I$ and Cu$^{2+}$ ion concentration is clearly observed with the $R^2$ of 0.99 and a broad linear span of up to 850μM which is larger than ones reported by others [21-23]. The limitation of detection (LOD) is defined by $3\sigma/K_{SV}$, where the $\sigma$ and $K_{SV}$ are standard deviation ($n=10$) and the sensitivity of the calibration curve (slope), is 0.18 μM.

3.3. The selectivity of AIZS-GO QDs

The selectivity toward Cu$^{2+}$ ion was evaluated by measuring PL intensities of QDs in the presence of six other kinds of heavy metal ions of 500 μM in the same experimental condition as the Cu$^{2+}$ ion as shown in Fig. 4. It can be seen that in the presence of other 500 μM metal ions, the PL intensity of the QDs probe had slight changes, possibly due to the relatively weak binding ability between the carboxyl groups and other metal ions, which indicates that other cations exert small influence on determination for Cu$^{2+}$ ion, making the solution sensor in this paper a selective and practical probe.

![Fig. 4 Relative PL intensity of the QDs at pH=7.4 in the absence (red column) and presence (black column) of 500 μM solution containing a specified metal cation.](image)

4. Conclusions

In this work, cadmium-free AIZS QDs in aqueous solution were successfully used as a fluorescent probe for Cu$^{2+}$ ion detection in the samples. In the presence of Cu$^{2+}$ ion, the PL quenched due to the quantum dots aggregation caused by carboxylate copper complex formation through reaction between carboxyl group and Cu$^{2+}$ ion, and the relationship between $I_0/I$ and Cu$^{2+}$ ion concentration can be well described by the Stern-Volmer equation. The fluorescent probe possesses good selectivity toward Cu$^{2+}$ ion and a wide linear range of 0-850μM with short time response within one minute, which offers great potentials in copper (II) detection in drinking water.

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