

Colorimetric Detection of Copper Ions Based on Surface Modification of Silver/Platinum Cluster Nanozyme



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Abstract: A sensitive colorimetric method for detection of copper ions (Cu^{2+}) was developed based on surface modification of Ag/Pt nanoclusters (Ag/Pt NCs) and regulation of the peroxidase-like activity. It was found that 3-mercaptopropionic acid (MPA) could inhibit the catalytic ability of Ag/Pt NCs, however it would lose the inhibition toward catalytic ability of Ag/Pt NCs after oxidization by oxygen through the catalysis of Cu^{2+} . On the basis of this, a colorimetric method was developed for the detection of Cu^{2+} by measuring the colorimetric signal variation of the TMB- H_2O_2 reaction. This method exhibited high sensitivity and selectivity toward Cu^{2+} over a panel of other metal ions, in the linear range of 10–100 nM with a detection limit of 5.0 nM. The method was simple and low cost, and suitable for Cu^{2+} detection in real water samples.

Key Words: Silver/Platinum nanoclusters; Colorimetric detection; 3-Mercaptopropionic acid; Copper ion

1 Introduction

As an essential microelement, copper ion (Cu^{2+}) plays crucial roles in the physiological activities and the work of organs of human beings, such as brain, liver and heart^[1]. However, the uptake of excess Cu^{2+} will bring about toxic effect on human beings and high level of Cu^{2+} , also produce environmental toxicity^[2]. The accumulation of excess Cu^{2+} probably brings about neurodegenerative diseases through participating in the generation of reactive oxygen. Some other diseases such as cancer, diabetes, cardiovascular diseases, atherosclerosis and liver cirrhosis ascites, were also associated with Cu^{2+} ^[3].

The conventional detection methods for Cu^{2+} include atomic emission spectroscopy (AES)^[4], atomic absorption spectroscopy (AAS)^[5], inductively coupled plasma mass spectrometry (ICP-MS)^[6], and electrochemical sensors^[7]. Most of these methods showed highly selective and sensitive, but they were time-consuming, and required sophisticated instrumentation or highly trained operators, which limited

their practical application. Thus, the development of simple, low-cost, highly sensitive and selective assay for Cu^{2+} detection is very important for practical application.

Recently, colorimetric sensors based nanomaterials, as a new strategy, have attracted great interests in heavy metal ions detection. Compared with electrochemical^[8] and fluorescent methods^[9,10], colorimetric methods are much simpler through naked-eye or UV-vis spectrometry measurements. For example, Deng *et al.*^[11] reported a colorimetric method for the rapid detection of Cu^{2+} based on thermally treated bare gold nanoparticles (Au NPs), and Hua *et al.*^[12] reported a novel colorimetric method of Cu^{2+} -based the 'click' chemistry-induced aggregation of Au NPs. The above methods were based on controlling the surface plasmonic resonance absorption which was determined by the dispersion of Au NPs. However, the high concentrations of other metal ions in real samples probably bring about interference, which will hinder the practical application of these methods. Recently, many metallic NPs, such as Fe_3O_4 NPs, PtNCs and Co_3O_4 NPs, were reported to have enzyme-like activity and thus named as

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“enzyme mimics” or “nanozymes”^[13]. The catalytic activities of these enzyme mimics were affected significantly by surface modification^[14].

Taking advantage of this property, many sensitive colorimetric methods for detecting variety of targets, such as heavy metal ions^[15,16], melamine^[17] and *L*-cysteine^[18], were developed. Among various metallic nanozymes, platinum-containing hybrid nanomaterials were widely utilized in sensor fabrication due to their higher catalytic activity. For example, Lin *et al.*^[18] incorporated platinum NPs onto the surface of graphene oxide (PtNPs/GO) and realized rapid detection of *L*-cysteine. Gao *et al.*^[19] used Au@Pt nanohybrids to amplify the signal of colorimetric immunoassay. Zheng *et al.*^[20] reported that Ag/Pt NCs demonstrated much higher catalytic activity than Pt NCs. In our previous study, the Ag/Pt NCs were also used to fabricating sensitive colorimetric assays for *L*-cysteine and Hg²⁺, based on the inhibition of *L*-cysteine and Hg²⁺ toward the catalytic activity of Ag/Pt NCs^[21,22].

It was reported that *L*-cysteine could bind with Pt NPs by Pt-S bond, which inhibited the catalytic activity of Pt nanozyme^[23,24]. In addition, Cu²⁺ could mediate the catalytic oxidation of sulfhydryl compounds^[25]. On the basis of this, we utilized mercaptopropionic acid (MPA) to inhibit the catalytic activity of Ag/Pt NCs and Cu²⁺ to mediate the oxidation of MPA. As expected, a colorimetric detection of Cu²⁺ was developed. This method was simple, low-cost, highly selective and sensitive.

2 Experimental

2.1 Reagents and apparatus

AgNO₃ was purchased from Sigma-Aldrich (USA). K₂PtCl₄ was from Maya (Shanghai, China). 3,3',5,5'-tetramethylbenzidine (TMB) and sodium borohydride (NaBH₄) were purchased from Aladdin. Single-strand DNA was from Sangon Biotech (Shanghai). All the metal salts were purchased from the National Institute of Metrology (Beijing). All of the other reagents used were of analytical grade. Ultra-pure water prepared with a Milli-Q Pure system was used throughout the experiments.

The ultraviolet-visible (UV-vis) spectra were obtained by an ELx800 spectrometer (UV-2802pcs, Unico). The absorption values of solution were obtained with a microplate reader (Thermo, USA). The transmission electron microscopy (TEM) images of NCs were obtained by a field-emission transmission electron microscope at an accelerating voltage of 200 kV (JEM-2100, JEOL, Japan). A Bruker EMXplus-10/12 spectrometer (Bruker, Germany) with Microwave Bridge (receiver gain, 30; modulation amplitude, 2 Gauss; microwave power, 20 mW; modulation frequency, 100 kHz) was used to measure EPR signals.

2.2 Preparation of Ag/Pt NCs

Ag/Pt NCs were prepared according to the method with a slight modification^[21]. Briefly, 50 μL of AgNO₃ (150 μM), 120 μL of K₂PtCl₄ (125 μM) and 300 μL of ssDNA (2 μM) in phosphate buffer (10.0 mM, pH 7.4) were mixed thoroughly and incubated at 4 °C for 30 min in the dark. Afterwards, freshly prepared NaBH₄ (40 μL, 5 mM) was added to the solution under vigorously shaking. Finally, the mixture was incubated for 3 h (37 °C, 1500 rpm). The obtained Ag/Pt NCs with an average diameter of 4 nm (2.0 μM, calculated according to the concentration of DNA) can be preserved at 4 °C for at least 1 month in the dark.

2.3 Detection of Cu²⁺

Firstly, 90 μL of Cu²⁺ standard solutions (0–200 nM) were mixed with 10 μL of MPA (20 μM) in Tris buffer (10 mM, pH 6.0) in the wells of microplate and incubated for 10 min at room temperature. Then 10 μL of as-prepared Ag/Pt NCs solution (0.5 μM) was added to the wells and incubated for 15 min. Afterwards, 90 μL of substrate containing 30 μL of citrate buffer (0.01 M, pH 4.0), 40 μL of TMB (3 mM) and 20 μL of H₂O₂ (1 M) was added to each well and incubated for 15 min. The absorption values at 652 nm were recorded by a microplate reader.

2.4 Selectivity

To investigate the selectivity of the proposed method, various metallic ions (Hg²⁺, Mn²⁺, Zn²⁺, Fe³⁺, Co²⁺, Cr²⁺, Ag⁺, Ni²⁺, Cd²⁺, Al³⁺, Ba²⁺ and Pb²⁺) were detected by the above method. The concentrations of all the other metal ions were 10 μM.

2.5 Analysis of real samples

Tap water sample, lake water sample and pond water sample were respectively collected from our lab, Lihu Lake (Wuxi) and the campus (Jiangnan University). After filtered through a 0.22-μm membrane, the samples were detected by the above method and Graphite furnace atomic absorption spectroscopy (GF-AAS).

3 Results and discussion

3.1 Characterization of Ag/Pt NCs

TEM images demonstrated that the size of Ag/Pt NCs was approximately 5 nm (Fig.1A). After incubated with MPA, the Ag/Pt NCs were aggregated (Fig.1B). The EDX spectrum of Ag/Pt NCs confirmed the deposition of MPA on the Ag/Pt NCs surface (Fig.2). Interestingly, the Ag/Pt NCs kept mono-

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