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One-step synthesis of orange fluorescent copper nanoclusters for sensitive and selective sensing of Al^{3+} ions in food samples

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ABSTRACT

One-step approach was developed for the fast synthesis of copper nanoclusters (CuNCs), which were used as a fluorescent probe for the sensitive detection of Al^{3+} in food samples. For this, aqueous $CuSO_4$ was reduced into CuNCs by dithiothreitol (DTT) at room temperature within 30 min. The synthetic process was fast, simple and easy. The DTT-capped CuNCs (DTT-CuNCs) were characterized by UV–vis absorption, fluorescence, FT-IR, TEM and XPS. The DTT-CuNCs display orange fluorescence with a maximum emission at 590 nm while excitation at 360 nm. The aggregation-induced fluorescence enhancement property of DTT-CuNCs in presence of Al^{3+} was found. On this basis, we developed a simple, sensitive, selective turn-on fluorescent sensor for the detection of Al^{3+} in food samples. Under the optimized conditions, the enhanced fluorescence intensity exhibited a good linear relationship with Al^{3+} concentrations in the range from 0.01 μM to 7 μM with a detection limit of 0.01 μM. The DTT-CuNCs-based fluorescent probe has been successfully used to assay the content of aluminum in real food samples such as the fried food and pasta. These results demonstrate the great potential of the DTT-CuNCs-based fluorescence sensor for the routine estimation of Al^{3+} content in food samples.

1. Introduction

Aluminum is a widely used metal in our daily life (used as food additives, cookware and so on) [1,2]. The wide use of aluminum inevitably results in a health risk due to its neurotoxicity [3]. It has been reported that aluminum neurotoxicity in humans could induce the brain and bone disorders, leading to illnesses such as Alzheimer's disease and Parkinson's disease [4]. Also, dermal absorption of aluminum ions around breast would increase the incidence of breast cancer [5]. Thus sensitive and selective detection of aluminum ions is important from the view point of human health and food safety.

Various methods have been employed to detect Al^{3+} such as flame atomic absorption spectrophotometer [6], inductively coupled plasma atomic emission spectrometric [7], inductively coupled plasma mass spectrometry [8], electrochemical [9], photocolorimetric [10,11] and fluorescent method [12], of which the fluorescent one is very promising due to its advantages of simplicity, selectivity, sensitivity, low instrument cost and fastness. In particular, fluorescent copper nanoclusters (CuNCs) have received an increasingly attention owing to their unique physical and chemical property, such as photoluminescence, water soluble, good bioavailability, and readily available precursor for the preparation of CuNCs as compared to the high cost precursor for noble metal AuNCs and AgNCs [13]. Up to date, a wide diversity of CuNCs has been reported as fluorescent probes to detect various targets, including Fe^{3+} [14], Hg^{2+} [15], ClO^- [16], H_2O_2 [17], biothiols [18], and so on. However, to our best knowledge, no CuNCs based fluorescent probes have been reported for the sensing of Al^{3+} until now.

In order to prepare photoluminescent CuNCs, various capping ligands or templates, such as proteins (BSA [19,20], papain [21], trypsin [22]), DNA [23,24], and egg white [25], have been used. However, the synthetic procedures for CuNCs were commonly implemented through heating treatment under strong alkaline conditions [26] or using an additional reductant [27], which makes the synthesis process tedious, complicated, and time-consuming. On the other hand, compared to protein- and DNA-capped CuNCs, small molecules-capped CuNCs are less expensive. And various small molecules, including glutathione [28], histidine [29] and ascorbic acid [30], have been used as capping agents and reducing agents for the preparation of fluorescent CuNCs through sonochemical [31], microwave irradiation [32], or heating treatment [33]. Although the fluorescent CuNCs were facilely prepared by

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using the above mentioned small molecules, unfortunately most of the previous works concentrated on fabrication of blue-emitting CuNCs. For example, the cysteine-CuNCs were successfully synthesized by using cysteine both as reducing agent and stabilizer, which showed emission at 480 nm [34]. The 2-mercaptobenzoic acid also has been employed to prepare CuNCs with an emission peak at 420 nm [35]. However, employment of the blue-emitting CuNCs suffers from the interference from samples with autofluorescence in the short-wavelength range, thus inevitably limiting their further applications. Hence, development of facile, rapid, and cost-effective approach to synthesize fluorescent CuNCs emitting at long wavelength is highly desirable. Furthermore, none of these CuNCs capped with small molecules has been used to assay Al^{3+} to date.

Here, for the first time, we investigate the potential of fast preparation of the orange fluorescent CuNCs within 30 min by direct reduction of $CuSO_4$ in the presence of DTT without using any additional reluctant and organic solvent at room temperature. DTT was selected as a reducing agent due to its low redox potential (−0.33 V at pH 7) [36] and strong coordination ability for copper ion [37], which could prevent the oxidation of CuNCs in aqueous solution. The CuNCs display orange fluorescence with a maximum emission at 590 nm while excitation at 360 nm. The fluorescence of the CuNCs was obviously enhanced by Al^{3+} in aqueous solution. Factors affecting fluorescent response of the CuNCs in the presence of Al^{3+} were investigated in detail. The application of the CuNCs as fluorescent probe to detection of Al^{3+} in food samples was demonstrated. To our knowledge, this is the first report of employment of fluorescent CuNCs to detect Al^{3+}.

2. Experimental

2.1. Chemicals and reagents

Dithiothreitol (DTT) was purchased from Aladdin (Shanghai, China). Copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$), aluminum nitrate nonahydrate [$Al(NO_3)_3 \cdot 9H_2O$], and other chemicals were from Kelong Chemical Reagent Co. Ltd. (Chengdu, China). All chemicals and solvents were of reagent grade and used without further purifications. Ultra-pure water (18.2 MΩ) was produced in our lab.

2.2. Instrumentation

Fluorescence and UV–vis spectra were obtained by a Hitachi F-2700 fluorescence spectrophotometer (Tokyo, Japan) and a Hitachi U-4100 spectrophotometer (Tokyo, Japan), respectively. The pH of a solution was measured by a PHS-3D pH meter (Shanghai Precision Scientific Instrument Co. Ltd., China). The zeta potential and hydrodynamic diameter were measured on a Zetasizer Nano-ZS90 (Malvern, UK). The transmission electron microscopy (TEM) images were taken on a Tecnai G2 20 electron microscope (FEI, USA). X-ray photoelectron spectroscopy (XPS) characterizations were conducted by using a VG Multilab 2000X instrument (Thermal Electron, USA). Infrared spectrum was recorded with a Tenson 27 Fourier Transform Infrared spectrometer (Bruker, Germany).

2.3. Synthesis of DTT-CuNCs

For preparation of DTT-CuNCs, 2 mL of DTT solution (0.1 M) was added to a beaker with 4 mL of ultra-pure water. After adding 0.1 mL of $CuSO_4$ solution (0.1 M) under stirring, the colorless solution changed to white emulsion. The pH of the resultant solution was adjusted to 6.50 using NaOH, and the mixture was stirred for 30 min at room temperature to obtain colorless CuNCs. The resultant DTT-CuNCs were stored at 4 °C for further use.

2.4. General procedure for Al^{3+} detection using DTT-CuNCs as fluorescent probe

In a typical process, 0.1 mL of DTT-CuNCs solution (final concentration of 8 μM) was added into a serial of Al^{3+} solutions with different concentrations from 0.01 μM to 20 μM in the presence of 0.01 M HAc-NaAc buffer (pH 6.5). After the mixture was diluted to 10 mL with pure water, the fluorescence intensity at 590 nm was measured at excitation wavelength of 360 nm after the mixture was incubated at room temperature for 1 min. All fluorescence (FL) measurements were performed in triplicate, and the data were recorded as a mean. In order to investigate the effects of foreign substances, the fluorescence intensity of DTT-CuNCs in the presence of various metal ions including Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Fe^{2+}, Cu^{2+}, Cd^{2+}, Mn^{2+}, Fe^{3+} and non-metal ions such as $NH_4{}^+$, F^-, Cl^-, Br^-, $NO_2{}^-$, $NO_3{}^-$, $SO_4{}^{2-}$, $CO_3{}^{2-}$, $SO_3{}^{2-}$, $ClO_3{}^-$ and $PO_4{}^{3-}$ were measured to study the selectivity of DTT-CuNCs as fluorescence probe for sensing of Al^{3+}.

2.5. Procedure for Al^{3+} detection in food samples

The ashing method was used to pretreatment of food samples [38], including fried bread stick, chips, steamed buns and bean vermicelli, which were purchased from local supermarket. Briefly, after being dried at 60 °C for 6 h, the food samples (about 1 g) were grinded and put in porcelain crucible. The furnace temperature was slowly increased from room temperature to 550 °C in 1 h, and maintained 550 °C about 5 h to ensure that the samples were ashed completely. The ash residue was dissolved in 15 mL of HNO_3 (20%) and quantitatively transferred to a beaker, which was sonicated for about 20 min and placed on an electric hot plate to remove the remaining HNO_3. The resulting solution was transferred to a 50 mL volumetric flask and made up to volume with ultra-water. After filtration through a 0.45 μm mixed fiber membrane (Shanghai Xinya Purification Device Factory, Shanghai, China), the resulting filtrate was used for Al^{3+} analysis by the proposed method and graphite furnace atomic absorption spectrometry (GF-AAS).

3. Results and discussion

3.1. Synthesis and characterization of DTT-CuNCs

DTT was selected as reducing agent and capping agent to synthesize CuNCs because it possesses the strong coordination ability with Cu^{2+} and strong reduction property with redox potential of −0.33 V at pH 7 [36], and has been used for preparation of the fluorescent AuNCs [39]. The reagent amount, molar ratio of DTT to Cu^{2+}, solution pH and reaction time were controlled to optimize the synthetic conditions, and the best-performing CuNCs as fluorescent probe were obtained by 0.033 M DTT and 2.5 mg $CuSO_4 \cdot 5H_2O$ (molar ratio of DTT to Cu^{2+} of 20:1) at pH 6.0–6.8 for 30 min of reaction time (Fig. S1).

The obtained DTT-CuNCs display a new absorption peak at 275 nm, which is different from that of DTT and Cu^{2+} (Fig. 1A). The surface plasma resonance band of large copper nanoparticles at 500–600 nm was not observed in the UV–vis absorption spectra of the prepared CuNCs, suggesting the successful formation of CuNCs [40]. The CuNCs exhibit orange fluorescence under UV light irradiation (inset Fig. 1B) and the maximum emission and excitation of DTT-CuNCs were located at 590 nm and 360 nm, respectively (Fig. 1B). The emission wavelength showed almost no shift while the excitation wavelength was changed from 340 nm to 390 nm (Fig. 1C), indicting that the CuNCs show the excitation independent fluorescence properties. The FT-IR spectrum of DTT-CuNCs exhibits the characteristic bands of DTT as a ligand (Fig. 1D). However,