Synthesis of gold nanorods with longitudinal surface plasmon resonance wavelength up to 1245 nm using gallic acid as a reductant in the presence of a binary surfactant system

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Gold nanorods with the longitudinal surface plasmon resonance (LSPR) wavelength up to 1245 nm are obtained by using an improved seed-mediated wet chemistry growth method where gallic acid is used as a reductant in the presence of a binary surfactant system. The effects of the gallic acid and the seed on the synthesised gold nanorods are investigated by ultraviolet–visible–near infrared spectroscopy and transmission electron microscopy (TEM). It is found that by increasing the gallic acid amount from 200 to 600 μL, the LSPR wavelength shifts from 975 to 1170 nm; at the same time, the absorption intensity of both the transverse surface plasmon resonance and LSPR increases, indicating a more complete reduction of chloroauric acid. To achieve a longer wavelength of the gold nanorods' LSPR peak, the seed amount was changed to a condition of 600 μL gallic acid. A redshift of the LSPR wavelength from 1135 to 1245 nm can be obtained as the seed amount increases from 30 to 70 μL. Furthermore, it was found that the redshift of the LSPR peak with increasing seed amount is in accordance with the increase trend of the aspect ratio obtained by analysing the dimensions of the gold nanorods through the TEM images. The method offers a new strategy to obtain gold nanorods with tunable LSPR wavelengths, which have wide application in many areas, such as biosensing and ultrafast optical information.

1. Introduction: Gold nanorods exhibit unique optical properties and have gained wide attention in recent years [1, 2]. Due to the surface plasmon resonance (SPR) behaviour, gold nanorods display large absorption and scattering properties [1, 2]. In general, there are two distinct peaks in the absorption spectrum of gold nanorods. The two peaks in the absorption spectrum of gold nanorods are called the transverse SPR (TSPR) and the longitudinal SPR (LSPR) absorption peaks [2, 3]. The TSPR wavelength is typically at around 520 nm while the LSPR wavelength is at a larger wavelength [2, 3]. The LSPR wavelength of gold nanorods is dependent on the length-to-diameter aspect ratio (AR) [2, 3]. As the length-to-diameter aspect ratio (AR) of gold nanorods increases, the corresponding LSPR wavelength shifts to a larger wavelength [4, 5]. Moreover, the excitation of SPR can induce the near-field enhancement effect [6]. These properties make gold nanorods good candidates for use in many areas, such as plasmon-enhanced spectroscopies [7, 8], biosensing [1], biological imaging [3], and photonic devices [6].

Several approaches have been reported for the synthesis of gold nanorods, such as photochemical synthesis [9], electrochemical synthesis [10], and wet chemistry synthesis [11–13]. One important procedure for the wet chemistry synthesis of gold nanorods is seed mediated synthesis [11–13]. Usually, there are two steps in seed-mediated wet chemistry synthesis: first, a gold seed solution is prepared by reduction of chloroauric acid with sodium borohydride as the reducing agent; then, the gold seed solution is added into the growth solution which contains surfactant, chloroauric acid, and a mild reducing agent [11–13]. Great effort has been made to improve the seed-mediated synthesis of gold nanorods [14–18]. Different conditions such as reaction time [14], pH value [15], and additives [16–18] are studied. In particular, the surfactant is reported as an important factor in gold nanorods synthesis

[19–24]. Different surfactants are used to improve the gold nanorods growth in the seed-mediated wet chemistry synthesis [13, 14, 19–24]. For example, El-Sayed and co-workers [13] reported that by using a binary surfactant system, including hexadecyltrimethylammonium bromide (CTAB) and benzyldimethylhexadecylammoniumchloride (BDAC) in the growth solution, gold nanorods with an AR up to 10 can be obtained. Murray and co-workers [23] reported a dramatically improved synthesis of gold nanorods by using a binary surfactant system containing CTAB and sodium oleate (NaOL) in the growth solution and produced gold nanorods with larger diameters.

Most of these reports use ascorbic acid as the reductant in the growth solution. Recently, there have been reports about the improvement of gold nanorods synthesis by using different weaker reductants instead of the commonly used ascorbic acid reductant [25–27]. For example, Caseri and co-workers [25] reported that by using dihydroxybenzenes (hydroquinone, catechol, or resorcinol) or glucose, synthesised gold nanorods can have a larger AR. Zubarev and co-workers [26] reported that by using hydroquinone as the reductant in the growth solution, the LSPR wavelength of gold nanorods can be up to 1230 nm with a high yield. However, most of the reductants are toxic [25, 26]. Gallic acid is a natural plant phenol and can be used as a reductant for the synthesis of biocompatible gold nanoparticles [28]. Recently, Xu *et al.* [29] obtained gold nanorods with a LSPR wavelength as large as 995 nm by using gallic acid as a mild reductant in the presence of CTAB in the seedless growth method.

Inspired by the methods mentioned above, we use gallic acid as a reductant in the presence of a binary surfactant system to prepare gold nanorods using the seed-mediated growth method. The sizes of the gold nanorods are tunable by varying the amounts of gallic acid and the seed solution, such that the LSPR wavelength is well extended in our fabrication method.
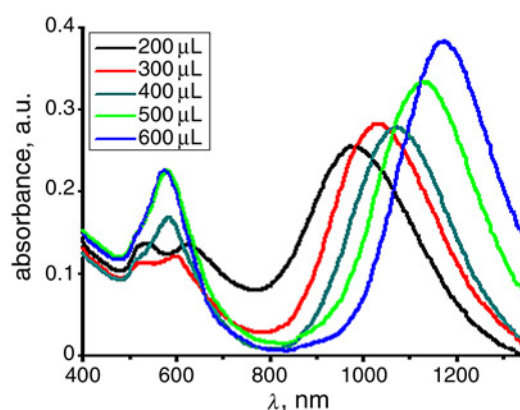
2. Experimental

2.1. Materials: CTAB was purchased from Amresco Inc. (USA). NaOL >97.0% was purchased from TCI America (USA). Chloroauric acid ($HAuCl_4 \cdot 4H_2O$), gallic acid ($C_7H_6O_5 \cdot H_2O$ 98.5%), hydrochloric acid (HCl 36–38%), and sodium borohydride ($NaBH_4$ 96%) were purchased from the Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). Silver nitrate ($AgNO_3$ >99.95%) was purchased from the Shanghai Shiyi Chemicals Reagent Co. Ltd. All of the chemicals were used as received without further purification. The water used in the experiments was double distilled water. Furthermore, all of the aqueous solutions, other than the chloroauric acid and the HCl solution, were prepared fresh daily.

2.2. Preparation of gold seeds: The gold seed solution was prepared as follows: a $HAuCl_4$ solution (5 mL, 5 mM) was mixed with a CTAB solution (5 mL, 0.2 M). The ice-cooled sodium borohydride solution (0.8 mL, 10 mM) was then added to the solution under stirring. During this process, the solution colour changed from yellow to brownish. The gold seed solution was kept undisturbed for 2 h at room temperature.

2.3. Synthesis of gold nanorods: NaOL solution and gallic acid solution were first heated to 50°C. In a typical synthesis, CTAB solution (1.5 mL, 0.2 M) and NaOL solution (0.3 mL, 0.1 M) were added to 2.5 mL of water. After the $HAuCl_4$ solution (0.5 mL, 5 mM) was added into the above solution, the mixed solution was ultrasonicated for 5 min. The solution became colourless. Following this, $AgNO_3$ solution (0.3 mL, 4 mM) was added, and the mixture was gently shaken. The HCl solution (0.3 mL, 1.2 M) was introduced to the solution to adjust the pH value. Then, the gallic acid solution (0.6 mL, 0.1 M) was added to the solution. The mixture was ultrasonicated for 5 min. Finally, different amounts of the gold seed solution were added into the solution and the solution mixture was gently shaken. The solution was allowed to react for 12 h at 30°C.

2.4. Characterisation: The absorption spectra of the synthesised colloidal gold nanorods solution were measured by using a Lambda 950 ultraviolet–visible–near infrared spectroscopy (UV–vis–NIR) spectrophotometer (PerkinElmer, USA) with a 1 cm quartz cuvette. For the absorption spectra measurements, the colloidal gold nanorods solutions were diluted by double distilled water. Transmission electron microscopy (TEM) images of the synthesised colloidal gold nanorods were obtained by using a Tecnai G2 F20 transmission electron microscope (FEI, USA). The gold nanorods for TEM observations were purified by centrifugation at 10 000 rpm for 10 min, washed with double distilled water, and recentrifuged at 10 000 rpm for 10 min. The precipitate was redispersed in double distilled water. The TEM samples were prepared by placing 10 μL of the gold nanorods solution on a copper grid and drying at room temperature.

3. Results and discussion:

In this Letter, gallic acid is used as a replacement of the traditional ascorbic acid reductant in the presence of a binary surfactant system composed of CTAB and NaOL in the seeded growth method. Different amounts of gallic acid solution were used in the growth solution in our experiments to investigate the effect of gallic acid on the synthesised gold nanorods. Fig. 1 shows the UV−vis−NIR absorption spectra of the synthesised gold nanorods solution when using amounts of gallic acid solution from 200 to 600 μL, while all the other chemicals added were kept unchanged. A redshift of the corresponding LSPR absorption peak position from 975 to 1170 nm can be seen in the absorption spectra with increasing amounts of gallic acid solution. At the same time, the absorption intensity of both the TSPR and LSPR increases, indicating a more complete reduction of $HAuCl_4$.
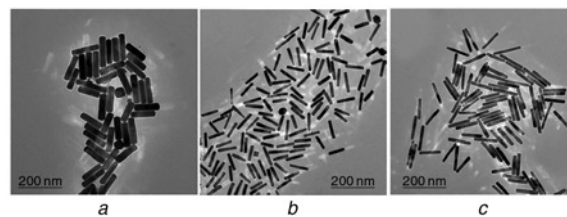

Figure 1 *UV–vis–NIR absorption spectra of the synthesised gold nanorods at gallic acid amounts from 200 to 600 μL*

The TEM images for the synthesised gold nanorods using gallic amounts of 200, 400, and 600 μL are presented in Fig. 2 to obtain detailed information about the synthesis of gold nanorods. The yield of the nanorods is greater than 70%, and the products are hemispherical capped cylindrical nanorods at all the gallic acid amounts. The values of the average diameter of the gold nanorods, which are obtained by analysing at least 100 particles from the TEM images, are 36, 21, and 18 nm for different amounts of the gallic acid solution of 200, 400, and 600 μL, respectively. The decreasing trend in the average diameter as well as a redshift of the LSPR peak position caused by the increasing amounts of gallic acid are similar to the observation reported by Lai *et al.* [30], who used ascorbic acid as the reductant. Gold nanorods with large diameters exhibit enhanced scattering properties and may be ideal for scattering-based applications [30], whereas larger LSPR peak positions in the near-infrared region have potential applications in biosensing and optoelectronic devices [1]. It can be seen that it is feasible to synthesise gold nanorods with tunable diameters from 36 to 18 nm as well as the LSPR wavelength from 975 to 1170 nm by simply varying the amount of gallic acid.
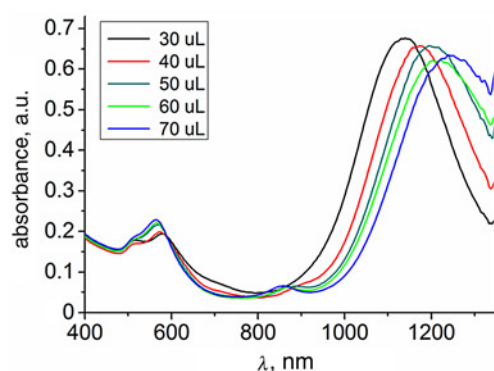
To obtain longer LSPR wavelengths of the synthesised gold nanorods, we performed another experiment with verified seed solution amounts while the amount of gallic acid solution was fixed at 600 μL. Fig. 3 shows the UV−vis−NIR absorption spectra of the gold nanorods for different amounts of seed solution from 30 to 70 μL while all the other chemicals were kept unchanged. We can see that when the amount of seed increases from 30 to 70 μL, the LSPR wavelength shifts from 1135 to 1245 nm. However, the increase of the seed amount decreases the intensity of the LSPR peak a little, which implies a lower yield of the gold nanorods.

The TEM images of the synthesised gold nanorods using different amounts of seed solution are shown in Figs. 4a–d, and the gold nanorods sizes obtained by analysing at least 100 particles from the TEM images are shown in Fig. 4e. The TEM images display
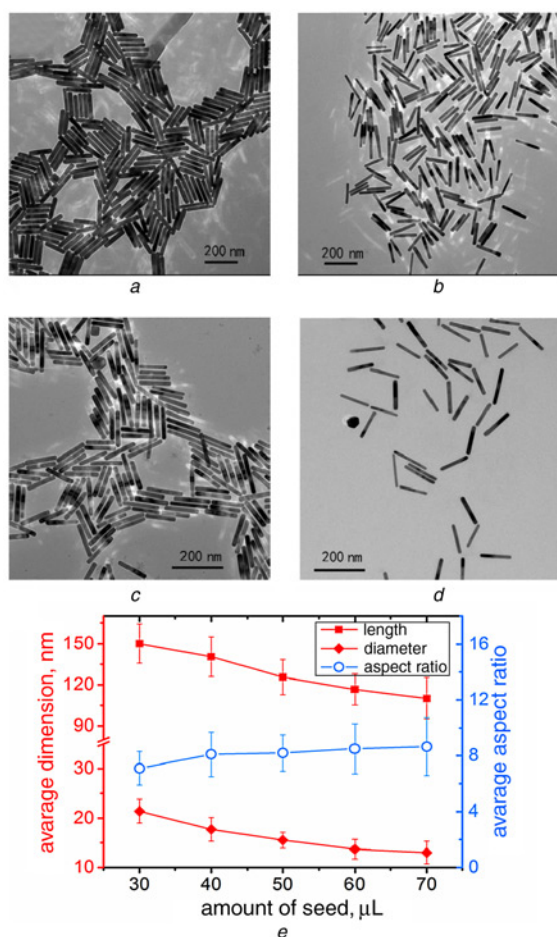

Figure 2 *TEM images of the synthesised gold nanorods for gallic acid amounts of 200, 400 and 600 μL*
a 200 μL
b 400 μL
c 600 μL

Figure 3 *UV–Vis–NIR absorption spectra of the gold nanorods solution synthesised by adding different amounts of seed from 30 to 70 μL*

monodisperse and rod-like gold nanoparticles. The yield of the nanorods becomes greater than 80%. As can be seen from Fig. 4e, the increase of the seed amount leads to the decrease of both the average length and the average diameter of the synthesised gold nanorods. In particular, when increasing the seed amount from 30 to 70 μL, the average length decreases from 150 to 110 nm, and the average diameter decreases from 21.4 to 13 nm. On the other

Figure 4 *TEM images obtained from the synthesised gold nanorods at different amounts of seed*
a 30 μL
b 40 μL
c 50 μL
d 70 μL
e Graphs showing length, diameter, and AR of the synthesised gold nanorods by using different amounts of seed as measured from their TEM images

Table 1 Measured LSPR peak position and the calculated one from (1)

Seed amount, μL	30	40	50	60	70
Measured λ_{LSPR}, nm	1135	1177	1208	1220	1245
Calculated λ_{LSPR}, nm	1095	1190	1199	1228	1242

hand, as can be seen in Fig. 4e, the decreases of both the length and the diameter become much slighter for larger seed amounts. This is in accordance with the relatively smaller redshift of the LSPR peak position when the seed amount becomes larger as depicted in Fig. 3.

It has been reported that in an aqueous solution, the LSPR wavelength (λ_{LSPR}) depends on the AR of the gold nanorods. The relationship between λ_{LSPR} and AR could be described as follows [3]:

$$\lambda_{LSPR} = 95AR + 420. \qquad (1)$$

The deduced LSPR wavelength results by AR using (1) and the experimentally measured ones are shown in Table 1. One can observe good agreement between the calculated results and measured ones, which implies good optical tunability of the gold nanorods by simply varying the AR of the particles in our experiment.

The reduction process in the growth solution in our experiments may be described through the following sequence [14, 23, 24]: (i) NaOL is used to partially reduce Au^{3+} into Au^+ in the mixed solution which is composed of CTAB, NaOL, and $HAuCl_4$; (ii) gallic acid is added to the growth solution, which results in a complete reduction of Au^{3+}; (iii) the gold seed solution is added to the growth solution, which can catalyse the reduction of Au^+ into Au, thereby initiating the growth of gold nanorods.

In our experiment, the largest LSPR wavelength of the gold nanorods reaches up to 1245 nm, which is larger than that reported by Ye *et al.* [23]. In their work, the largest peak position is 1150 nm. The improvement obtained by our method is achieved by the use of gallic acid as a reductant instead of ascorbic acid. Hydrophobic molecules, like heptane and paradioxybenzene, can be inserted into the hydrophobic part of the CTAB and help stabilise the rod-like micellar template of the CTAB, further increasing the AR of the gold nanorods [15, 29]. Gallic acid may work in a similar way [29]. This could explain why the longer LSPR peak position can be obtained compared with that of ascorbic acid. In [29], the largest LSPR peak position is 995 nm using gallic acid as a reductant in the presence of CTAB in the seedless growth method. The difference of our experiments compared with [29] comes from the use of NaOL as the cosurfactant in the seed mediated growth method. As a comparison, we also used gallic acid in the seedless growth method in the presence of the binary surfactant system composed of CTAB and NaOL and the largest LSPR peak position of the synthesised gold nanorods is 1100 nm. So both the NaOL and the seed solution benefit from the increase of the LSPR wavelength.

4. Conclusion: We have synthesised gold nanorods using gallic acid as a reductant in the presence of a binary surfactant system composed of CTAB and NaOL in the seed mediated growth method. With the increasing amount of the gallic acid, a more complete reduction of chloroauric acid can be achieved such that the dimensions and the LSPR position can be tuned by the gallic acid amount. The LSPR wavelength of the nanorods can be further extended up to 1245 nm by increase of the seed amount and the red shift of the LSPR position is found to be in accordance with the increase trend of the AR. Furthermore, comparisons of our experimental results with the results reported in [23, 29] show that gallic acid, as well as the NaOL and the seed solution, benefit from the increase of the LSPR wavelength

of gold nanorods. Our method offers a new strategy for the synthesis of gold nanorods with tunable LSPR peak positions and may have wide application in biosensing and ultrafast optical information.

6 References

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