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Ultrasensitive colorimetric detection of manganese(II) ions based on anti-aggregation of unmodified silver nanoparticles

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ABSTRACT

We report a facile, selective, and sensitive colorimetric assay for Mn^{2+} ions based on the anti-aggregation of unmodified silver nanoparticles (AgNPs). In the absence of Mn^{2+} ions, the addition of L-arginine to the AgNPs dispersion caused the aggregation of AgNPs via Ag–N covalent interaction, and the color of the solution changed from yellow to colorless. While the presence of Mn^{2+} ions can prevent the aggregation of AgNPs due to the formation of the complex between Mn^{2+} ions and L-arginine, accompanying with a distinct color change from colorless to yellow with the increase of Mn^{2+} ions. Under the optimal experimental conditions, the absorbance at 390 nm was linearly proportional to the Mn^{2+} ions concentration in the ranges from 0 to 700 nM, and from 5 μM to 70 μM, with a detection limit of 20 nM. Also, it was successfully used for the detection of Mn^{2+} ions in environmental water samples.

1. Introduction

Manganese is a required trace element in human body, which acts as cofactors for a great number of enzymes with many functions. For example, manganese enzymes are absolutely indispensable for detoxification of superoxide free radicals in organisms [1]. However, high levels of exposure to manganese are harmful and may cause manganism. Signs of toxicity of manganese include violent acts, depression, and hallucinations. Prolonged exposure to manganese can lead to a Parkinson-like syndrome [2]. Compared with other valence states of manganese, Mn^{2+} ions are stable in environmental water. As a result, many efforts have been devoted to develop various assays for Mn^{2+} ions with high sensitivity and good accuracy. Traditionally, Mn^{2+} ions are mainly detected by instrument analysis, such as atomic absorption spectrometry [3], X-ray florescence spectroscopy [4], inductively coupled plasma mass spectroscopy [5], and inductively coupled plasma atomic emission spectroscopy [6]. Although these methods have a good accuracy and sensitivity, yet they need costly instrument and laborious pre-treatment steps, making them unsuitable for on-spot rapid detection.

In recent years, noble metal nanoparticles as colorimetric probes have drawn great interest owing to their unique advantages, such as high extinction coefficient, size- and morphology-dependent optical properties, strong surface plasmon resonance (SPR) properties, and allowing on-spot detection with the naked eye [7]. Various colorimetric assays have been developed for the detection of metal ions using gold nanoparticles (AuNPs) or silver nanoparticles (AgNPs), including Hg^{2+}, Cu^{2+}, Ag^{+}, Pb^{2+}, Cr^{3+}, Co^{2+} ions and etc. [8–14]. Notably, AgNPs have lower price and higher extinction coefficients than those of AuNPs. To date, only few AgNPs-based colorimetric assays for Mn^{2+} ions have been established [15–17]. Most of the assays are based on the Mn^{2+} ions-induced aggregation of small molecules modified or functionalized AgNPs. Nevertheless, the utilization of functionalized AgNPs not only increases the operation complexity, but also enhances the cost. Besides, the aggregation-based approaches are easily affected by various external factors (temperature, salt, and thiols), leading to bad selectivity and accuracy. As opposed to the aggregation-based approaches, anti-aggregation-based methods may conquer the corresponding drawbacks because they can reduce or eliminate the possibility of interference. However, the colorimetric assays for Mn^{2+} ions based on anti-aggregation of AgNPs have not yet been developed, to the best of our knowledge.

In the present work, for the first time, we propose a rapid, facile, sensitive, and selective colorimetric assay for Mn^{2+} ions based on the aggregation of unmodified AgNPs via deactivating the aggregation reagent (L-arginine) by Mn^{2+} ions. The developed colorimetric approach showed the high sensitivity (20 nM) which is superior to the previously reported nanoparticles-based assays for the detection of Mn^{2+} ions, and good selectivity over other common metal

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ions. In order to prove the practicality of this colorimetric assay, it was successfully applied to the detection of Mn^{2+} ions in real water samples.

2. Experimental details

2.1. Chemicals and instruments

Silver nitrate ($AgNO_3$), manganese(II) chloride ($MnCl_2$), sodium chloride (NaCl), calcium nitrate ($Ca(NO_3)_2$), magnesium chloride ($MgCl_2$), potassium chloride (KCl), nickel nitrate ($Ni(NO_3)_2$), zinc nitrate ($Zn(NO_3)_2$), cobalt dichloride ($CoCl_2$), ferric trichloride ($FeCl_3$), ferrous dichloride ($FeCl_2$), and sodium borohydride ($NaBH_4$) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). L-arginine and tri-sodium citrate were obtained from Aladdin Reagent Co. Ltd (Shanghai, China). All the chemical reagents were at least of analytical grade and used as received. The aqueous solutions were prepared with ultrapure water ($18.2\,M\Omega\,cm^{-1}$) from a Millipore Milli-Q system (Merck Millipore, USA).

The morphology and size of the AgNPs were characterized using a HT7700 transmission electron microscopy (TEM, HITACHI, Japan). Ultraviolet–visible (UV–vis) absorption spectra were determined via a UV-1800 UV–vis spectrophotometer (Shimadzu, Japan). Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was performed with an iCAP6500 plasma emission spectrophotometer (Thermo Scientific, USA).

2.2. Synthesis of citrate-stabilized AgNPs

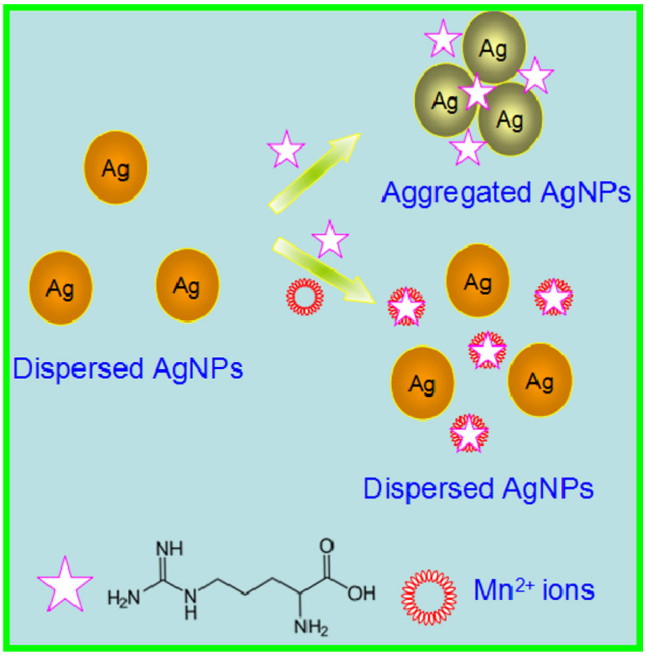
The citrate-stabilized AgNPs (citrate-AgNPs) were prepared according to the reported procedure with slight modification [18]. Typically, 5 mL of 20 mM $AgNO_3$ aqueous solution and 3 mL of tri-sodium citrate (1%) were added into a beaker flask. After that, 50 μL of fresh $NaBH_4$ solution (0.05 M) was quickly injected into the mixture under vigorous stirring, and the solution was kept continually stirring for another 30 min to produce a yellow solution. Finally, the as-prepared AgNPs was stored at 4 °C before use. The concentration of AgNPs solution was estimated to be 0.28 nM according to Beer's law with an extinction coefficient of ca. $5.56 \times 10^8\ M^{-1}\ cm^{-1}$ at 390 nm [19].

2.3. Colorimetric detection of Mn^{2+} ions

For detection of Mn^{2+} ions using AgNPs dispersion, different concentrations of Mn^{2+} ions (0–60 μM) and 0.3 mL of 7 mM L-arginine were added into Britton–Robinson (B-R) buffer solution (pH 9.4), and then 545 μL AgNPs was added to above solution. The total volume of the solution was 3 mL. Finally, the mixture was incubated at room temperature for 40 min. Afterwards, photographs and UV–vis absorption spectra were taken.

2.4. Detection of Mn^{2+} ions in real water samples

Lake water and river water were collected from Center Lake of Southwest University of Science and Technology campus and Fujiang River (Mianyang, China), respectively. Tap water was obtained from our own laboratory. They were filtered through the funnel and diluted to 10 times with B-R buffer solution (pH 9.4). After that, a series of Mn^{2+} ions standard solution were respectively added into the diluted lake water, river water, or tap water. These real water samples were analyzed using the developed assay or ICP-AES.



Scheme 1. Schematic illustration of the detection mechanism of Mn^{2+} ions based on the aggregation of unmodified AgNPs.

3. Results and discussion

3.1. Detection mechanism

The detection mechanism of Mn^{2+} ions is illustrated in Scheme 1. The citrate–AgNPs were well-dispersed owing to the electrostatic repulsion of negatively charged citrate ions on the surface of AgNPs. In the absence of Mn^{2+} ions, the addition of L-arginine to the citrate–AgNPs dispersion caused an aggregation of citrate-AgNPs and the color of the solution changed from yellow to colorless. The reason for the aggregation of AgNPs was that L-arginine with rich nitrogen atoms had stronger affinity with AgNPs than the citrate ions, which could substitute citrate ions via Ag–N covalent bond [20]. Once Mn^{2+} ions were pre-mixed with L-arginine followed by mixing with citrate–AgNPs solution, the covalent interaction of L-arginine with AgNPs would be inhibited thanks to the higher binding affinity of L-arginine for Mn^{2+} ions. In this case, a turnover process from aggregation to dispersion state of AgNPs occurred, depending on the concentration of Mn^{2+} ions. Meanwhile, the color of AgNPs dispersion gradually changed from colorless to yellow. Accordingly, the AgNPs-L-arginine system allowed the colorimetric detection of Mn^{2+} ions with the UV–vis spectroscopy or naked eye.

In order to verify the validity of the detection mechanism of Mn^{2+} ions, UV–vis spectroscopy and TEM observation were performed. As shown in Fig. 1, a characteristic SPR band of AgNPs dispersion is observed at 390 nm and the dispersion color is light yellow (curve a). In the absence of Mn^{2+} ions, the addition of 0.7 mM L-arginine to AgNPs dispersion caused the decrease of the absorbance at 390 nm, and the color of the dispersion turned colorless (curve b), indicating that the aggregation process occurred. However, when L-arginine was pre-treated with Mn^{2+} ions, the absorbance of AgNPs dispersion at 390 nm greatly increased, and the dispersion color changed back to yellow, demonstrating that AgNPs was dispersed. It should be noted that the absorbance of AgNPs dispersion in the presnece of Mn^{2+} ions and L-arginine is higher than that of crude AgNPs dispersion. The phenomenon can be explained as a superposition of AgNPs dispersion and the metal