Synthesis of gold nanorods with a longitudinal surface plasmon resonance peak of around 1250nm

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Abstract
We prepared gold nanorods and joined them to chemicals such as tetrachloauric (III) acid trihydrate, silver nitrate, hydroquinone, hexadecyltrimethylammonium bromide, sodium hydroxide and sodium borohydride using the seed-mediated method. The combination of hydroquinone, with or without salicylic acid, influences the size of the gold nanorods, and this is demonstrated by the results of TEM images, UV–vis spectra and the value of the longitudinal surface plasmon resonance peak with respect to the UV–vis spectra. By changing the Ag+ ion and hydroquinone concentration and the combination of hydroquinone and salicylic acid, the size of the gold nanorods can be controlled and this is manifested by longitudinal surface plasmon resonance peaks forming between 875 and 1278 nm. In particular, sample E2 achieved a longitudinal surface plasmon peak at 1273 nm and an aspect ratio of more than 10 by modifying the hydroquinone to 2.5 mM and salicylic acid to 0.5 mM concentration in the growth solution.

Keywords: gold nanorods, salicylic acid, hydroquinone, silver nitrate, aspect ratio
Classification numbers: 2.09, 4.02

1. Introduction

Gold nanorods (AuNRs) are a useful gold nanostructure in various science and technology fields due to their optical, catalytic and electronic properties derived from their strong length dependent surface plasmon resonance (SPR) absorption in the near-infrared region, and one-dimensional morphology for nano-scale assembly applications [1–6]. In the SPR spectrum of AuNRs there exist peaks of two types: those for transverse surface plasmon resonance and those for longitudinal surface plasmon resonance (LSPR). The wavelength of SPR spectra depends on the size and structure of the material. Hence, for the efficient utilization of AuNRs it is necessary to control not only their size, but also their shape.

AuNRs have been synthesized by the seed-mediated method and the photochemical method [7–9]. Two steps are involved in the seed-mediated method: fresh preparation of gold seeds using sodium borohydride (NaBH4) as the reducing agent, and the expansion of gold seeds into AuNRs in a growth solution. One limitation of this method is that gold seeds cannot be preserved over an extended period. Another problem is that the yield is rather low. To grow longer AuNRs with aspect ratios ranging from 4.6 to 10, a binary surfactant mixture composed of hexadecyltrimethylammonium bromide/benzyldimethylhexadecylammonium chloride (CTAB/BDAC) was used [10].

Vigderman and Zubarev showed that a maximum LSPR peak position was reached at an intermediate hydroquinone (HQ) concentration of 5 mM [11]. Our method displays a similar trend, although the LSPR maximum appears at...
2.1. Materials

The following chemicals were purchased commercially and used as-received without any further purification. Tetra-
chloroauric (III) acid trihydrate (HAuCl₄·3H₂O, 99.5%), silver nitrate (AgNO₃, 99.99%), salicylic acid (SA, 99.5%),
hydroquinone (HQ, 99%), sodium hydroxide (NaOH, 99%) and sodium borohydride (NaBH₄, 98%) were purchased from
Merck; hexadecyltrimethylammonium bromide (CTAB, 99%) was purchased from India. All solutions were prepared
with deionized water. Prior to performing nanoparticle synthesis protocols, the glassware and stir bars were cleaned
with aqua regia (3:1 v/v HCl (37%): HNO₃ (65%)) solutions.

2.2. Characterization

Ultraviolet–visible–near infrared (UV–vis–NIR) spectra were recorded on a UV–vis–NIR-V670, JACCO spectro-
photometer. The morphology and size of the AuNRs were investigated using transmission electron microscopy
(TEM) (JEM-1400, JEOL, Japan) and scanning electron microscopy (SEM) (JSM 7401F, JEOL, Japan).

2.3. Method of synthesis

2.3.1. Seed preparation. First, a seed solution for AuNR growth was prepared by slowly mixing 100 μl of 0.025 M
HAuCl₄ into 10 ml of 0.1 M CTAB. To this mixture, 460 μl of freshly prepared 0.01 M ice-cold NaBH₄ aqueous
solution, prepared using 100 ml of 0.01 M NaOH and 3.78 mg NaBH₄, was added quickly to the gold salt and
CTAB mixture while stirring and kept standing for 30 min, leading to a change in color from light yellow to light
brown.

2.3.2. Synthesis of nanorods. In a typical process, a growth solution of AuNRs is prepared by adding 1.75 μmol AgNO₃
into the mixture of 1 mmol CTAB, 2.5 μmol HAuCl₄ and 50 μmol (HQ). In the next step, 80 μl of the seed solution is
added to the growth solution and left overnight before cleaning through two centrifugation cycles of 10,000 rpm for
20 min.

The UV–vis absorption spectra were taken to characterize these nanorods with wavenumber form from 400 to
1300 nm. The morphologies and size of the nanoparticles were characterized by TEM. Before the TEM observation,
5 ml of the AuNR solution is centrifuged for 20 min at a speed of 3000 rpm in order to remove CTAB and to
concentrate the nanoparticles. Using TEM more than 100 particles were investigated and the width, length and aspect
ratio of the AuNRs were determined.
Figure 2. TEM images of the samples at different silver concentrations: (a) 0 mM, (b) 0.15 mM, (c) 0.25 mM, (d) 0.35 mM and (e) 0.4 mM; other preparation parameters are [CTAB] = 0.1 M, [HAuCl₄] = 0.025 M, [HQ] = 0.1 M and 80 μl seeds. (f) Diagram of the LSPR peaks of AuNRs and (g) the UV–vis spectrum of the growth of the AuNR solution prepared by changing the AgNO₃ concentration.
Table 1. Aspect ratio and yield of AuNRs at different Ag⁺ concentrations without SA.

| AgNO₃ (mM) | LSPR (nm) | Aspect ratio | Yield of AuNRs (%) |
|------------|-----------|--------------|-------------------|
| 0.00       | —         | —            | 0                 |
| 0.15       | 854       | 3.77         | 76                |
| 0.25       | 1027      | 4.76         | 77                |
| 0.35       | 1138      | 6.09         | 100               |
| 0.40       | 1072      | 5.44         | 89                |

3. Results and discussion

The AuNR fabrication method consists of the preparation of gold seeds (with a diameter of about 20 nm) and subsequent nanoparticle growth in a growth solution containing HAuCl₄, CTAB, AgNO₃ and HQ.

To elucidate their three-dimensional structure, the AuNRs were coated onto a copper substrate and investigated by SEM imaging in vertically standing assemblies (figure 1(a)). From this image it is clear that the particles have a rod-like morphology with a circular cross-section rather than a belt-like morphology with a rectangular cross-section. Figure 1(b) shows the XRD pattern of the AuNRs. The diffraction peaks of the AuNRs appeared at 38.4°, 44.6°, 64.7° and 77.7° corresponding to the (111), (200), (220) and (311) crystalline plane diffraction peaks of gold (JCPDS file No. 04–0784) [14].

3.1. Tuning the aspect ratio and the LSPR peak of AuNRs without salicylic acid

The first part of this study concerns an investigation of the growth of AuNRs with the influence of different silver ion concentrations in the growth solution. In figures 2(a)–(e) TEM images of AuNRs with different AgNO₃ concentrations are shown. In sample A1 (figure 2(a)), a AuNR is not formed due to the absence of Ag⁺ in the growth process. There exists only one transverse absorption peak at 500 nm in the UV–vis spectrum of sample A1 (figure 2(g)). Conversely, an Ag⁺ ion in the growth solution is the agent of nanorod formation. The longitudinal band is expected to appear far beyond the spectral range in the near-infrared region with positions dependent on the aspect ratios of the nanorods. The LSPR peak of AuNRs is illustrated in figures 2(f) and (g). These results show that the length of the nanorod depends on Ag⁺ ion concentration, as shown in table 1. The length of the AuNRs increases with the increase of Ag⁺ ion concentration and the length starts to decrease at 0.35 mM AgNO₃. Moreover, the length of the AuNRs was determined to be around 51 nm (sample A2), 57.71 nm (sample A3), 63.74 nm (sample A4) and 49.38 nm (sample A5) from the TEM images in figures 2(b)–(e).

The length of the AuNRs prepared at different HQ concentrations was also determined. Figures 3(a)–(e) show TEM images of different aspect ratio AuNRs prepared using various concentrations of HQ while keeping all other variables constant.

Figure 3(f) and table 2 show the effect of different HQ concentrations on the LSPR peak. The LSPR peak changes from 1063 to 1178 nm according to the change in the nanorod lengths. When the concentration of HQ increased from 3 to 7 mM in the growth solution, the AuNR aspect ratio increased, leading to longer AuNRs. A further increase in HQ to 4 mM leads to the formation of shorter AuNRs. Using 4 mM HQ gave the most red-shift LSPR peak at about 1178 nm, while the largest tested concentration of 7 mM, gave an LSPR peak at about 1063 nm and a small fraction of spherical nanoparticles in the solution was formed. The average aspect ratio of these rod particles varied at 6.29, 6.58, 6.02, and 5.31 when the HQ concentrations were 3.0, 4.0, 5.0, and 7.0, respectively. The length, the diameter and the aspect ratio of the AuNRs were estimated from twenty representative AuNRs in each sample’s TEM image.

3.2. Effect of salicylic acid on the growth of nanorods

In an experiment to improve the yield and length of AuNRs, Ye et al [6] discovered that the addition of SA during nanorod growth can significantly increase the amount of AuNRs formed with aromatic additive as both a co-reducing and reinforcement agent of the CTAB template. As shown in figures 4(c) and (d), an increase in SA (table 3) had an effect on the size and the position of the plasmon absorption of nanoparticles. A further increase in SA to 0.5 mM led to a blue-shift of the plasmon absorption.

In this experiment the positions of the LSPR peaks determined by UV–vis spectra are 1234 nm (sample C4) and 1167 nm (sample C1) in the growth of AuNRs with and without SA, as shown in figures 4(c) and (d). This shows that the role of SA in the growth process is to control the size and shape of the AuNRs. In figure 4(b), the AuNRs exhibit average dimensions of 79.07 nm length and 11.37 nm diameter (corresponding to an aspect ratio of 6.95).

3.3. Tuning the aspect ratio and the LSPR peaks of AuNRs with salicylic acid

Under identical experimental conditions, a small amount of salicylic acid (SA) is added to the growth step. The aspect ratio (AR) of nanorods can be controlled by varying AgNO₃ and HQ (figures 5 and 6).

To grow AuNRs with larger aspect ratios, the silver ion content added to the NR growth solution is systematically adjusted. Similar to the synthesis without SA, the presence of silver is necessary for rod formation. In the experiment, the length and the LSPR peaks of AuNRs were determined at varied Ag⁺ ion concentrations (table 4 and figure 5).

The optical properties of these AuNRs was characterized using UV–vis absorption spectra (figures 5(f) and (g)). In figures 5(f) and (g), normalized UV–vis spectra of the representative AuNR sample with LSPR peaks from 1002 to 1254 nm are presented. The maximum LSPR peak
Figure 3. TEM images of the samples at different HQ concentrations: (a) 3 mM, (b) 4 mM, (c) 5 mM, (d) 6 mM and (e) 7 mM; other preparation parameters are [CTAB] = 0.1 M, [HAuCl₄] = 0.025 M; [Ag⁺] = 0.1 M and 80 μl seeds. (f) Diagram of the LSPR peaks of the AuNRs and (g) UV–vis spectra of solutions prepared with different concentrations of HQ for growing AuNRs.
of ∼1254 nm in the experiment with the use of SA is higher than that without SA (LSPR peak of ∼1138 nm).

The effect of HQ concentration in the growth solution was determined by varying it from 2.0 mM to 4.0 mM, and the UV–vis spectra of the resulting AuNRs are shown in figure 6(d).

Experimentally, the influence of HQ concentration on the optical properties of AuNRs was studied by altering the amount of HQ (table 5), whereas the amounts of CTAB, silver nitrate, HAuCl₄, and SA were fixed at 5 ml, 225 μl, 100 μl and 250 μl, respectively. As shown in figure 6, increasing the HQ concentration combined with the presence of SA in the growth solution, produced AuNRs with an aspect ratio of 8–10, as seen in the representative TEM image shown in figure 6. In addition, it is possible to produce a red-shift up to 1273 nm and decrease the number of spherical particles to almost to zero. At the lowest HQ concentration (2.0 mM), AuNRs with a plasmon resonance peak at 1270 nm (sample E1) are formed. Increasing the HQ concentration to 2.5 mM leads to the formation of AuNRs with an LSPR peak at 1273 nm (sample E2), and its further increase continues to a blue-shift in the LSPR peak with the wavelength decreasing to 1254 nm (sample E3) at 3.0 mM HQ. Little change in the peak position is evident when the HQ concentration reaches 3.5 mM. This means that 125 μl of HQ was enough for the current reduction and this is less than the 200 μl of HQ solution required in the growth solution without SA. Interestingly, when 125 μl of HQ is used with the presence of SA, it does induce elongation

### Table 2. Aspect ratio and yield of AuNRs at different concentrations of HQ without SA.

| HQ (mM) | LSPR (nm) | Aspect ratio | Yield of AuNRs (%) |
|---------|-----------|--------------|-------------------|
| 3.00    | 1167      | 6.29         | 83                |
| 4.00    | 1178      | 6.58         | 100               |
| 5.00    | 1138      | 6.02         | 100               |
| 6.00    | 1075      | 5.94         | 85                |
| 7.00    | 1063      | 5.31         | 94                |

### Table 3. LSPR peaks at different concentrations of salicylic acid (SA).

| Sample | [SA] (mM) | LSPR (nm) |
|--------|-----------|-----------|
| C1     | 0         | 1167      |
| C2     | 0.3       | 1212      |
| C3     | 0.4       | 1220      |
| C4     | 0.5       | 1234      |
| C5     | 0.6       | 1220      |
| C6     | 0.7       | 1212      |

Figure 4. TEM images of the samples at concentrations of SA: (a) 0 mM, (b) 0.5 mM. (c) Diagram of the LSPR peaks of AuNRs and (d) UV–vis spectra of the growth of AuNRs from a solution prepared with different concentrations of SA: 0, 0.3, 0.4, 0.5, 0.6 and 0.7 mM; other preparation parameters are [CTAB] = 0.1 M, [HQ] = 0.1 M; [HAuCl₄] = 0.025 M; [Ag⁺] = 0.1 M and 80 μl seeds.
Figure 5. TEM images of AuNRs and UV–vis spectra of the samples at different concentrations of [Ag⁺]: (a) 0 mM, (b) 0.25 mM, (c) 0.35 mM, (d) 0.45 mM and (e) 0.55 mM. Other preparation parameters are [CTAB] = 0.1 M; [HQ] = 0.1 M; [HAuCl₄] = 0.025 M; [SA] = 0.5 mM and 80 µl seeds. (f) Diagram of the LSPR peaks of the AuNRs and (g) UV–vis spectra of a solution prepared with different concentrations of silver nitrate for growing AuNRs.
LSPR peak at 1273 nm of the AuNRs compared to the case of 200 μl of HQ (LSPR peak at 1185 nm).

Therefore, on adding 125 μl HQ into the growth solution, the corresponding concentration of HQ in the growth solution is 2.5 mM and gives the most red-shifted LSPR peak at 1273 nm. These nanorods are straight and uniform with average length of 102.78 nm and an average diameter of 9.99 nm, resulting in average aspect ratio of 10.29. On the other hand, the yield of AuNR formation is larger than 98%.

Figure 5 shows that a maximum LSPR peak position was reached at an intermediate HQ concentration of 2.5 mM, and this dropped off at concentrations above and below that value. This suggests that the HQ concentration of 2.5 mM is already near its ideal concentration for obtaining the highest possible value of LSPR peak.

The largest concentration of 4.0 mM gives an LSPR peak at about 1176 nm (sample E4), as seen in the representative histograms shown in figure 6(c). Control experiments show that reducing the HQ concentration in the growth solution to ~3.0 mM in the absence of SA leads to the deterioration not only of LSPR wavelength, but also of the yield of AuNR formation.

4. Conclusion

In summary, AuNRs were synthesized with and without SA using the seed-mediated method. The combination of SA and HQ led to an increase in the length of the AuNRs compared to the case using only HQ in the growth process. In particular, the wavelength of the LSPR peaks of the AuNRs can reach a value of 1273 nm. Moreover, the wavelength of

Table 4. Aspect ratio and yield of AuNRs at different Ag⁺ concentrations with [SA] = 0.5 mM.

| AgNO₃ (mM) | LSPR (nm) | Aspect ratio | Yield of GNRs (%) |
|------------|-----------|--------------|------------------|
| 0.00       | —         | —            | 0                |
| 0.15       | 1002      | 6.09         | 95               |
| 0.25       | 1002      | 6.09         | 95               |
| 0.35       | 1234      | 6.95         | 96               |
| 0.45       | 1254      | 7.81         | 99               |

Table 5. Aspect ratio and yield of AuNRs at different concentrations of HQ with [SA] = 0.5 mM.

| HQ (mM) | LSPR (nm) | Aspect ratio | Yield of GNRs (%) |
|---------|-----------|--------------|------------------|
| 2.0     | 1270      | 8.13         | 99               |
| 2.5     | 1273      | 10.29        | 100              |
| 3.0     | 1254      | 7.82         | 100              |
| 3.5     | 1216      | 7.05         | 98               |
| 4.0     | 1185      | 6.89         | 99               |
the LSPR peaks of the AuNRs can be controlled from 854 to 1273 nm by Ag$^+$ ion and HQ concentrations.

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