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Colorimetric detection of iron ions (III) based on the highly sensitive plasmonic response of the *N*-acetyl-L-cysteine-stabilized silver nanoparticles

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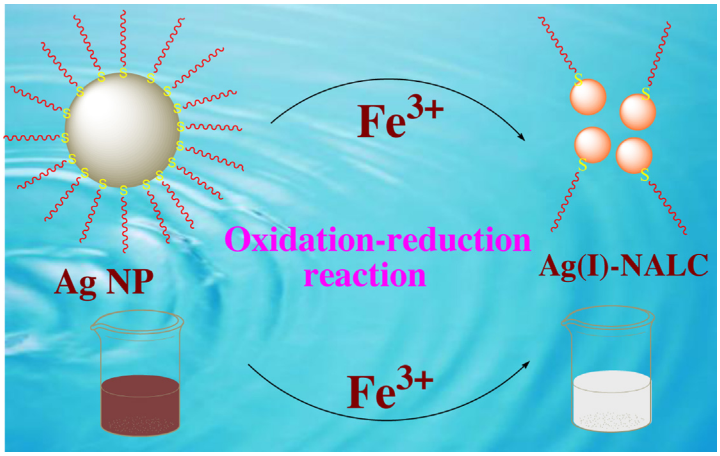
HIGHLIGHTS

- *N*-acetyl-L-cysteine-stabilized Ag nanoparticles are synthesized by a chemical reduction method.
- The surface plasmon resonance intensity of the silver nanoparticles decreases with Fe^{3+} concentration.
- The silver nanoparticles can be used for sensitive and selective detection of Fe^{3+} ions in water.
- A new detection mechanism of oxidation–reduction reaction between Ag NPs and Fe^{3+} ions is proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

We report here a facile colorimetric sensor based on the *N*-acetyl-L-cysteine (NALC)-stabilized Ag nanoparticles (NALC–Ag NPs) for detection of Fe^{3+} ions in aqueous solution. The Ag NPs with an average diameter of 6.55 ± 1.0 nm are successfully synthesized through a simple method using sodium borohydride as reducing agent and *N*-acetyl-L-cysteine as protecting ligand. The synthesized silver nanoparticles show a strong surface plasmon resonance (SPR) around 400 nm and the SPR intensity decreases with the increasing of Fe^{3+} concentration in aqueous solution. Based on the linear relationship between SPR intensity and concentration of Fe^{3+} ions, the as-synthesized water-soluble silver nanoparticles can be used for the sensitive and selective detection of Fe^{3+} ions in water with a linear range from 80 nM to 80 μM and a detection limit of 80 nM. On the basis of the experimental results, a new detection mechanism of oxidation–reduction reaction between Ag NPs and Fe^{3+} ions is proposed, which is different from previously reported mechanisms. Moreover, the NALC–Ag NPs could be applied to the detection of Fe^{3+} ions in real environmental water samples.

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1. Introduction

In modern society, more and more people pay attention to their living standard, including usual daily food, drink, and surrounding environment. Metal elements are essential components for living body. The metals in the form of ions can coordinate with protein, nucleic acid, vitamin and hormone to generate metalloprotein and metalloenzyme etc. which play critical roles in regulating the important biochemical and physiological processes of life [1,2]. However, any metal ion with too higher and/or lower level would destroy the balance of metabolism. Thus quantitative determination of metal ions concentration is the key to ensure the metal ions on healthy level. Iron is one of essential trace element and it is a necessity for many physiological processes in human and animal bodies [3,4]. Iron ions in body are usually responsible for the transfer and transport of oxygen and block materials. The lack of iron ions will result in a lot of physiological and pathological diseases, such as iron-deficiency anemia, methemoglobinemia, liver and kidney damage, diabetes and heart diseases, and so on. Thus, qualitative and quantitative detection of Fe^{3+} is required to ensure body health [3–5].

Nowadays, many analytical techniques, such as atomic absorption spectrometry, inductively coupled plasma mass spectrometry and inductively coupled plasma emission spectrometry, have been applied to the detection of metal ions. However, these methods usually need sophisticated equipments and tedious sample preparation steps. Recently, chemsensors fabricated from fluorescent nanoparticles, such as carbon dots, graphene quantum dots, and noble metal nanoparticles or nanoclusters for sensing of metal ions have attracted wide attention due to their good selectivity, high sensitivity and easy operation [6–8]. Colorimetric assay has also been extensively utilized to detect heavy metal ions in aqueous solution because of the cost-efficient and less time-consuming procedures compared to other methods [9–12]. For example, Yin et al. developed a facile colorimetric sensor for ultrasensitive determination of Cu^{2+} based on catalytic oxidation of L-cysteine [13]. Meanwhile, metal nanoparticles and nanorods have recently received increasing interest in colorimetric assay because of the pronounced surface plasmon resonance (SPR), highly stable dispersion, good biocompatibility, and tunable physical and chemical properties dependent on size and shape [14–17]. Among the coinage metal nanoparticles (Cu, Ag, Au), it is well-known that silver has the strongest surface plasma resonance, even with the size down to 2 nm. Therefore, most of SPR-related fundamental investigations and sensing applications have focused on silver nanoparticles. For instance, Duan et al. realized the colorimetric detection of Hg^{2+} based on silver nanoparticles [18]. Annadhasan et al. reported the simultaneous detection of Hg^{2+}/Mn^{2+} by using green-synthesized silver nanoparticles [19]. In another report, silver nanoparticles were also used to detect copper ions with paper-based devices [20]. It should be pointed out that although such method has achieved much development, to the best of our knowledge, the sensitive detection of Fe^{3+} based on plasmonic silver nanoparticles has not yet been reported. Herein, we aim to synthesize appropriate silver nanoparticles for the colorimetric sensing of Fe^{3+} with high sensitivity and selectivity.

For preparing metal nanoparticles, it is common to use organic protecting ligands to improve the stability and dispersity of nanoparticle. As an example, oleylamine-stabilized Au–Ag alloy nanoparticles with tunable size and surface plasmon resonance frequency have been reported [21]. In another work, cysteamine was also utilized as efficient protecting ligand to prepare Ag nanoparticles in aqueous medium [22]. Among the used stabilizing agents, amino acid (AA) containing both amino-group and carboxyl group could show either hydrophilic or hydrophobic property. Due to the unique structure and properties, AA with either acidic or basic characteristic has been widely used to stabilize metal nanoparticles. For example, water-soluble gold nanoparticles have been successfully synthesized by using tryptophan and L-cysteine as protecting ligands [23,24]. Sastry and his co-workers successfully synthesized Ag and Au nanoparticles by using cysteine and lysine as capping ligands, respectively [25,26]. As far as we know, there is scarce report of the usage of *N*-acetyl-L-cysteine as protecting ligand for the preparation of noble metal nanoparticles, except for its participation in the synthesis of small Au and Ag nanoclusters [27]. Recently, *N*-acetyl-L-cysteine-protected silver nanoparticles have been reported as optical sensors and colorimetric assay for Ni^{2+} ions detection [28].

Here, by using the strong interaction between cysteine (—SH) and silver, we present a simple method to prepare *N*-acetyl-L-cysteine-stabilized Ag nanoparticles (denoted as NALC–Ag NPs) without tedious post-synthesis step. The prepared Ag nanoparticles are water-soluble and show strong surface plasmon resonance around 400 nm. It was found that the SPR intensity of the as-synthesized Ag nanoparticles decreases when Fe^{3+} ions were gradually introduced into the solution. Moreover, the color of the Ag nanoparticle solution showed a change upon addition of different concentrations of Fe^{3+}. On the basis of the SPR intensity of the silver nanoparticles, the sensitive detection of Fe^{3+} has been successfully realized. The sensitivity and limit of detection were calculated to be 0.00578 μM^{-1} and 80 nM, respectively. Meanwhile, the color change of the Ag colloidal solution can be distinguished by naked eyes, which can also be used to directly check whether the presence of Fe^{3+} or not in the solution. More importantly, different from the previously reported detection mechanisms based on ligand-induced aggregation of Ag nanoparticles and formation of nanoalloys, the present study demonstrates a new sensing mechanism based on Fe^{3+}-induced decomposition of Ag nanoparticles, resulting in highly sensitive plasmonic response.

2. Experimental

2.1. Materials

Silver nitrate ($AgNO_3$), potassium hydroxide (KOH), and ethanol (CH_3CH_2OH) were purchased from Beijing Chemical Reagent. *N*-acetyl-L-cysteine ($C_5H_9O_3N_3S$) and L-cysteine were obtained from Alfa Aesar. Sodium borohydride ($NaBH_4$) was purchased from ACROS. Standard stock (10 mM) solution of metal ions (Hg^{2+}, Ca^{2+}, Fe^{3+}, Na^{+}, Cu^{2+}, K^{+}, Ni^{2+}, Co^{2+}, Pb^{2+}, Ag^{+}, Mn^{2+}, Mg^{2+}, Zn^{2+}, Cd^{2+}, MnO_4^{-} and $Cr_2O_7^{2-}$) were prepared with ultrapure water from the respective metal salts (NaCl, KCl, $CuCl_2 \cdot H_2O$, $ZnCl_2$, $CaCl_2$, $FeCl_3 \cdot 6H_2O$, $AgNO_3$, $MgSO_4$, $Hg(NO_3)_2 \cdot 1/2H_2O$, $MnCl_2$, $NiCl_2 \cdot 6H_2O$, $Pb(NO_3)_2$, $CoCl_2 \cdot 6H_2O$, $Cd(CH\ COO)_2 \cdot H_2O$, $KMnO_4$ and $K_2Cr_2O_7$). All chemicals were used as received without any further purification. Water was supplied by a Nanopure water system (18.3 MΩ cm).

2.2. Instruments

UV–vis spectra were recorded on UV-3000PC Spectrophotometer (Shanghai Mapada Instruments Co., Ltd.). X-ray photoelectron spectroscopy (XPS) measurements were performed by using AVG Thermo ESCALAB250 spectrometer (VG Scientific) operated at 120 W. Fourier-transformed infrared spectroscopy (FTIR) study was conducted on a Vertex 70 FTIR with a KBr wafer technique, i.e., the solid mixture of KBr and Ag NP (NALC) were ground into fine powder and then pressed into transparent sheet by sheeting-out mill. The size and morphology of the as-synthesized Ag NPs were examined by using a Hitachi H-600 transmission electron microscope (TEM) operated at 100 kV. High resolution transmission electron microscope (HRTEM) images were obtained from a JEM-2010 (HR) microscope operated at 200 kV. Dynamic light

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