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Influence of amount of CTAB and ascorbic acid concentration on localized surface plasmon resonance property of gold nanorod

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ABSTRACT

Gold nanorods (AuNRs) are prepared through seeded growth approach. Synthesis parameters of the amount of cetyltrimethylammonium bromide (CTAB), and concentration of ascorbic acid (AA) were studied. We were aiming for an aspect ratio of 3 which could be achieved by a nanorod feature in the range of 45 nm length and 15 nm width. The absorption spectra are observed with an UV–visible NIR spectrophotometer and analysed theoretically. It is known that there are two plasmon resonance peaks for gold nanorod corresponding to transverse surface plasmon resonance (TSPR) and longitudinal surface plasmon resonance (LSPR), respectively. It is found that as the concentration of CTAB increases, the yield of NRs increases. As the concentration of AA increased from 0.05 to 0.2 M, LSP shifts to longer wavelength but upon further increasing the concentration, LSP shifts back to shorter wavelength. A linear relationship between LSPR wavelength and surrounding medium dielectric constant is obtained, which is in good agreement with the theoretical results.

1. Introduction

Surface plasmon resonance (SPR) method has made an important contribution to the observation of bimolecular interactions [1,2]. For this type of sensor a relatively simple approach can be used by taking advantage of the nanoparticles of noble metals. When light is incident upon noble metal nanoparticles (NPs) which are uniformly coated on the surface of a dielectric material, absorption occurs if the optical frequency is in resonance with the collective oscillation of the conduction electrons, this phenomenon is known as localized surface plasmon resonance (LSPR) [3,4]. The plasmon resonance band can be changed by changing certain physical characteristics such as the size, shape, composition, relative distance and refractive index of the surrounding medium [3]. Among the available noble metal NPs, gold (Au)NPs have been widely studied and applied in many areas due to their unique optical, electronic and molecular-recognition properties [5–7]. It has been shown that the optical absorption spectrum of AuNPs is dependent on size, surrounding medium and mainly the shape of the NP. The aspect ratio is the value of the long axis (length) divided by the short axis (width) of a cylindrical or rod-shaped particle (nanorod, NR). Increase in aspect ratio increases the energy separation between the resonance frequencies of the long and short bands [8,9]. The non-spherical shape of the particle causes two different dipoles to form when interacting with light. The transverse dipole (diameter) and the longitudinal dipole (length) account for the oscillating electrons throughout the particle. The interaction between the two dipoles causes the longitudinal peak to be observed in the visible to NIR region. The longitudinal peak is much more intense than the transverse peak and can be tuned by changing the aspect ratio of the gold nanorods [8].

Much progress has been made in the synthesis of spherical AuNPs in the past decades [9–13], and the influence of particle radius on the physical, chemical, optical, electronic and catalytic properties of the material have been broadly studied. Several synthesis methods have been used to prepare AuNR, such as template method [9], electrochemical methods [10], seeded growth method [11], photochemical method [12] and so on. However, most methods have several drawbacks such as low processing yield, long reaction time and tedious synthesis steps. In this study, we will synthesize gold nanorods by seeded growth method, which is a simple and effective method to produce high yields nanorods. CTAB is widely used in the synthesis of NRs (or NPs) in all reduction paths. The properties of AuNRs with varying amount of CTAB and concentration of AA will be studied. The TSP and LSP of the solution were characterized using UV–visible NIR spectrophotometer. The results demonstrate that sufficient CTAB amount is important in order to

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obtain AuNRs and the reduction rate of Au ions was dependent on the AA concentration.

2. Theoretical analysis

Using an extension of the Mie theory, the physical mechanism for a dual mode LSPR sensor based on AuNR can be explored theoretically. The cross sections for absorption and scattering of light due to light introduced on AuNPs are defined as: [14]

$$C_{abs} = k_0 v \left[\frac{\varepsilon_m - \varepsilon_d}{L_i(\varepsilon_m + 2\varepsilon_d)} \right], C_{sca} = \frac{{k_0}^4}{6\pi} v \left[\frac{\varepsilon_m - \varepsilon_d}{L_i(\varepsilon_m + 2\varepsilon_d)} \right]^2 \quad (1)$$

where, k_0 is defined as $k_0 = 2\pi N/\lambda$, N is the number of particles per unit volume, λ the wavelength of the interacting light. v the volume of each particle. ε_m the permittivity of surrounding medium. ε_d the permittivity of sphere or elliptical rod. L_i is the geometrical factor of the ith resonant. They are defined as:

$$L_1 = \frac{1-e^2}{e^2} \left(-1 + \frac{1}{2e} \ln \left(\frac{1+e}{1-e} \right) \right), L_2 = L_3 = 1 - 2L_1, e = 1 - \frac{b^2}{a^2} \quad (2)$$

The ratio a/b is the aspect ratio of the AuNR. In addition [8],

$$\varepsilon_m = -\varepsilon_d \left(1 + \frac{1}{L} \right) \quad L \in (0, 1) \quad (3)$$

The geometrical factor L is dependent on the aspect ratio of the rod. The value is between 0 and 1, but not exactly 0 or exactly 1. As the AuNR becomes more elliptical, the value for L increases causing the absorbance band shift towards the infrared. This is why the SP absorption band is very sensitive to size along major axis, and aspect ratio. The sensor theory leads us to the conclusion that gold nanorods support two surface plasmon resonances. These two resonances can form the basis for a sensor that distinguishes between background refractive index changes and surface-binding of an analyte. By measuring the change in resonance wavelength and peak extinction for both resonances of a nanorod, one can separately quantify changes in solution index and surface concentration of the analyte. The extinction coefficient of randomly oriented particles in the dipole approximation is: [15,16]

$$\gamma = \frac{k_0 v \varepsilon_m^{3/2}}{3} \sum_i \frac{\left(\frac{1}{L_i^2} \right) \varepsilon_{d_{img}}}{\left(\varepsilon_{d_{rea}} + \frac{1-L_i}{L_i} \varepsilon_m \right) \varepsilon_{d_{img}}^2} \quad (4)$$

$\varepsilon_{d_{rea}}$ and $\varepsilon_{d_{img}}$ are the real and imaginary part of the material dielectric function. With the known complex dielectric constant of gold, Eq. (4) can be plotted as the authors did in [8]. From theoretical analysis, it can be concluded that two maxima are present in the simulated absorption spectra corresponding to the transverse and longitudinal resonances. The absorption maximum of the transverse mode shifts to shorter wavelength with increasing aspect ratio. The absorption maximum of the longitudinal mode red-shifts with increasing gold nanorod aspect ratio. However, the effect on the longitudinal mode is much more pronounced. Furthermore, the relative intensity ratio of the longitudinal to the transverse mode increases with increasing aspect ratio. Both maxima shift to longer wavelength and the intensity of both resonances increases with an increasing medium dielectric constant.

3. Synthesis process

In this work, the synthesis of AuNRs is produced using the seeded growth method. The CTAB seeds were prepared by reducing the gold ions (Au^{3+}) to atomic gold atoms using a strong reducing gent sodium borohydride ($NaBH_4$), in the presence of CTAB. In a

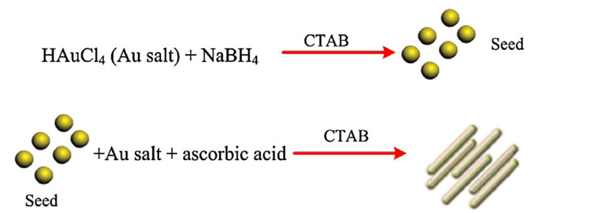

Fig. 1. Schematic illustration synthesis of AuNRs with the seed-mediated method.

50 mL tube, 9.75 mL 0.2 M CTAB stock solution and 250 μL of 0.01 M chloroauric acid ($HAuCl_4$) were c ombined and stirred vigorously. 600 μL of 0.01 M freshly prepared ice-cold $NaBH_4$ was added to the flask. The solution was stirred for 2 min. 60 μL of 0.01 M $AgNO_3$ solution was added and inverted to mix the reagents. Different amounts of $AgNO_3$ yield different rod dimensions, increasing the amount of $AgNO_3$ will increase the aspect ratio and result in a red shift in the longitudinal plasmonic band on the UV–visible spectra [8,11]. 500 μL 0.01 M $HAuCl_4$ was added to the tube and inverted to mix. 55 μL of freshly prepared 0.1 M ascorbic acid (AA) solution was added and the tube inverted to mix. 15 μL CTAB capped seeds were added and the tube was gently mixed. The solution was allowed to sit overnight to let the rods grow, an experimental schematic is shown in Fig. 1. The rods were purified via centrifugation for 20 min using 10,000 rpm then resuspended in deionized water. They were then centrifuged for 10 min using 10,000 rpm and also resuspended in deionized water. The TSP and LSP of the solution were characterized using UV–visible NIR spectrophotometer (UV-3600, Shimadzu). Size and shape of the AuNRs were observed using transmission electronmicroscopy (TEM) (PhilipsCM12, Version 3.2).

4. Results and discussions

Fig. 2 shows the TEM image and absorption spectrum of the AuNRs synthesized in the experiment. The spectrum shows two absorption peaks at 709 nm and 518 nm corresponding to the LSP and TSP, respectively. The NRs have an aspect ratio of 3.1.

The concentration of CTAB is the dominant factor to induce the anisotropic shape of NRs [11]. However, the effect of the concentration of CTAB on the formation of gold NRs was not studied. TSP and LSP of AuNRs synthesized with varying CTAB concentrations of 0.05, 0.10, 0.15 and 0.25 M are shown in Fig. 3. The absorbance values in the spectra represent the yield of AuNRs. It is found that as the concentration of CTAB increases, the yield of NRs increases which can be seen from the decreasing TSP intensity and increasing LSP intensity. This result can be explained by the enhanced CTAB adsorption on the surface of the growing particle. The adsorption of surfactant onto an interface involves the straightforward processes of diffusion of surfactant molecule from the bulk to the surface. The adsorption of monomer onto the

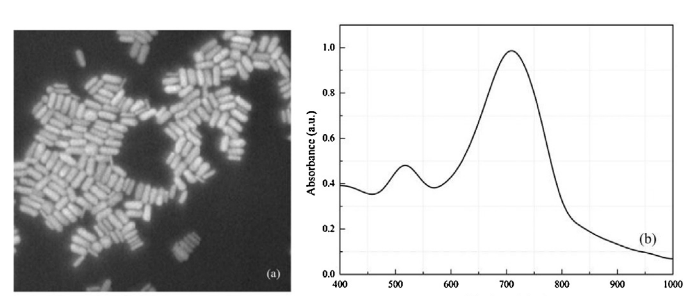

Fig. 2. (a) TEM image of AuNRs, the scale bar is 50 nm. (b) UV–visible NIR. spectra of AuNRs.