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Polyethyleneimine-templated copper nanoclusters via ascorbic acid reduction approach as ferric ion sensor

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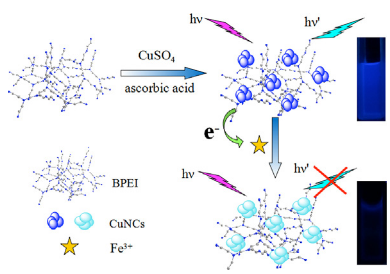
HIGHLIGHTS

- A new method for synthesis of the BPEI-CuNCs is established.
- A facile approach for Fe^{3+} ion sensing by fluorescence quenching is developed.
- The method for Fe^{3+} sensing has high sensitivity and excellent selectivity.

GRAPHICAL ABSTRACT



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ABSTRACT

In this report we reported a facile one-pot method for synthesis of water-soluble and stable fluorescent CuNCs at room temperature, in which branched polyethyleneimine (BPEI) served as capping scaffold and ascorbic acid as reducing agent. The prepared BPEI-CuNCs exhibited excellent properties such as good water-solubility, photostability and high stability toward high ionic strength. Based on the electron transfer induced fluorescence quenching mechanism, this fluorescence probe was used for the sensitive and selective determination of ferric ions (Fe^{3+}) in aqueous solution. The limit of detection was 340 nM in the linear range of 0.5–1000 μM, which was lower than the maximum level of Fe^{3+} permitted in drinking water by the U.S. Environmental Protection Agency. The method was successfully applied to the detection of Fe^{3+} in tap water, Yellow River water and human urine samples with the quantitative spike recoveries ranging from 95.3% to 112.0%.

1. Introduction

Recently, ultra-small fluorescence metal nanoclusters (NCs), consisting of several to hundreds of metal atoms, have attracted great attention due to their unique physical, optical and electrical properties [1–5]. As their dimensions approach the Fermi wavelength of electrons, these noble-metal NCs have size-tunable electronic transitions and exhibit strong luminescence properties [6–9]. Among the noble-metal NCs, Au and Ag nanoclusters, displaying bright fluorescence and chemical stability, have gathered wide studies for use in sensing and imaging in the past decade [10–15]. However, the research on the preparation and application of copper clusters (CuNCs) has on its early stage. Vazquez-Vazquez et al. prepared a series of small atomic CuNCs by the microemulsion technique [16]. Vilar-Vidal et al. reported a electrochemical synthesis method for preparation of stable CuNCs which were reduced at the cathodic surface [17]. As the CuNCs

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exhibited intrinsic characteristics such as good fluorescence property and chemical stability, they were emerging as promising probes in environmental and biological sensing.

Polyethyleneimine (PEI), a type of polyamine that contains a high density of primary, secondary, and tertiary amine groups, has been widely served as effective templates and protection agents for synthesis and surface modification of different nanomaterials [18–20]. For example, fluorescence Ag clusters were synthesized using PEI as capping agent for hydrogen peroxide and glucose sensing [18]. The PEI-modified CdTe quantum dots were also reported to selective detection of Cd^{2+} ions [21]. Inspired by the fact that amine groups have excellent chelation ability with Cu^{2+} ions, PEI can polyvalent interact with Cu^{2+} and provide as scaffold to formation of CuNCs. Ling et al. reported the synthesis of PEI-templated CuNCs by a chemical reduction method using hydrazine hydrate as reducing agent [22]. However, the synthetic method had some disadvantages such as the necessity of high temperature heating operation and the usage of organic reagent, which would prevent their further applications. In the present study, we established a facile one-pot approach to synthesize water-soluble and highly stable fluorescent CuNCs, which employed branched polyethyleneimine (BPEI) as capping scaffold and ascorbic acid (AA) as reducing agent for the first time (Scheme 1). AA, which was a mild and environmental-friendly reducing agent, replaced the toxic organic reagent. The whole synthesis process was conducted at room temperature. The prepared fluorescent BPEI-CuNCs exhibited blue emission at 430 nm with the absolute quantum yield of 2.1%.

It is known that the level of Fe^{3+} ions is an important factor in the evaluation of water quality. In addition, the presence of Fe^{3+} in biological systems has to be efficiently moderated as both its deficiency and overloading can impair cellular functions and induce various biological disorders [23,24]. Therefore, determination of Fe^{3+} ions is undoubtedly of great significance in environment and health monitoring. At present, a variety of sensor platforms for the detection of Fe^{3+} ions have been developed by using gold nanoparticles, carbon nanoparticles, organic dye molecules, and gold nanoclusters, etc. [23,25–29]. However, up to now, none explored the fluorescent CuNCs probes for Fe^{3+} sensing. Herein, we demonstrated that the prepared BPEI-CuNCs were employed for sensitive and selective Fe^{3+} ions sensing in aqueous media. The detection mechanism was based on the electron transfer induced fluorescence quenching of the BPEI-CuNCs (Scheme 1). This method was successfully applied for detection of Fe^{3+} ions in tap water, Yellow River water, and urine samples with good spiked recoveries.

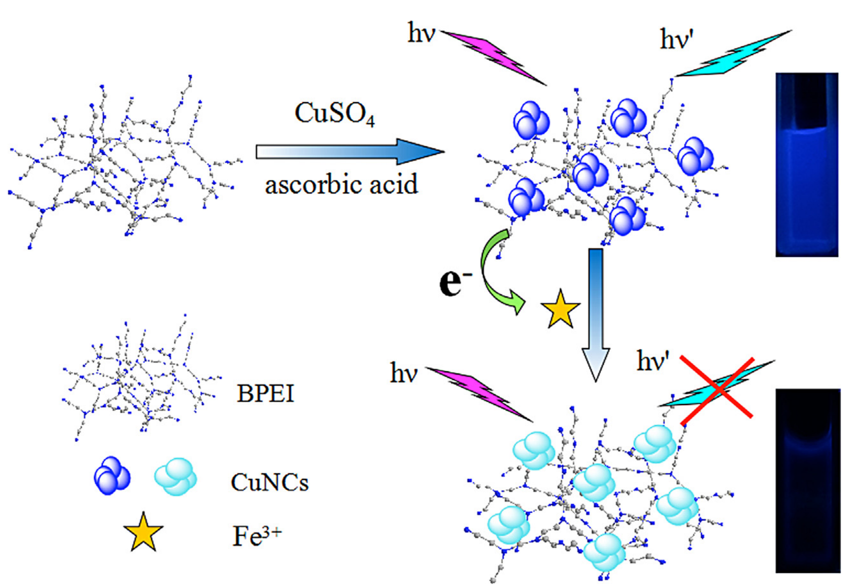
2. Experimental

2.1. Chemicals and materials

All chemicals and reagents were of analytical grade and used as received. Ultrapure water was used from a 1820-V AXL water purification system (Chongqing, China). Branched polyethyleneimine (MW 1.8 K) was purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China). Branched polyethyleneimine (MW 0.6 K, 10 K, and 25 K) were obtained from Alfa Aesar (Heysham, U.K.). $CuSO_4\cdot 5H_2O$ was purchased from Shanghai Bodi Chemical Co., Ltd. (Shanghai, China). Ascorbic acid and all amino acids were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Aqueous solutions of K^+, Na^+, Ag^+, Fe^{2+}, Ni^{2+}, Co^{2+}, Ba^{2+}, Ca^{2+}, Mn^{2+}, Hg^{2+}, Mg^{2+}, Pb^{2+}, Zn^{2+}, Al^{3+}, and Fe^{3+} were prepared from KCl, NaCl, AgCl, $FeCl_2$, $NiCl_2$, $Co(Ac)_2$, $BaCl_2$, $CaCl_2$, $MnCl_2$, $HgCl_2$, $MgCl_2$, $Pb(NO_3)_2$, $ZnCl_2$, $AlCl_3$, and $FeCl_3$, respectively. Aqueous solutions of NO_3^-,Cl^-, Ac^-, Br^-, SO_3^{2-}, $HPO_4^{2-}$$HPO_4^{2-}$, SO_4^{2-}, and citrate^{3-} were prepared from $NaNO_3$, NaCl, NaAc, NaBr, Na_2SO_3, Na_2HPO_4, Na_2SO_4, and trisodium citrate, respectively. In the experiment for investigation of the sensitivity of the BPEI-CuNCs toward various pH conditions, pH values of the solutions from pH 2.0 to 11.0 were adjusted by adding HCl or NaOH in order to avoid the electrolyte-induced perturbations by buffer solutions.

2.2. Instruments and methods

Transmission electron microscopy (TEM) images of the BPEI-CuNCs were obtained using a Tecnai G2F30 instrument. A drop of the BPEI-CuNCs solution was placed on a copper grid coated with a thin layer of amorphous carbon film and dried for the TEM analysis. X-ray photoelectron spectroscopy (XPS) measurement was performed by using a PerkinElmer PHI-5702 multifunctional photoelectron spectrometer. Specimen for XPS analysis measurement was prepared as followed: a drop of the BPEI-CuNCs solution was dispersed on a 1 cm × 1 cm mica sheet and let it dry. After several cycles of alternate droping and drying, the sample



Scheme 1. The synthetic strategy of the BPEI-CuNCs and the mechanism of the BPEI-CuNCs probe for Fe^{3+} sensing.