



One-pot synthesis of fluorescent DHLA-stabilized Cu nanoclusters for the determination of H₂O₂



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ABSTRACT

A facile one-pot approach has been developed to prepare orange-emitting Cu nanoclusters (NCs) using tetrakis(hydroxymethyl)phosphonium chloride as a reducing agent and lipoic acid as a capping agent under an alkaline medium at room temperature. The as-prepared Cu NCs exhibited excellent water solubility, large Stokes shift, long lifetime and good dispersion. After the addition of polyvinyl pyrrolidone, the fluorescence intensity of dihydrolipoic acid-stabilized Cu NCs (DHLA-Cu NCs) was greatly enhanced, and their fluorescence signal remained stable for 5 weeks storage in the dark at room temperature. Based on H₂O₂-induced fluorescence quenching, DHLA-Cu NCs showed high sensitivity and selectivity for the detection of H₂O₂ in aqueous solution with a detection limit of 0.3 μM, and were applied successfully to the detection of H₂O₂ in human urine samples.

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1. Introduction

Metal nanoclusters (NCs), typically consisting of several to tens of metal atoms, provide a significant bridge between metal atoms and nanoparticles [1]. Because of their attractive properties, such as excellent stability, extremely small size and easy modification, thiolate-protected metal NCs have received a great deal of attention in recent years [2,3], especially thiolate-protected Au NCs and Ag NCs which are considered to be attractive candidates for chemical sensing and bioimaging [4]. For example, glutathione-capped Au NCs (GSH-Au NCs) can be utilized as a fluorescence “turn-off” probe for Cu²⁺ ions sensing based on the aggregation-induced fluorescence quenching [5]. On the basis of S²⁻ etching-induced mechanism, GSH-Ag NCs offer highly sensitive and selective detection of S²⁻ [6]. NIR-emitting PEGylated Au NCs are capable of tumor imaging and cancer therapy owing to their high targeting efficiency and long tumor retention [7].

Cu is an easily-obtained and cheap metal and widely used in daily life. In recent years, Cu NCs have received increasing attention for their applications in catalysis and chemical sensing. For example, red emissive Cu NCs in supramolecular hydrogels are reported to have excellent catalytic performance in the methylene blue-hydrazine reduction system [8]. L-cysteine-capped Cu NCs are

applied in highly sensitive and selective detection of Hg²⁺ ion on the basis of the interactions between Hg²⁺ and L-cysteine [9]. However, current reports concerning the synthesis of thiolate-stabilized Cu NCs are relatively sparse in comparison to those for Au NCs and Ag NCs [10]. It is a challenge to synthesize highly stable and extremely tiny Cu NCs because they are easily surface oxidized in air and unstable in colloidal dispersion [11,12]. In order to address this issue, in recent years, several groups have devoted themselves to study the synthesis of thiolate-stabilized Cu NCs with high stability and extremely small size. One-pot synthesis of 2-mercapto-5-n-propylpyrimidine-protected Cu NCs was achieved in the ethanol phase using a wet chemical reduction method, but the obtained Cu NCs were unstable and only soluble in the organic phase [13]. One-pot synthesis of red-emitting Cu NCs using D-penicillamine as the capping agent was also reported, although the as-prepared Cu NCs displayed an intriguing aggregation-induced emission feature and good stability, they presented a fluorescence signal only in acidic media (pH < 6.0) [14]. Recently, blue-emitting Cu NCs using lipoic acid (LA) modified with polyethylene glycol as a capping agent and NaBH₄ as a reducing agent were prepared, but the strong reducing agent NaBH₄ was easy to generate no fluorescent larger nanoparticles, and the modification of the ligands increased the operational burden [15]. Therefore, it is highly desirable to develop a facile approach for preparing fluorescent Cu NCs with excellent stability.

Tetrakis(hydroxymethyl)phosphonium chloride (THPC) is a type of mild reducing agent, and has been used for the preparation of Au

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NCs and Au/Ag alloy NCs [16,17]. In our study, a facile one-pot approach was developed to prepare orange-emitting dihydroliipoic acid-stabilized Cu NCs (DHLA-Cu NCs) using THPC as a reducing agent and commercial LA as a capping agent. The optical properties and microstructure of DHLA-Cu NCs were characterized using UV–vis absorption, fluorescence, Fourier transform infrared (FT-IR), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). The fluorescence intensity of the DHLA-Cu NCs was enhanced by the addition of polyvinyl pyrrolidone (PVP). Based on H₂O₂-induced fluorescence quenching, DHLA-Cu NCs displayed high sensitivity and selectivity towards H₂O₂.

2. Experimental

2.1. Materials and reagents

LA, GSH, THPC, mercaptosuccinic acid (MSA), 11-mercaptoundecanoic acid (MUA), 6-mercapto-1-hexanol (MH), 4(2-Hydroxyethyl) piperazine-1-ethanesulfonic acid (HEPES) and PVP were obtained from Sigma-Aldrich (USA). Copper nitrate and other chemicals were obtained from Sinopharm Chemical Reagent Co., Ltd. (China). All the reagents were used as received without further purification. Ultrapure water with a resistivity of 18.2 MΩ cm⁻¹ obtained from a Millipore purification system (USA) was used for the experiments.

2.2. Instruments

FT-IR spectra were obtained on a Nicolet 330 spectrophotometer (Thermo Electron Corp., USA). TEM images were collected using a TECNAI F-30 (Philips-FEI, Netherlands). UV–vis absorption spectra were recorded from a UV 2550 UV–vis spectrophotometer (Shimadzu, Japan), and fluorescence spectra were obtained from an F-4500 spectrophotometer (Hitachi, Japan). The fluorescence lifetimes were determined on a FluoroMax-4 spectrofluorometer (Horiba JobinYvon, France). The electronic binding energies of DHLA-Cu NCs were measured using XPS analysis, which was conducted with a PHI Quantum 2000 Scanning ESCA Microprobe (Physical Electronics, USA) equipped with a monochromatised microfocussed Al X-ray source. All of the binding energies were calibrated using C1s as a reference energy (C1s=284.6 eV).

2.3. Synthesis of DHLA-Cu NCs

Typically, 4.1 mg of LA was solubilized in 19.8 mL of an aqueous solution containing 0.4 mL of 1 M NaOH solution, followed by the addition of 0.2 mL of 0.1 M Cu(NO₃)₂ under vigorous stirring. After stirring for 5 min, 7.2 μL of 80% THPC was added slowly to the mixture. The DHLA-Cu NCs were obtained after vigorous stirring at room temperature for 15 min. This as-prepared fluorescent Cu NCs solution was neutralized by the drop-wise addition of 1 M HCl and stored at 4 °C for further used.

2.4. Determination of H₂O₂

Different concentrations of H₂O₂ and interference solutions were freshly prepared before use. To investigate the sensitivity towards H₂O₂, different concentrations of H₂O₂ were added into the 40 mM HEPES buffer solution (pH 7.4) containing the same amount of DHLA-Cu NCs and the mixture was equilibrated for 30 min before spectral measurement. To test the selectivity towards H₂O₂, solutions containing the same amount of DHLA-NCs but with different interference were added in 40 mM HEPES buffer (pH 7.4) and equilibrated for 30 min before spectral measurement. The fluorescence intensity at 590 nm was recorded for the

fluorescence measurements using the excitation wavelength of 365 nm, and both of the slit widths for the excitation and emission were set at 10.0 nm.

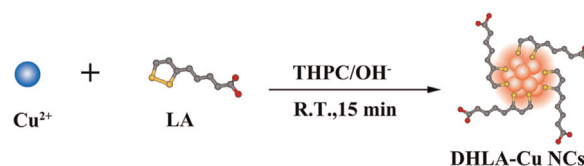
3. Results and discussion

3.1. Synthesis and characterization of the DHLA-Cu NCs

The preparation process for the DHLA-Cu NCs was illustrated in Scheme 1. The alkaline medium played two important roles in the DHLA-Cu NCs preparation. It could cleave the disulfide bond of LA, and release the free mercapto groups [18,19], which exhibited the excellent ability of stabilizing the nucleated cluster due to the strong interaction between Cu and S. From FT-IR spectra of natural LA and LA incubated in an aqueous alkaline solution (Fig. S1 in the Supporting information), it was observed that LA maintained most of its native structure in the alkaline condition, and the S–H stretching band appeared at 2497 cm⁻¹, revealing that LA generated free mercapto groups in alkaline conditions. In addition, the mild reducing reagent, THPC, would be more suitable for Cu²⁺ reduction in order to prepare the DHLA-Cu NCs in the alkaline condition. UV–vis spectra (Fig. S2 in the Supporting information) exhibited no characteristic peak after the addition of THPC into the mixture of LA and Cu²⁺ in a neutral condition, while a broad absorption band around 325 nm was obtained after the addition of THPC. The lack of a characteristic surface plasmon band of larger Cu nanoparticles indicated the formation of the DHLA-Cu NCs. These results suggested that THPC was essential for the preparation of the Cu NCs in an alkaline medium.

Generally, with the size decrease of the metal nanoparticles, their physical and chemical properties change dramatically. When the size approaches the Fermi wavelength of electrons, metal nanoparticles exhibit a marked photoluminescence property due to discrete energy levels and quantum confinement [20]. Therefore, to obtain their fluorescence emission, an extremely small size of metal NCs is necessary. The as-prepared DHLA-Cu NCs were characterized using TEM. As indicated in Fig. 1a, the TEM image showed that the DHLA-Cu NCs were well dispersed with an average diameter of 1.8 nm and no aggregation was found. The fluorescence features of the DHLA-Cu NCs were also analyzed as shown in Fig. 2. A strong symmetric emission of the Cu NCs appeared at 590 nm with an excitation maximum at 342 nm. In contrast to organic dye, the large Stokes shift (248 nm) avoided crosstalk between the excitation and emission spectra. The aqueous solution of the Cu NCs was faint yellow in color and exhibited a bright orange emission under 365 nm UV light (inset of Fig. 2). The decay profile of the DHLA-Cu NCs was monitored (Fig. 1b), and the fluorescence decay spectrum fitted with three exponential curves, suggesting the possible existence of three components at 0.8 ns (1%), 91.1 ns (12%) and 583.6 ns (87%). The fluorescence lifetime of 573.2 ns was obtained using the weighted average method [21], which is related to the surface state governed by the interaction between metal core and surface ligands [22,23].

FT-IR spectroscopy and XPS were used to study the surface chemistry of the DHLA-Cu NCs. In comparison with LA in the alkaline condition, the FT-IR spectrum of the DHLA-Cu NCs (Fig. S1



Scheme 1. Schematic illustration of the preparation process of DHLA-Cu NCs.

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