



Fast synthesis of porous copper nanoclusters for fluorescence detection of iron ions in water samples

Yihong Huang^{a,*}, Hanqiang Zhang^{b,c,**}, Xiaofen Xu^c, Jiangcong Zhou^c, Fenfen Lu^c, Zhusen Zhang^{b,c}, Zhibiao Hu^c, Jiangshui Luo^{b,c,**}

^a Fujian Longking Co. Ltd., Longyan 364000, Fujian, China

^b Collaborative Innovation Center of Clean Energy, Longyan University, Longyan 364000, Fujian, China

^c Fujian Provincial Key Laboratory of Clean Energy Materials, College of Chemistry and Materials Science, Longyan University, Longyan 364000, Fujian, China

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ABSTRACT

Copper nanoclusters (Cu NCs) have attracted great research interest in recent years owing to its unique physical, electrical and optical properties. Macromolecules have been widely used as templates to synthesize fluorescent Cu NCs. In this study, a simple method for synthesis of albumin chicken egg capped porous copper nanoclusters (p-Cu NCs) was developed for the first time. The obtained p-Cu NCs exhibited intense emission and excitation peaks at 280 nm and 340 nm, respectively. Besides, the p-Cu NCs fluorescence probe could be quenched by Fe³⁺ ions in aqueous solutions. Therefore, the p-Cu NCs can be excellently candidate as fluorescent probe for the detection of Fe³⁺ ions. Under optimized conditions, this fluorescent probe exhibited a wide linear response concentration range (0.2 to 100 μM) to Fe³⁺ with a detection limit of 0.0234 μM. In addition, the fluorescent probe has been successfully used for the detection of Fe³⁺ in natural water samples with satisfactory result.

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1. Introduction

Metal nanoclusters (NCs), a molecular species, which consist of one kind molecular metal atoms or two or more metal atoms bonded to each other [1–3]. The sizes of metal NCs are near the Fermi wavelength of electrons endow and it composed of several to a few hundreds of metal atoms [4,5]. Due to large Stokes shifts, excellent photostability, low toxicity and unique size-dependent fluorescence properties, metal NCs have received much attention in a variety of analytical and biological applications [6–8]. Among different metal NCs, Cu NCs have attracted great research interests in recent years owing to unique physical, electrical and optical properties [9–12]. In addition, copper is inexpensive, abundant and readily available from commercial sources than many noble metals, such as platinum, gold and silver.

It is commonly known that macromolecules have been widely used as templates to synthesize fluorescence Cu NCs, due to their abundant binding sites that can potentially bind and further reduce certain metal ions to offer better scaffolds [6,13]. Moreover, Cu NCs capped different macromolecules bring out different properties and applications. For example, Yang et al. [14] synthesized L-cysteine stabilized Cu NCs

and used for fluorescence detection of Hg²⁺. Hu et al. [15] applied glutathione capped Cu NCs for selective and sensitive detection of Hg²⁺ in water and food stuff. Zhong et al. [16] utilized bovine serum albumin coated Cu NCs as a regenerable fluorescent probe for Cu²⁺. Feng et al. [17] employed polyethyleneimine-templated Cu NCs as ferric ion sensor. Jia et al. [18] used D-penicillamine stabilized Cu NCs and applied for biosensing and catalytic applications. Therefore, it is very necessary to choose an appropriate template to synthesize Cu NCs and used for a particular application.

In this research, albumin chicken egg (ACE) was chosen as template to synthesize porous Cu NCs (p-Cu NCs) via a simple method. The p-Cu NCs showed excellent fluorescent properties. In addition, the p-Cu NCs acting as a fluorescence probe possessed good sensitivity and selectivity for Fe³⁺ ions in aqueous solution. It is important to highlight that this fluorescence probe was applied for detection of Fe³⁺ in tap water samples and showed a satisfactory result.

2. Experimental

2.1. Materials and Instrumentation

Albumin chicken egg was purchased from Sigma-Aldrich (America), metal salts (Fe(NO₃)₃, CuSO₄, HgCl₂, Pb(NO₃)₂, AlCl₃, BaCl₂, CaCl₂, CdCl₂, CoCl₂, LiNO₃, MgCl₂, Ni(NO₃)₂, Sr(NO₃)₂, Zn(NO₃)₂) were purchased from Xilong Chemical Co., Ltd. (Guangdong, China). All reagents were

* Corresponding author.

** Corresponding authors at: Collaborative Innovation Center of Clean Energy, Longyan University, Longyan 364000, Fujian, China.

E-mail addresses: yihonghuang921@163.com (Y. Huang), hanqiangzhang@126.com (H. Zhang), proticils@gmail.com (J. Luo).

analytical reagent grade and all the solutions were prepared with deionized water (18.2 M Ω).

Transmission electron microscopy (TEM) images were performed on Tecnai G2 F20 S-TWIN Microscope (FEI Company, America). Fourier transform infrared spectroscopy (FT-IR) was recorded on Thermo NICOLET iS 10 (Thermo Fisher Scientific, America). Ultraviolet visible (UV-vis) absorption spectrum was carried out on UV-2600 (SHIMADZU, Japan). Fluorescence spectra were measured by RF-5301 (SHIMADZU, Japan) with a 1.0 cm quartz cell. The fluorescence lifetime was analyzed by FLS-980 (Edinburgh, UK). Atomic absorption spectroscopy (AAS) was recorded on AA-7000F (SHIMADZU, Japan).

2.2. Preparation of p-Cu NCs

p-Cu NCs have been prepared according to previous report with some modification. Typically, 2 mL CuSO₄ solution (20 mM) was added to 10 mL ACE solution (15 mg/mL) with vigorous stirring. After stirred at room temperature for 5 min, the bluish solution was slowly adjusted to pH 12 using NaOH solution. And then, the mixed solution was allowed to stir at 55 °C for 8 h. After that, this solution was dialyzed against distilled water through dialysis bag with a molecular weight cutoff of 3500 Da for 48 h to remove unreacted small molecules, and the final solution was diluted to 100 mL. The as-prepared p-Cu NCs were stored at 4 °C for further use.

2.3. Fluorescence Detection of Fe³⁺ Ion

For a typical detection, 1 mL of p-Cu NCs was diluted to 10 mL with distilled water (1 mM PBS). Under the same experimental conditions, a series of Fe³⁺ ion with different concentrations was added and mixed thoroughly. This mixture solution was subjected to fluorescence measurements on a fluorescence spectrophotometer with the excitation wavelength of 280 nm. All experiments were taken at room temperature.

2.4. Detection in Tap Water Samples

In the present work, the tap water samples were collected from Longyan University in Fujian. Prior to use, the tap water samples were filtered through 0.22 μ m membranes to remove large particles. Then Fe³⁺ ions with different concentrations were spiked by standard addition recovery method for further analysis.

3. Results and Discussion

3.1. Characterization of p-Cu NCs

TEM was used to measure the morphology of p-Cu NCs and the result was provided in Fig. 1A. As shown in Fig. 1A, the p-Cu NCs show porous structure and the size is about 30 nm. Besides, to explore the surface groups of p-Cu NCs, the FT-IR spectrum of p-Cu NCs was also recorded. It can be seen from Fig. 1B, the peaks at 1651, 1541 and 1305 cm⁻¹ are correspond to the typical secondary structures of proteins [1,19]. The peaks at 1072 and 900 cm⁻¹ are ascribed to the C—C stretching vibrations modes of egg white proteins. These results indicated that ACE was capped on the surface of Cu.

3.2. Optical Properties of p-Cu NCs

The UV-vis absorption spectrum and fluorescence spectra of p-Cu NCs were depicted in the Fig. 2A. The p-Cu NCs have an absorption peak at 285 nm, which was ascribed to the quasi-continuous electronic energy band structure and quantum confinement effects of p-Cu NCs [20,21]. In addition, the p-Cu NCs show the excitation and emission peaks at 285 and 340 nm, respectively.

In order to further investigate the fluorescence property, the influence of excitation wavelength to emission spectra of p-Cu NCs was also researched and the 3D contour map mode was provided in the Fig. 2B. Under the different excitation wavelength condition, the maximum emission wavelength of p-Cu NCs was almost no change and located at 340 nm. This result disclosed that the emission wavelength of p-Cu NCs is independent of the excitation wavelength. Besides, the p-Cu NCs display maximum fluorescence intensity when the excitation wavelength located at 280 nm. Consequently, subsequent fluorescence experiments were carried out at 280 nm emission wavelength.

3.3. Optimization of the Sensing System

In this system, this fluorescence p-Cu NCs were designed to fluorescent sensor Fe³⁺. There are several main factors could affect the experiment results, such as pH value and reaction time. In order to research the effect of pH for the fluorescence sensing system, the fluorescence intensities of p-Cu NCs in the presence and absence 50 μ M Fe³⁺ were measured with different pH values. As shown in Fig. 3A, the fluorescence quenching intensities of p-Cu NCs in the aqueous solution were almost few changed under the acidity and neutral condition, but it was gradually decreased with increasing pH values. Therefore, pH 5 was used to measure in the subsequent experiment at this system.

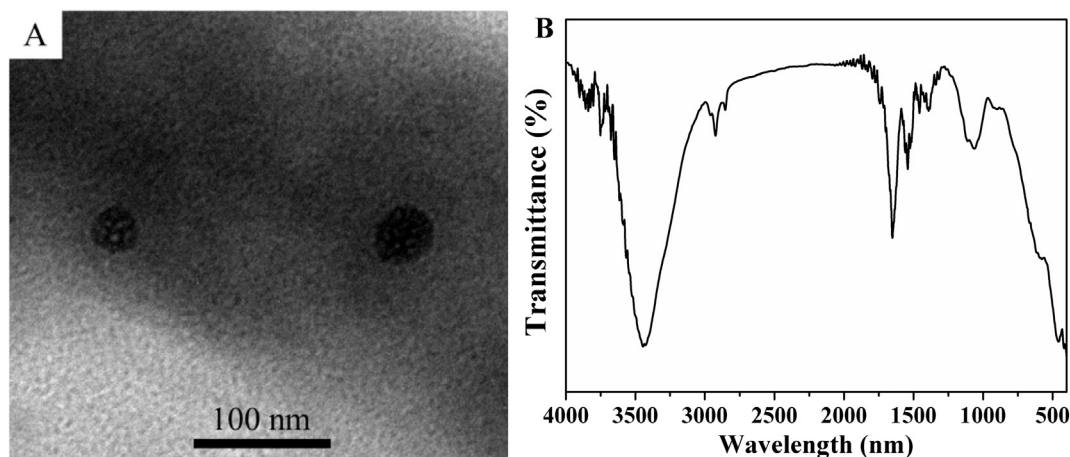


Fig. 1. (A) TEM image and (B) FT-IR spectrum of p-Cu NCs.

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