Original article

Tuning plasmon absorption of unmodified silver nanoplates for sensitive and selective detection of copper ions by introduction of ascorbate

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A B S T R A C T

Silver nanoplates as novel optical sensors for Cu^{2+} detection have been demonstrated. Silver nanoplates are synthesized *via* previous H_2O_2–$NaBH_4$ cyclic oxidation–reduction reactions. With introduction of ascorbate as mild reductants, Cu^{2+} ions are reduced into Cu^+ and the Cu^+ is further reduced to Cu, which is deposited on the surface of the silver nanoplates. The deposition of the Cu on the surface of the silver nanoplates allows a significant red-shift of their plasmon absorption. Therefore, trace Cu^{2+} can be detected. The shift of the plasmon absorption wavelength of silver nanoplates is proportional to the Cu^{2+} concentration over a range of 40–340 μmol L^{-1} with a limit of detection of 9.0 μmol L^{-1}. Moreover, such silver nanoplate-based optical sensors provide good selectivity for Cu^{2+} detection, and most other metal ions do not disturb its detection. Moreover, the practicality of the proposed sensor was tested. This Cu^{2+} assay is advantageous in its simplicity, selectivity, and cost-effectiveness.

1. Introduction

With unique optical/electronic properties for potential applications, silver nanoplates (also nanoprisms or nanodisks) have been intensively studied [1–4]. The lateral dimensions being much larger than the thickness provides silver nanoplates an extreme degree of anisotropy, which favors highly tunable localized surface plasmon resonance absorption and maximum electromagnetic-field enhancement [4–7]. Such attractive features make them promising nanomaterials for chemo/bio sensing applications [1,3,7]. For instance, the shape-dependent plasmon absorption shifts of silver nanoplates have yielded various colorimetric sensors [3,8,9]. Also, silver nanoplates have been exploited for use in metal-enhanced fluorescence and surface-enhanced Raman scattering sensors in sensing applications [1,7,10–14].

Although copper is an essential element for life, excess copper levels exert toxicity to living organisms and lead to serious environmental contamination [15]. Therefore, Cu^{2+} recognition and detection is necessary, and optical sensors/probes for

detection of copper ions have been continuously studied. For instance, various chromogenic/fluorophoric probes for copper ion detection have been reported [16–19]. Despite their high sensitivity and selectivity, these sensors have certain drawbacks, including water-insolubility and time-consuming preparations. Fortunately, various emerging functional nanomaterials have been exploited as novel optical sensors/probes for copper ion detection with advantages of water-solubility and simple preparations. For example, a copper/silver nanocluster has served as a fluorescent probe for copper ion detection [20]. Also, a polyamine-functionalized carbon quantum dot probe for detection of Cu^{2+} has also been developed [21]. Moreover, nanomaterial-based colorimetric assays for Cu^{2+} detection by naked eye inspection have received intensive attention. For instance, a colorimetric assay for copper ions detection based on catalytic leaching of silver-coated gold nanoparticles has been established [22]. Also, functionalized-gold nanoparticles have been used as colorimetric probes for copper ions [23–28]. However, these colorimetric probes involved time-consuming modification of the gold nanoparticles. Therefore, modification-free nanomaterials for sensing copper ions are preferred.

Here, we describe a new silver nanoplate-based optical sensor for Cu^{2+} detection. Silver nanoplates are synthesized *via* previously

established H_2O_2–$NaBH_4$ cyclic oxidation-reduction reactions [29]. With introduction of ascorbate as a mild reductant, Cu^{2+} ions are reduced into Cu^+, and the Cu^+ is further reduced into Cu, which is deposited on the surface of the silver nanoplates. The deposition of the Cu on the surface of the silver nanoplates causes significant red-shifts of the surface plasmon resonance absorption. Therefore, trace Cu^{2+} can be detected. Such silver nanoplate-based optical sensors provide good selectivity for Cu^{2+} detection and most other metal ions do not disturb its detection. This sensing strategy for Cu^{2+} detection is advantageous for its simplicity, selectivity, and cost-effectiveness.

2. Experimental

2.1. Materials

Silver nitrate, ascorbic acid, sodium borohydride, and sodium citrate were purchased from Sigma–Aldrich. H_2O_2 solutions (30 wt%) and analytical grade $CuSO_4 \cdot 5H_2O$ were obtained from Sinopharm Chemical Reagent Co., Ltd.

2.2. Instruments

TEM (HR-TEM) and energy dispersion spectroscopy element analyses were performed on a JEOL JEM-2100 transmission electron microscope and JSM-6380 scanning electron microscope, respectively. Absorption spectra were recorded by PerkinElmer-Lambda 35 UV–vis spectrophotometer.

2.3. Synthesis of silver nanoplates

Silver nanoplates were prepared via a previously reported method [29]. Typically, a 24.75 mL aqueous solution containing silver nitrate (0.05 mol L^{-1}, 50 µL), trisodium citrate (75 mmol L^{-1}, 0.5 mL) and H_2O_2 (30 wt%, 60 µL) was vigorously stirred. Sodium borohydride ($NaBH_4$, 100 mmol L^{-1}, 250 µL) was rapidly injected into this mixture to initiate the cyclic oxidation–reduction reactions toward silver. When the color of the solution turned blue, silver nanoplates had been synthesized. The total 25 mL solution contains 125 µmol L^{-1} silver nanoplates (calculated with silver amount).

2.4. Detection of copper ions

The as-prepared silver nanoplates were purified by centrifugation and redispersed into citrate buffers (10 mmol L^{-1}, pH 5.0). For copper ion detection, 62.5 µmol L^{-1} silver nanoplate solution was incubated with 5.0 mmol L^{-1} ascorbate and various amount of Cu^{2+} ranging from 0.0–800 µmol L^{-1} for 30 min and then subjected to UV–vis spectroscopy measurements.
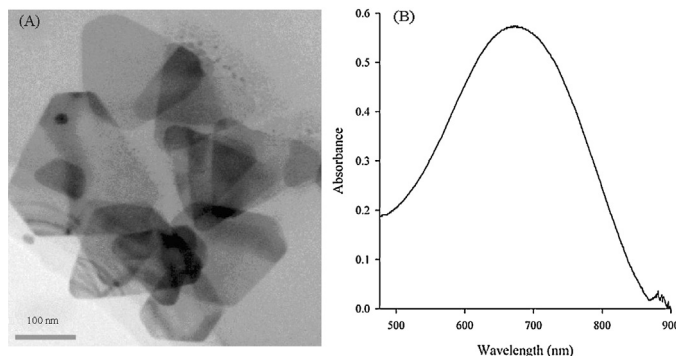

Fig. 1. (A) TEM image and (B) the absorption spectrum of silver nanoplates (125 µmol L^{-1}).

3. Results and discussion

3.1. Synthesis and characterization of silver nanoplates

By a facile previously reported cyclic oxidation-reduction reaction [29], blue silver nanoplate colloids were synthesized. TEM analysis in Fig. 1A shows their morphology and size features. Results indicate they are polymorphous. Fig. 1B shows their absorption spectrum with a characteristic peak at 670 nm.

3.2. Sensing mechanism

As shown in Fig. 2, the addition of copper ions causes the initial 670 nm plasmon absorption peak of silver nanoplates to be significantly red-shifted to 714 nm. On the other hand, the absorbance of free Cu^{2+} (340 µmol L^{-1}) in this wavelength range is very small, even when ascorbate present. When ascorbate was present, Cu(II) was reduced into Cu(I), and the induced Cu(I) was further reduced to Cu(0) [30], and the reduced Cu was further deposited onto the surface of the silver nanoplates. The elemental analyses of energy dispersion spectroscopy of the dried silver nanoplates derived after the sensing reaction show that the surface composition of the silver nanoplates contains an average level of 27.4% Cu (ten silver nanoplates are measured). This result confirms that copper is indeed deposited on the surface of the silver nanoplates due to ascorbate reduction of copper ions. Although the trace deposited Cu obscures discernible variation of the silver nanoplate dimensions and shape, as confirmed by TEM analyses, the HR-TEM analyses indicate that the original clear surface crystal lattice structure of silver nanoplate turns indiscernible due to the deposition of a noncrystalline Cu layer, as shown in Fig. 2B and C. The in-plane dipole resonance of silver nanoplates has been proven to be very intense, and its wavelength is extremely dependent on the height, edge length, and tip sharpness of silver nanoplates [5,7,31]. In addition, the plasmon absorption is extremely sensitive
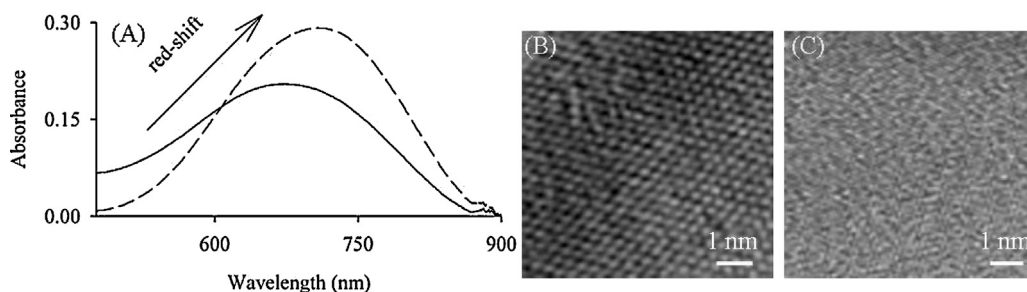

Fig. 2. (A) Silver nanoplate (62.5 µmol L^{-1}) absorption spectra in the absence (solid curve) and presence (dashed curve) of copper ions (340 µmol L^{-1}). The HR-TEM images of the surface structure of single silver nanoplates in the absence (B) and presence (C) of copper ions by introduction of ascorbate as a reductant. The deposition of a noncrystalline Cu layer on the silver nanoplate completely obscures the crystal lattice of the original silver nanoplate.