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Synthesis of yeast extract-stabilized Cu nanoclusters for sensitive fluorescent detection of sulfide ions in water

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ABSTRACT

In this work, we have presented a novel strategy to utilize as-synthesized yeast extract-stabilized Cu nanoclusters (Cu NCs) for sensitive and selective detection of S^{2-}. The fluorescence intensity of Cu NCs was enhanced significantly in the presence of both $Na_2S_2O_8$ and S^{2-}. By virtue of this specific response, a Cu NC-based fluorescent turn-on sensor was developed, which allows the detection of S^{2-} in the range of 0.02–0.8 μM with a detection limit of 10 nM. The enhancing mechanism was also discussed based on fluorescence decay, transmission electron microscopy (TEM) and dynamic light scattering (DLS) studies, indicating that S^{2-} enhanced the Cu NCs emission mainly through sulfide-induced aggregation of Cu NCs. Furthermore, we demonstrated the usability of the present approach for the detection of S^{2-} in water samples, which illustrates its great potential for the environmental monitoring and water quality inspection fields.

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1. Introduction

Detection of sulfide ion (S^{2-}) is important in the assessment of environmental quality due to its wide distribution in natural water and wastewater. As a traditional toxic pollutant, excessive existence of S^{2-} can cause serious environmental problems and poses hazards to living systems as well as human health (Bagarinao, 1992; Morse et al., 1987; Xiong et al., 2015). It has been reported that exposure to low concentration of S^{2-} could cause dizziness, while contact with high concentration of S^{2-} would lead to unconsciousness, irritation in mucous membranes, permanent brain damage or even asphyxiation (Fiorucci et al., 2005; Peng et al., 2011). At present, several techniques have been reported for the detection of S^{2-}, such as electrochemical methods (Salimi et al., 2006; Liu et al., 2008), gas chromatography (Antonisse and Reinhoudt, 1999), ion chromatography (Giuriati et al., 2004), fluorescence (Cao et al., 2011; Chen et al., 2011; Cui et al., 2013; Liu et al., 2012; Yu et al., 2013) and chemiluminescence methods (Huang et al., 2007). Among them, fluorescence-based assay shows great advantages over other methods due to its high sensitivity, rapid detection and simplicity of operation. Especially, recently-developed fluorescent nanomaterials offer new opportunities for establishing novel S^{2-} fluorescence analysis methods due to their excellent photophysical properties and good biocompatibility (Xiong et al., 2015).

Fluorescent metal nanocluster is a novel class of ultrasmall fluorescent nanomaterials composed of several to a few hundreds of metal atoms. They possess many attractive features including excellent photostability, large stokes shifts, low toxicity and unique size-dependent fluorescence properties, thus making metal nanoclusters promising as attractive fluorescent probes for a variety of analytical and biological applications (Lu and Chen, 2012; Shang et al., 2011; Zhang and Wang, 2014a). Among different metal NCs, Cu NCs have received increasing attention in recent years for their applications in catalysis and chemical sensing (Jia et al., 2013, 2014; Wei et al., 2011). For example, Hu et al. (2013) used bovine serum albumin (BSA) stabilized Cu NCs as peroxidase mimetic for application in colorimetric assay of H_2O_2 and glucose. Gao et al. (2015) used GSH-protected Cu_6 NCs as novel electrochemical sensing materials for glucose detection. Nevertheless, compared to Au and Ag, although Cu is an easily-obtained, cheap metal and widely used in daily life, the preparation of highly stable and ultrafine size controlled fluorescent Cu NCs still remains challenging, which is mainly due to its susceptibility to oxidation upon exposure to air and the instability in colloidal dispersion.

Recently, biological macromolecules such as peptides and proteins have been widely utilized as templates for synthesizing highly fluorescent metal NCs, due to their abundant binding sites that can potentially bind and further reduce certain metal ions to offer better scaffolds (Hu et al., 2015). Yeast extract is a commercially available biological product which is widely used as food additives, flavorings, or as nutrients for bacterial culture media. It

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is made from the same fresh yeast as that is used in bread, beer and wine production by extracting the cell contents without the surrounding cell wall. Importantly, the yeast extract contains many kinds of natural components from yeast cell, such as proteins, amino acids, carbohydrates, vitamins and minerals (Yamal et al., 2013), which could be excellent candidates for the preparation of nanomaterials. Herein, we report for the first time the synthesis of fluorescent Cu NCs by using yeast extract as both reducing and stabilizing agents. The as-synthesized Cu NCs exhibited intense blue fluorescence maximized at 450 nm and excellent water-solubility and stability. Interestingly, our as-prepared Cu NCs exhibited highly specific and sensitive response towards S^{2-}, which allows the development of a new, robust fluorescent assays for monitoring the level of S^{2-} in real water samples.

2. Materials and instrumentation

2.1. Materials

Yeast extract (LP0021) was bought from Oxoid. $CuCl_2 \cdot 2H_2O$, $Na_2S \cdot 9H_2O$, $Na_2S_2O_8$ and other salts were purchased from Aladdin Industrial Corporation (Shanghai, China). They are analytical grade chemical reagents and used without further purification unless for special needs. Deionized water with a resistivity of 18.2 MΩ/cm was used for all experiments.

2.2. Instrumentation

The fluorescence spectra were measured with a Shimadzu RF-5301 spectrofluorimeter using a 10 mm quartz cuvette. Fluorescence lifetime measurements were measured with Edinburgh FLS920 dedicated Fluorescence Spectrometer. Transmission electron microscope (TEM) images were taken on FEI Tecnai G2 F20 instrument. Dynamic light scattering measurements (DLS) was performed on Brookhaven Instruments Corporation ZetaPALS.

2.3. Synthesis of Cu NCs

All glassware used in the experiment was cleaned in a bath of freshly prepared 3:1 HCl/HNO_3 and rinsed thoroughly in water prior to use. In a typical synthesis, an aqueous solution of yeast extract (8 mL, 100 mg) was mixed with an aqueous solution of $CuCl_2$ (2 mL, 100 mM) at room temperature. The solution was stirred at room temperature for 2–3 min. Finally, the mixture was allowed to reflux for 12 h at 100 °C, and the color changed from light blue to deep green gradually. After reaction, the Cu NCs were purified by centrifugation (14,000 rpm, 10 min) in order to remove the solid from the supernatant. The final solution was stored at 4 °C when not in use.

2.4. Fluorescence detection of S^{2-}

For the typical assay of S^{2-}, 0.1 mL of the Cu NCs suspension (0.25 mg/mL) was diluted with 2.8 mL of phosphate buffer solutions (10 mM, pH 5.0), followed by the addition of 0.05 mL $Na_2S_2O_8$ (30 mM) and different concentrations of S^{2-}, respectively. The mixed solution was left reacted at room temperature for 20 min and finally subjected to measuring the fluorescence emission spectra with the excitation wavelength of 370 nm at room temperature. The slot widths of the excitation and emission were 5.0 and 10.0 nm, respectively.

2.5. Detection in water samples

Hot spring and tap water samples were collected from the Taoyuan campus of Northwest University in Xi'an. Prior to use, the natural water samples were filtrated through 0.22 μm membranes to remove the suspended solids, then diluted to 100 times by phosphate buffer solution (10 mM, pH 5.0). Subsequently, S^{2-} were spiked to water samples at different concentration, and then used for the detection with the same procedure as that described in Section 2.4.

3. Results and discussion

3.1. Characterization of yeast extract-synthesized Cu NCs

The fluorescent Cu NCs were synthesized through an ordinary reflux procedure by using yeast extract as both reducing and stabilizing agents. The as-prepared Cu NCs exhibited a deep green color, and emitted an intense blue fluorescence under a UV lamp (365 nm). Fig. 1A shows the spectra of Cu NCs in aqueous solution.

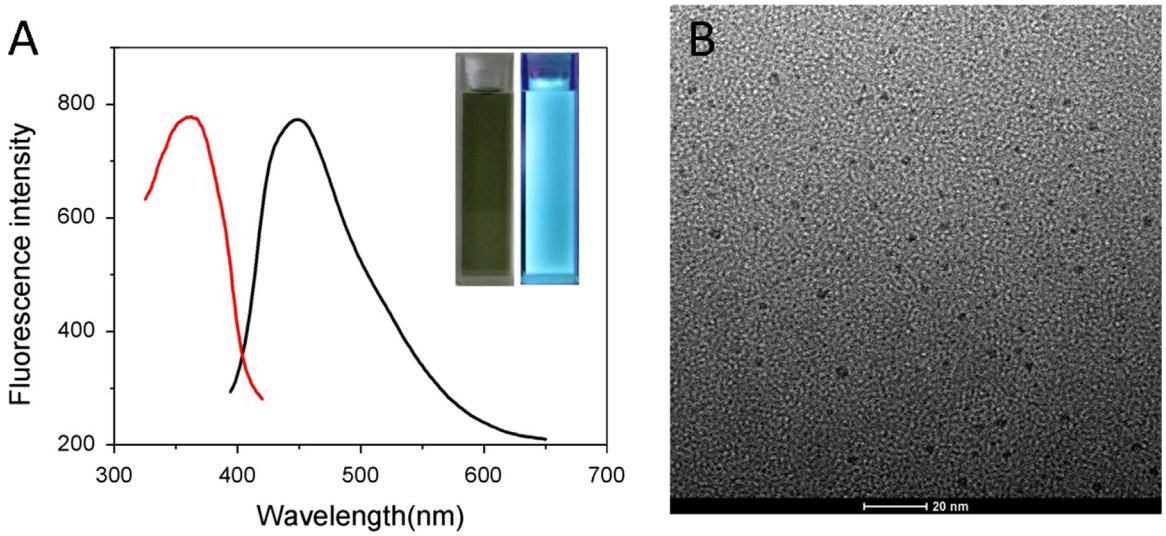

Fig. 1. (A) Fluorescence excitation (red line) and emission spectra (black line) of as-prepared Cu NCs. Inset: photographs of the as-prepared Cu NCs under the irradiation of the daylight (left) and 365 nm UV light (right); (B) TEM image of as-prepared Cu NCs. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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