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RESEARCH PAPER

Detection of Lead Ion Based on Aggregation-induced Emission of Copper Nanoclusters

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Abstract: A turn-on fluorescence analysis method was established for detection of Pb^{2+} based on aggregation-induced emission. Glutathione-protected non-noble metal copper nanoclusters (Cu NCs@GSH) showed nearly no fluorescence. However, the fluorescence intensity of Cu NCs@GSH was remarkably improved in the presence of Pb^{2+} and showed bright orange fluorescence. A fluorescence method for detection of Pb^{2+} was established based on this principle. The fluorescence change of the Cu NCs@GSH solution showed a linear relationship with Pb^{2+} concentration within the range of 200–700 μM. The limit of detection was 106 μM (S/N = 3). This method is simple, rapid and highly selective, and can be used for the visual qualitative detection of Pb^{2+} under ultraviolet (UV) lamp.

Key Words: Aggregation-induced emission; Copper nanoclusters; Lead ion (II)

1 Introduction

Fluorescent metal nanoclusters (NCs) as a new class of fluorophores was widely applied to detection of metal ions[1–5] and biological small molecules[6–9], cell imaging[10–12], and environment analytical[13] etc. Deng *et al*[14] found Met-Au NCs could serve a fluorescent "turn-off" sensor for the selective detection of Cu^{2+}. Gao et al prepared Cu NCs with tannic acid as protective ligands to detect Fe^{3+} based on strongly quenching through an electron transfer mechanism[15]. Yang et al prepared Cu NCs with L-cysteine as a template for sensitive and selective detection of Hg^{2+} on the basis of the interactions between Hg^{2+} and *L*-cysteine[16]. Generally, many methods have been successfully developed for detecting metal ions based on fluorescence-quenching mechanism. However, due to the ubiquitous nature of fluorescence quenching, these methods did not show obvious advantages in terms of sensitivity or selectivity[17].

In 2001, Tang group[18] first discovered that silicon miscellaneous cyclopentadiene derivatives exhibited a dramatic photoluminescence enhancement in their solid phase, which was called aggregation-induced emission (AIE). Currently, AIE was not only used in the design of the synthesis of strong fluorescent NCs, but also showed broad application prospects in the chemical sensor, biological fluorescent probes and so on[19,20]. Dou *et al*[21] developed a new approach to synthesize highly fluorescent Au@Ag NCs via AIE based on the weakly fluorescent parental Au NCs in 2014. Guo *et al* reported a label-free optical probe for Ca^{2+} detection using the AIE based on Au(I)-thiolate complexes[22]. Li *et al*[23] discussed a possible mechanism that Ag^{+} could enhance the fluorescence intensity, and established a highly sensitive and selective method to detect trace amount of Ag^{+} using AIE-Au NCs as a sensor. For metal ions detection, "turn-on" fluorescence analysis method had distinct advantages in terms of sensitivity or selectivity, because it produced positive response signal in the presence of target material. Extensive AIE research focused on the noble Au NCs and Ag NCs, however, there were few reports about Cu NCs. Jia *et al*[24,25] first found that Cu NCs could carry out AIE

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by some kind of solvent. So far, metal ions-induced-aggregation was not reported.

Herein, we found that the fluorescence intensity of the original weakly fluorescent Cu NCs could be enhanced by Pb^{2+} based on AIE. Thereby a fluorescence method for "turn-on" detection of Pb^{2+} was established based on this principle. Cu NCs@GSH as probe could be used for the visual qualitative detection of Pb^{2+} under ultraviolet (UV) lamp.

2 Experimental

2.1 Instruments and reagents

The fluorescence measurements were carried out using an F97Pro fluorescence spectrophotometer (Lengguang Tech, Shanghai, China). The transmission electron microscopy (TEM) images were acquired on a Tecnai G2 F20 S-TWIN TEM (FEI). The pH value was measured by a PHS-3C pH meter (Shanghai Precision Scientific Instruments Co., Ltd., China).

L-glutathione reduced (GSH), $Cu(NO_3)_2{\cdot}3H_2O$, $ZnCl_2$, $CrCl_3$, $CoSO_4{\cdot}7H_2O$, $MnCl_2{\cdot}4H_2O$, $NiSO_4{\cdot}6H_2O$ and $Fe(NO_3)_2{\cdot}9H_2O$ were purchased from Sangon Biotech Co., Ltd. (Shanghai, China). $Pb(NO_3)_2$ was obtained from Sigma-Aldrich Co., Ltd. (Shanghai, China). $CaCl_2$ were purchased from Damao Reagent Co., Ltd. (Tianjin, China). $MgCl_2$ were from Xilong Chemical Co., Ltd. $Hg(NO_3)_2{\cdot}H_2O$ was from J&K Chemicals. All the materials were used without further purification.

2.2 Synthesis of Cu NCs@GSH

Cu NCs@GSH was synthesized reference to the literature method[11]. Briefly, the Cu NCs were synthesized by mixing 5 mL of $Cu(NO_3)_2{\cdot}3H_2O$ aqueous solution (20 mM) with 5 mL of GSH solution (80 mM) at room temperature, and a yellow solution was obtained. Then, NaOH solution (1 M) was added to adjust the pH of reaction solution to 5. The mixture gradually changed to pale yellow. The obtained solution was subjected to ultrafiltration using 3000 MW filter to remove the unreacted GSH and Cu^{2+}.

2.3 Measurement

The purified Cu NCs solution was diluted by 10 times before using. Then 50 μL of Pb^{2+} with different concentrations were mixed with 450 μL of 10-fold diluted Cu NCs. The fluorescence spectra were recorded on a fluorescence spectrometer at 360 nm as excitation wavelength.

3 Results and discussion

3.1 AIE of Cu NCs@GSH

As shown in Fig.1A, the fluorescence emission of the Cu NCs solution was set at 624 nm when the excitation wavelength was set at 360 nm, which was consistent with the previous references. TEM image of Cu NCs@GSH was depicted in Fig.1B. There were no larger metal particles or aggregation, and the average size was about 2.6 nm. These results demonstrated that Cu NCs were successfully synthesized.

As shown in Fig.2a, Cu NCs@GSH solution diluted by 10 times showed almost no fluorescence under UV light (λ = 365 nm). The transparent solution changed to milky in the presence of 400 μM Pb^{2+}, and intense orange-yellow fluorescence emission was observed, as shown in Fig.2b. The intensity of fluorescence enhanced instantly by 9-fold. The fluorescence emission was blue-shifted from 624 nm to 607 nm. This phenomenon might attribute to strong electrostatic adsorption between Pb^{2+} and carboxyl group on the surface of Cu NCs@GSH[26], which made the GSH-Cu compound in the solution close to each other by GSH-Pb^{2+}-GSH[27,28], and the charge transferred from ligands to metal ions, which resulted in fluorescence intensity being enhanced instantly[29]. Additionally, Luo *et al*[30] pointed out that the emission wavelength could blue shifted due to the closer interactions between Au^+ and Au^+ on the surface of Au NCs when AIE had been occurred. We speculated that the blue-shift of emission band was attributed to the stronger interactions between Cu^+ and Cu^+ on the surface of Cu NCs.

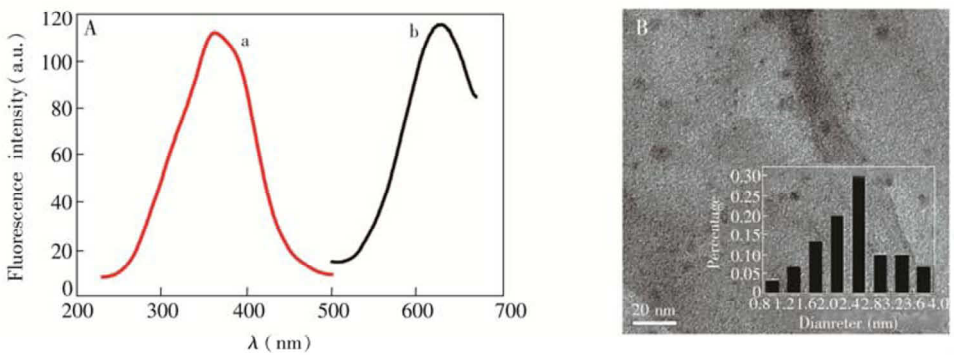

Fig.1 Fluorescence excitation (a) and emission (b) spectra (A) and TEM image (B) of glutathione protected copper nanoclusters (Cu NCs@GSH). Inset: distribution of particle size of Cu NCs@ GSH