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Colorimetric determination of Hg(II) by combining the etching and aggregation effect of cysteine-modified Au-Ag core-shell nanorods

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ABSTRACT

In this report, a simple and effective approach for colorimetric detection of Hg^{2+} based on surface etching and aggregation effect of cysteine-modified Au-Ag core-shell nanorods has been investigated. When the addition of Hg^{2+} has a low concentration under 60 μM, electrostatic interaction-induced intense aggregation of colloidal Au-Ag core-shell nanorods takes place. Thus the longitudinal plasmonic absorption peak decreases rapidly, which also leads to the colloidal color become shallow. Whereas when the addition of Hg^{2+} has a high concentration greater than 60 μM, the adherent cysteine molecules break away from the surface of nanorods due to the intense Hg-S bond. Then the bare nanorods have been etched under the action of Hg^{2+}. The decrease of the Ag shell results in the red shift of the longitudinal absorption peak, which further leads to the color change of the colloids. The sensing based on particle aggregation-induced absorption decrease has a linear response for Hg^{2+} from 1 to 60 μM with a theoretical detection limit of 0.273 μM. The sensing based on etching effect-induced red shift has a logarithmic response for Hg^{2+} from 60 to 250 μM with a theoretical detection limit of 1.065 μM. Interference test and real samples detection results show that Hg^{2+} could be specifically detected by using this probe based on Au-Ag core-shell nanorods.

1. Introduction

Noble metallic nanoparticles have been studied widely due to their strong and tunable light absorption and scattering within the visible region based on localized surface plasmon resonance (LSPR) [1]. The origin of LSPR could be attributed to the collective oscillation of conduction band electrons at the particle surface, which greatly depends on the particle geometry, interparticle interaction and local dielectric environment [2]. Therefore, chemical and biologic molecule-induced tiny change of particle geometry, aggregation and dielectric coating could results in large change of the optical and spectral properties of the colloidal particles. Thus noble metal, such as gold and silver, nanoparticles have promising widely applications in (bio)chemical sensing, detection and imaging [3,4].

Surface etching is an effective method to change the shape of metal nanoparticles and then tuning their optical properties. Thus spectral and colorimetric sensors based on etching of noble metal nanoparticles have attracted great attention due to their distinct variation in absorption spectrum and color associated with morphology changes [5–8]. Based on enzymatic-like reaction mediated etching of gold nanorods, Zhang et al. reported an ultrasensitive visual method for on-site detection of glucose in human urine [9]. In their method, gold nanorods were efficiently etched by hydrogen peroxide, which was generated by glucose-glucose oxidase enzymatic reaction. The etching of gold nanorods leads to a decrease of the particle aspect ratio and a blue-shift of longitudinal LSPR. Under optimized condition, the sensitivity toward glucose has been obtained with a detection limit of 0.1 μM and a visual detection limit of 3 μM. The H_2O_2-based sensing applications have also been used in the etching of silver nanoparticles. Zhang et al. reported the colorimetric detection of hydrogen peroxide and lactate based on the etching of the carbon based Au-Ag bimetallic nanoparticles [10]. When adding H_2O_2 owing to the etching effect of H_2O_2 towards silver, the characteristic LSPR absorbance peak of Au-Ag/C nanoparticles declined and red-shifted with the colloid color changing from reddish orange to light pink. This colorimetric strategy could be applied to directly detect of lactate by naked eye and spectrum with the linear range of 0.1–22 mM and 22–220 mM. By using the etching of silver nanoprisms, colorimetric detection of catalase and catalase-positive bacteria (*E. coli*) has also been studied [11]. The formation of silver nanoprisms with LSPR at long wavelengths is

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facilitated by the oxidative etching of the particles in the presence of a reducing agent and citrate. When enzymes disrupts the redox balance, the shape and size of the nanoparticles change to yield a color variation from blue to purple, red, orange and yellow. It has been found that the multi-color transition of silver colloids can provide quantification of catalase and *E. coli* by eye. Zhu et al. reported a colorimetric sensing method for detecting Pb^{2+} based on the accelerated etching of gold nanorods [12]. In the method, the sodium thiosulfate-induced dissolution rate of gold nanorods could be accelerated by the addition of Pb^{2+}. Then the accelerated etching results in the shape change of the gold nanorods to gold nanospheres, which further leads to a qualitative spectral change from double band to single band LSPR. Thus a distinct irreversible color change of the gold colloid from blue to red takes place and could be used to detect Pb^{2+} with excellent selectivity and high sensitivity. Recently, a new strategy for high-performance colorimetric detection of Hg^{2+} based on anti-etching of silver nanoprisms has been reported [5]. In the presence of Hg^{2+}, the formation of Ag-Hg alloy could protect the silver nanoprisms from iodide ions-induced etching and the colloidal color remains blue. A good linear relationship between the LSPR shift and Hg^{2+} concentrations indicates that the silver nanoprisms-based probe could be used for the detection of Hg^{2+}.

Particle aggregation is the other effective approach to change the inter-particle distance and interaction, which further tunes their optical properties. When biomarkers, organic molecules and inorganic ions work as bridges connecting the colloidal nanoparticles and result in the aggregation, the plasmon coupling will leads to the appearance and red shift of the new LSPR peak corresponding to the longitudinal plasmon resonance. Therefore, the analytes could be detected sensitively by measuring the wavelength shift and intensity increase of the LSPR peak in the absorption spectrum. Thus spectral and colorimetric sensing based on aggregation of noble metal nanoparticles have also been widely studied in recent years [13–18]. In the nanochain structure consisting of several gold nanoparticles, a new longitudinal LSPR, which could be adjusted from visible to near infrared range, has been observed in absorption spectra due to the particle aggregation [19]. This plasmonic coupling in gold nanochain could be applied in bio-assay for ractopamine through the change of colloidal color and LSPR absorption peak with naked eye or absorption spectra. Deng et al. reported a sensitive and selective method for PPi sensing in synovial fluid of arthritis patients with gold nanoparticles as the signal readout [20]. The addition of Cu^{2+} to the gold colloid containing cysteine causes the particle aggregation, resulting in the wine red-to-blue color change and the appearance of a new absorption at 650 nm. The subsequent addition of PPi well solubilizes the aggregated gold nanoparticles with the changes in both the color and the absorption spectrum. Thus the concentration of PPi could be visualized with the naked eyes through the color change of the colloid and quantitatively determined by spectroscopy. Zhu et al. reported an ultra-sensitive sensing of AFP Based on multi-spectral information from face-to-face aggregation of gold triangular nanoplates [21]. Due to the AFP-induced face-to-face aggregation of the gold nanoplates, both the absorbance intensity and the peak wavelength of the in-plane dipole LSPR are sensitive to the AFP concentration. By analyzing the intensity decrease and wavelength shift of the absorption peak, AFP could be detected with a detection limit of 0.2 pg/mL. Huang et al. reported a novel anti-aggregation gold nanoparticle-based colorimetric sensing method for detecting Hg^{2+} [22]. The method was based on the aggregation of gold colloid in the presence of an aggregation agent inhibited by Hg^{2+} because of high affinities between Hg^{2+} and the aggregation agents. Under optimized conditions, the sensitivity of the sensing method for detecting Hg^{2+} ions is ca. 25 nM. Hg^{2+} ions have also been detected using silver nanorods as a probe [23]. Based on the aggregation and re-aggregation of silver nanorods in the presence of dithiothreitol, Karthig et al. studied the selective and sensitive determination of Hg^{2+} in aqueous solution. This developed sensing method had good linearity under the optimal conditions with a limit of detection of 0.15 pM.

These previous reports indicate that both the etching and aggregation of metal nanoparticles could be finely used in the spectrum sensing and colorimetric detection. Is it possible for us to develop a new sensing method by combining the etching and aggregation effect? In this way, the improved sensing performances such as sensitivity and detection range are expected to be obtained. In this paper, cysteine-modified Au-Ag core-shell nanorods have been synthesized and used for detection of Hg^{2+}. Under different concentration range of Hg^{2+}, the effect of aggregation and etching takes place, respectively. Thus, both the intensity decrease and wavelength shift of the LSPR peak could be used in Hg^{2+} sensing, which greatly enlarges the detection range.

2. Experimental

2.1. Reagents

Cetyl trimethyl ammonium bromide ($C_{19}H_{42}BrN$; CTAB), L-Ascorbic acid ($C_6H_8O_6$; AA), sodium borohydride ($NaBH_4$) and silver nitrate ($AgNO_3$) were purchased from Sigma-Aldrich (USA). L-Cysteine ($C_3H_7NO_2S$) was purchased from Wolsen (China). Chloroauric acid ($HAuCl_4{\cdot}3H_2O$), $HgCl_2$, $CaCl_2$, $Cr(NO_3)_3$, $Pb(NO_3)_2$, $NaNO_3$, $MnC1_2$, $MgCl_2$, KCl, $AlCl_3$, $CuCl_2$, NH_4Cl were obtained from Shanghai Chemical Reagent Co. Ltd. (China). Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were obtained from Xi'an Hairmer Co. Ltd. (China). All the reagents were of analytical grade and were used without further purification. The ultrapure water with 18.2 MΩ cm was used throughout the experiments. Other specs of the ultrapure water are TOC (total organic carbon) ≤5 ppb, RNases ≤0.01 ng/mL and DNases ≤4 pg/μL.

2.2. Preparation of Au-Ag core-shell nanorods

Gold nanorods were prepared according to the seed mediated growth method reported by Nikoobakht and El-Sayed [24]. Briefly, CTAB solution (5 mL, 0.1 M) was mixed with 250 μL of 0.01 M $HAuCl_4$ and stirred. To this stirred solution, 600 μL of ice-cold 0.01 M $NaBH_4$ was added under stirring, which resulted in the formation of abrownish-yellow seed solution with vigorous stirring for 5 min. Then the solution was kept at 25 °C in the absence of stirring. For the preparation of growth solution, the mixture of 9.5 mL of 0.1 M CTAB and M_i mL of 0.01 M $AgNO_3$ solution was firstly added to 400 μL of 0.01 M $HAuCl_4$, and then ascorbic acid (250 μL, 0.1 M) was added with gentle mixing. Here, M_i is the volume of added $AgNO_3$ solution, which is increased from 5 to 75 μL in order to control the aspect ratio of the gold nanorods. Afterwards, 250 μL of the seed solution was added. The mixture was maintained at 27–30 °C overnight without any further stirring. These colloidal gold nanorods were used to prepare Ag-Au core-shell nanorods.

The preparation of Au-Ag core-shell nanorods is similar to the previous reported method [25,26]. In summary, the colloidal gold nanorods were centrifuged at 8000 rpm/min for 15 min firstly, and then were dispersed in the same amount of CTAB (0.08 M) solution. N_i mL of 0.01 M $AgNO_3$ solution, 0.4 mL of 0.1 M AA solution and 1 mL of 0.1 M sodium hydroxide solution were added to 5 mL above prepared gold nanorods colloid with water bath heating at 65 °C for 4 h. Here, N_i is the volume of added $AgNO_3$ solution, which is increased from 50 to 450 μL. By tuning the volume of added $AgNO_3$, Au-Ag core-shell nanorods with different Ag nanoshell thicknesses were prepared.

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