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Precise modulation of gold nanorods aspect ratio based on localized surface plasmon resonance

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ABSTRACT

Gold nanorods (GNRs) aspect ratio is significant to GNRs-based biomedical sensors. In this paper precise modulation of GNRs aspect ratio was realized by H_2O_2 oxidation based on localized surface plasmon resonance (LSPR) of GNRs. The oxidation process was studied in detail. A linear relationship was revealed between H_2O_2 oxidation time and the longitudinal LSPR wavelength of GNR, the latter depending on GNRs aspect ratio. Using the relationship GNRs aspect ratios could be modulated by H_2O_2 oxidation time. Oxidation time deduced aspect ratio was verified by transmission electron microscope (TEM) characterization and the average error is 2.92%. Influences of temperature and pH value on the modulation process were investigated. Increase in temperature (from 30 °C to 60 °C) or solution acidity (pH value from 2.6 to 1.2) facilitated the oxidation process. The proposed method is characterized by its simplicity and efficiency, and would find extensive application prospects in GNRs-based biomedical sensing fields.

1. Introduction

Noble metal nanoparticles have attracted worldwide attention because of their unique optical properties [1]. A noteworthy characteristic of noble metal nanoparticles is their well-known localized surface plasmon resonance. LSPR exhibits a strong absorption band in the ultraviolet-visible (UV–vis) absorption spectrum when incident photon frequency is resonant with the collective oscillation of the conduction electrons on metal surface [2,3]. Gold nanoparticles, such as nanospheres, nanorods, etc., are most widely studied due to their stable chemical properties compared to other metals [4]. Gold nanorods (GNRs) are especially promising in biomedical sensing field, characterized by their tunable anisotropic optical property and wide spectrum range (ranging from visible light to near infrared region) [5]. GNRs possess of two LSPR bands in their UV–vis absorption spectrum, belonging to the longitudinal and transverse surface plasmon resonance, respectively [6,7]. The longitudinal plasmon absorption band (LPAB) arises from the light absorption and scattering along the particle long axis, and the transverse plasmon absorption band (TPAB) corresponds to the light absorption and scattering along the short axis direction [8]. The former is highly sensitive to the dielectric properties of surrounding environment as well as particle aspect ratio, based on which some plasmonic applications have been developed [9].

The parameter of GNRs aspect ratio has a decisive influence on their optical properties since it changes the rod light scattering and absorption cross-section, and affects the localized surface plasmon resonance spectrum [10,11]. GNRs with specific aspect ratios have found wide applications in optical devices or biomedical sensing fields. For example, GNRs with aspect ratio of 1.7 were used as a substrate for surface enhanced Raman scattering (SERS) [12], and GNRs with aspect ratio of 2.14 were prepared for multimodal optical imaging of cancer cells [13]. In addition, GNRs with specific aspect ratios were conjugated with biomolecular targeting or recognition ligands to achieve molecular specificity aiming at biomedical sensing [1]. For example, GNRs with aspect ratios of 3.2 were used as fluorescent biosensor for the detection of hepatitis B virus DNA [14], and GNRs with aspect ratio of 3.5 were functionalized by suitable antibody to realize ultra-sensitive cancer biomarker detection [15]. Therefore, it is of important significance to prepare GNRs with required aspect ratio.

GNRs were usually synthesized through seed-mediated growth [16], electrochemical synthesis [17], photochemical preparation [18] and porous aluminum template method [17]. Among them, seed-mediated growth was mostly adopted at present due to their high yield, simple operation and mild reaction environment [16].

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However, growth of gold nanorods with desired aspect ratio is difficult since the particle shape and size depends on several experimental parameters, such as acid condition, ascorbic acid (AA) volume, $AgNO_3$ concentration, incubation temperature, etc. [6]. Tedious pre-experiments need to be finished to seek suitable parameters before final growth. According to the reports [9,19–21], GNRs were oxidized when oxidizing agent was introduced. The authors studied the shape transformation of GNRs under the presence of H_2O_2. However, the quantitative relationships between particle aspect ratio and key parameters, such as H_2O_2 concentration, oxidation time, reaction temperature, etc., were neglected. On the other hand, it is well known that GNRs aspect ratio has a deceive influence on its longitudinal plasmon resonance [22]. Decrease in aspect ratio leads to obvious blue shift in LPAB wavelength [22], providing an intuitive monitoring method for GNRs aspect ratio. These researches stimulate our research to modulate GNRs aspect ratio by H_2O_2 oxidation based on localized surface plasmon resonance of GNRs.

In this work, influence of H_2O_2 concentration, oxidation time and reaction temperature on GNRs were investigated in detail aiming at GNRs aspect ratio modulation. The LPAB wavelengths of GNRs were revealed to decrease linearly with the prolongation of H_2O_2 oxidation time, the latter depending on GNRs aspect ratio. The quantitative relations between GNRs aspect ratio, LPAB wavelength, and H_2O_2 oxidation time were obtained, so that GNRs aspect ratio could be calculated from H_2O_2 oxidation time. The calculated aspect ratio was verified by TEM characterization and error was analyzed. Influences of reaction temperature and solution acidity on the oxidation process were studied. As a result, GNRs aspect ratio could be quantitatively modulated by H_2O_2 oxidation process based on the localized surface plasmon resonance of GNRs.

2. Experiments

Reagents and apparatus: Hydrogen tetrachloroaurate (III) trihydrate ($HAuCl_4 \cdot 3H_2O$, AR), hexadecyltrimethylammonium bromide (CTAB, AR), sodium borohydride (96%), L-ascorbic acid (99.7%), hydrochloric acid (36%–38%) and hydrogen peroxide (30%) were purchased from Sinopharm Chemical Regent Co., Ltd (Shanghai, China). Silver nitrate (99.8%) was purchased from Ling Feng Chemical Regent Co., Ltd (Shanghai, China). UV–vis absorption spectra were recorded on a UV-2450 spectrophotometer (Shimadzu, Japan). Transmission electron microscope images were obtained on a JEM-2100F transmission electron microscope (JEOL, Japan).

Synthesis of GNRs: CTAB-capped GNRs were fabricated through seed-mediated growth method [16,23,24]. Firstly 10 mL $HAuCl_4$ solution (5×10^{-4} M) was mixed with 10 mL CTAB solution (0.2 M) in a beaker. Then a freshly prepared, ice-cold $NaBH_4$ solution (0.01 M, 1.5 mL) was injected into the $HAuCl_4$-CTAB mixture within 2 min under fast magnetic stirring. The solution color turned brown yellow immediately, indicating the formation of CTAB-stabilized gold seeds sol [23]. Then the sol was kept standing for 2.5 h at 30 °C water bath before further application to gold nanorods synthesis. As for gold nanorods growth 10 mL $HAuCl_4$ solution (0.001 M) was mixed with 10 mL CTAB solution (0.2 M) in a beaker. Then 0.5 mL $AgNO_3$ (0.01 M), 180 μL freshly prepared ascorbic acid (0.08 M), and 40 μL HCl (1.2 M) solutions were added into the beaker followed by addition of 40 μL Au seeds sol. The mixture was quickly stirred for 2 min, and then left undisturbed at 30 °C water bath for 16 h to incubate GNRs.

GNRs Oxidization by H_2O_2: Firstly, 5 μL of 6 M HCl was added into 4 mL as-prepared GNRs sol to adjust pH value to 1.8. Then 100 μL of 0.124 M H_2O_2 was added. The mixture was put into 50 °C water bath in which oxidization reaction proceeded. 7 min later the mixture was transferred into a sample cell of UV–vis spectrophotometer, cooled by 20 °C water bath to stop the oxidization process, followed by immediate UV–vis test. (It has been proofed by compensatory test that the oxidization reaction stopped when water bath temperature was lower than 20 °C. The result was not shown in this paper.) Then the sample was taken out, 50 °C water bath heated to react for another 1 min, 20 °C water bath cooled and UV–vis tested again. This process was repeated 23 times to trace the variation of LPAB wavelength versus reaction time until the total reaction time was 30 min.

Influences of reaction temperature and pH value on H_2O_2 oxidization: For temperature effect investigation the procedure described in the previous paragraph was repeated at 30, 40, 50, 60 and 70 °C water bath at pH = 1.8, respectively. The initial incubation time in water bath at each temperature was 8 min and then gradually increased to 25 min. As for pH effect study the procedure was repeated at pH of 1.2, 1.8, 2.1 and 2.6 (adjusted by 6 M HCl solution) in 50 °C water bath, respectively. The initial incubation time was 12 min and then gradually increased to 26 min.

3. Results and discussion

3.1. The effect of H_2O_2 oxidation on GNRs

Fig. 1 shows the series UV–vis absorption spectra of GNRs oxidized by different concentrations of H_2O_2 for 15 min. The as-prepared gold nanorods possess of two plasmon bands at 520 and 731 nm (curve a), ascribed to the transverse and longitudinal plasmon resonance, respectively. After addition of 7 mM H_2O_2 (0.124 M), obvious blue shift occurred in LPAB wavelength (669.7 nm) while the TPAB peak remained unchanged (curve b). As the amount of H_2O_2 solution increased, the LPAB peak further blue shifted (curve c and d) until merging together with the TPAB peak (curve e and f). The photos of those products under different H_2O_2 amounts are shown in Fig. 2A. For as-prepared gold nanorods the color is dark blue, and the products possessing of UV–vis absorption curve b, c, d, e and f are dark green, sky-blue, purple, pink and light yellow, respectively. TEM images present the morphology evolution of GNRs during H_2O_2 oxidation. For the as-prepared sample standard nanorods were observed (Fig. 2B, a). Then the rod length became shorter (Fig. 2B, b and c), followed by occurrence of a small quantity of nanospheres (Fig. 2B, d). Finally only

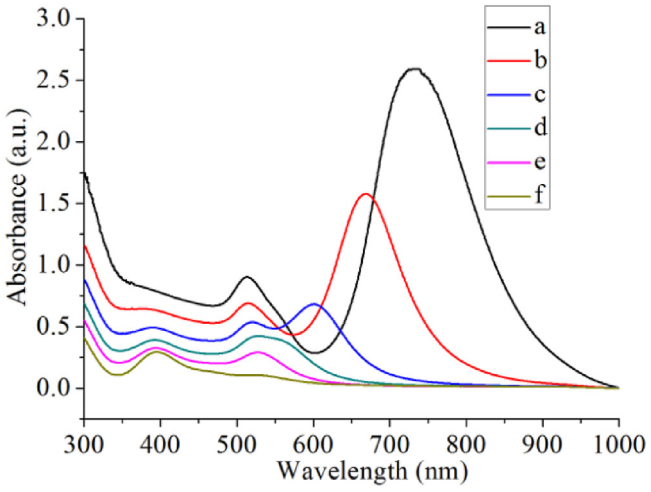

Fig. 1. UV–vis absorption spectra of GNRs before (a) and after being oxidized by H_2O_2 with different concentrations: (b) 7 mM, (c) 10 mM, (d) 18 mM, (e) 23 mM and (f) 24 mM.