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Synthesis of Au nanorods in a low pH solution via seed-media method*

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The gold (Au) nanorods with various aspect ratios are obtained by a seed-media method in low pH growth solution. Transmission electron microscopy (TEM) and UV-visible spectrophotometry are utilized to characterize the Au nanorods, and the longitudinal absorption peak positions of Au nanorods show different shifting trends of the growth evolutions in various low pH (1∼3) solutions. Other influential factors on the shape of Au nanorod are also systematically studied under low pH reaction condition. The positions of longitudinal peak shift between 600 nm and 900 nm, with the aspect ratios of Au nanorods varying from 2 to 5 both in the simulation and experimental results. The simulation results are in agreement with experimental ones.

Keywords: Au nanorods, seed-media method, aspect ratio, surface plasmon absorption

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1. Introduction

Over the past two decades, the interest in the unique optical properties of metal nanorods has become increasingly popular because of their great potential applications in optical switch,[1] polarizer,[2–5] biological sensing,[6] etc. Due to the excellent stability, gold (Au) nanorods have been regarded as an important polarizing material. The various processes for synthesizing the Au nanorods have been reported, such as template method,[7–9] electrochemical method,[10,11] and seed-media method.[12,13] The seed-media method has the advantages of its well-shaped controllability and high yield.[14,15] The typical seed-media method for synthesizing Au nanorods is as follows: Au^{3+} ions are first reduced into Au atoms on the seed surface in the growth solution containing the surfactant of cetyltrimethylammonicum bromide (CTAB) and then Au atoms form nanostructure.

Moreover, Au nanorods exhibit distinct optical properties of plasma absorption, depending on aspect ratio.[16] The plasma resonance splits into two plasma absorption modes consisting of the longitudinal plasmon resonance and the transverse plasmon resonance, which has been reported by Gans.[17] However, the effect of reaction factor on aspect ratio of Au nanorod has barely been reported in detail under the condition of low pH growth solution.

In the present study, the Au nanorods are synthesized by the seed-media method using the hydrogen tetrachloroaurate (III) trihydrate ($HAuCl_4{\cdot}3H_2O$), CTAB, ascorbic acid (AA), silver nitrate ($AgNO_3$), sodium borohydride ($NaBH_4$), and HCl as the initial materials. Transmission electron microscopy (TEM) and UV-visible spectrophotometry are utilized to characterize the morphologies and absorption properties of Au nanorods. The optical properties of Au nanorods are studied by testing and calculating method.

The purposes of the present study are a) to study the effect of pH value on the aspect ratio of Au nanorod in the process of growth, b) to search the influencing factors on the aspect ratio of Au nanorod synthesized at pH = 1.6, and c) to investigate the absorptions of Au nanorods with various aspect ratios by calculating and experimental methods.

2. Experiment

Hydrogen tetrachloroaurate (III) trihydrate ($HAuCl_4{\cdot}3H_2O$), silver nitrate ($AgNO_3$), odium borohydride ($NaBH_4$), cetyltrimethylammonium bromide (CTAB), ascorbic acid (AA), HCl (37%) were purchased from Shanghai Chemical Co., Ltd., Shanghai, China. Ultrapure water with a resistivity higher than 18.2 MΩ·cm was produced by millipore (UPT-11-10T, ULUPURE, China).

i) Preparation of seed solution The 0.7288-g CTAB was first dissolved in 19-ml water, and then 1-ml aqueous solution of $HAuCl_4$ (0.5 mM) was added into CTAB aqueous solution. The solution appeared dark yellow. After that, 1.2-

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ml icy $NaBH_4$ solution (0.01 M) freshly prepared was added into reaction solution. The solution became brown immediately. The breaker was left in a water bath (30 °C) for 2.5 h. The seed solution was then ready for future use.

ii) Preparation of Au nanorods The growth solution was prepared in a typical process, appropriate amounts of $HAuCl_4$ (0.5 mM), $AgNO_3$ (4 mM) solution, ascorbic acid (0.08 M) aqueous solution, HCl (3.7 wt%), and seed solution were sequentially added into 20-ml CTAB (proper concentrations) aqueous solution. The growth solution was left in a water bath (30 °C) without being disturbed for 15 h. Then the solution was centrifuged under 8000 r/min to obtain gold nanorods.

The pH of growth solution was adjusted by adding HCl solution and measured using Lab pH Meter (MP521, SANXIN, China). The morphologies and sizes of Au nanorods were characterized by Transmission Electron Microscope (TEM, JEM 2010, JEOL, Japan). The absorption of Au nanorods solution was tested by UV-visible spectrophotometry (SHIMADZU, UV-1601).

3. Results and discussion

3.1. The effect of pH on the aspect ratio of Au nanorod

In the process of growth, without HCl addition (pH of the growth solution $\sim$ 2.8), the intensity of absorption spectrum becomes stronger and the longitudinal peak position is blue-shifted as the reaction takes place, and the longitudinal peak finally reaches 788 nm after 45 min as shown in Fig. 1(a). This means the aspect ratio of Au nanorods decreases with time going by, which is accordant with the result of Ref. [14]. Sau and Murphy[14] considered that the elongating of rod is accompanied by the widening of rod in the stage of growth, while the elongating rate of rod is slower than the widening rate. We assume the ratio of elongating rate to widening rate to be R. So at pH = 2.8, $R < 1$. However, the interesting thing that can be observed from Fig. 1(c) is that the longitudinal peak position is red-shifted from 640 nm to the ultimate 735 nm in 320 min at pH = 1.6, so $R > 1$. Moreover, the longitudinal peak position is always nearly 745 nm at the pH of 2.1 according to Fig. 1(b), and R could be considered to be equal to 1. On the other hand, the final longitudinal peak position of rods is blue-shifted (788 nm–735 nm) and time spent on reaction increases from 45 min to 320 min with pH value decreasing from 2.8 to 1.6. It could be supposed that the weaker reduction ability of AA at lower pH reduces the production rate and yield of Au atoms, consequently, the reaction time extends and the aspect ratio decreases. As to the different shifting trends of Au nanorods in the process of growth at different values of pH, it might be a factor that varying concentrations of Au atoms deriving from Au ion reduction by AA can adjust the value of R. The higher the value of pH, the lower the concentration of Au atoms is, and then the lower the value of R is.

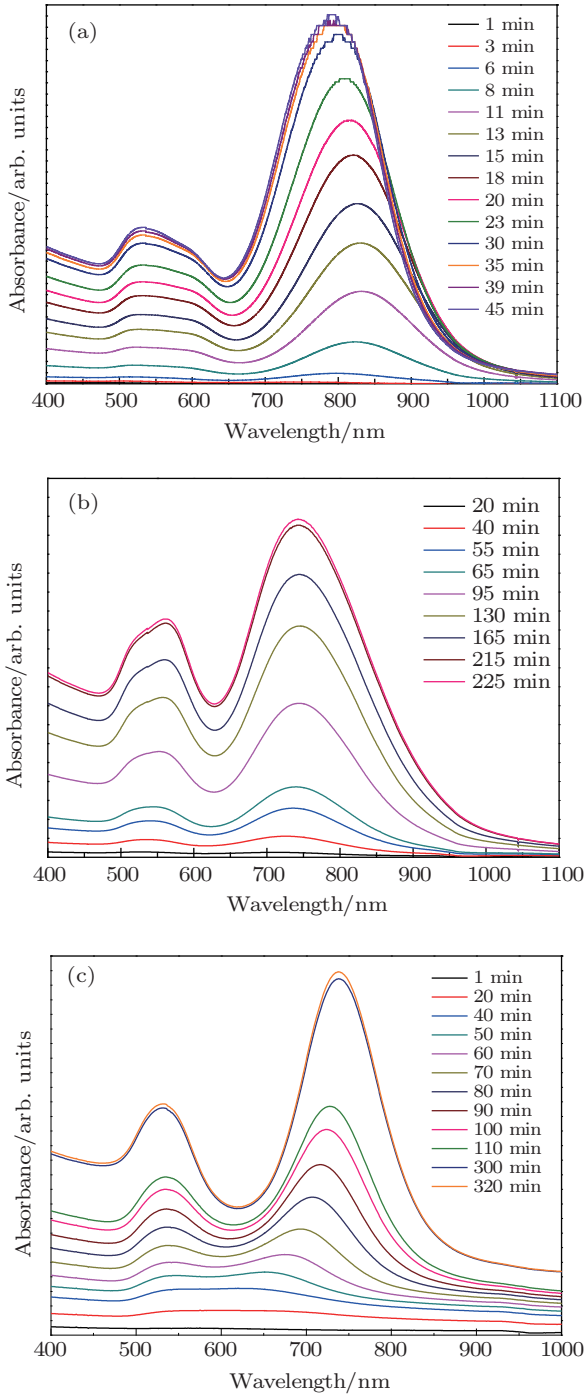


Fig. 1. (color online) Time-dependent absorption spectra of gold nanorods synthesized at pH values of (a) 2.8, (b) 2.1, and (c) 1.6, after addition of seeds to the growth solution and with $V_{HAuCl_4} = 2$ ml, $V_{AgNO_3} = 0.5$ ml, $V_{AA} = 180$ µl, $V_{seeds} = 40$ µl, $m_{CTAB} = 0.7288$ g in all the cases.

3.2. Other factors influencing the aspect ratio of Au nanorod at pH = 1.6

Au ions are reduced to Au atoms, and then the Au atoms participate in the growth of nanorods. The growth will not be terminated as long as Au atoms and CTAB are sufficiently supplied. Therefore, the concentration of Au ions also affects the aspect ratio of final shaped nanorods.[14] The aspect ratio of nanorod increases as the concentration of Au ions increases, but decreases as the concentration of Au ions further

increases as shown in Fig. 2(a). The high concentration of Au ions leading to the precipitate of complex of Au–Br–surfactant is formed from the binding of Au ions and surfactant, which affects the growth of nanorods.[15]

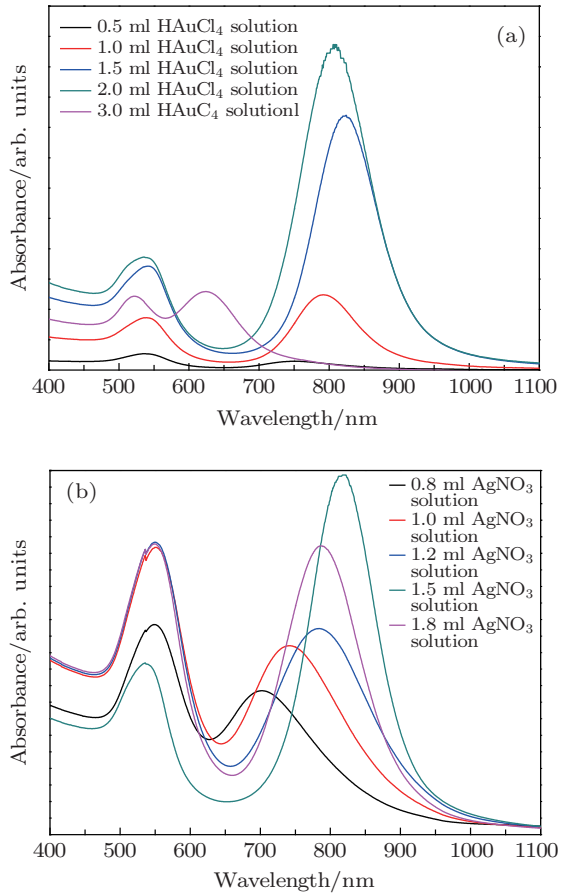


Fig. 2. (color online) UV-visible absorption spectra of gold nanorod samples prepared (a) in $HAuCl_4$ solutions with various concentrations of Au ions and (b) in $AgNO_3$ solutions with various concentrations of Ag ions. In the case of panel (a), $V_{AgNO_3} = 0.5$ ml, $V_{AA} = 180$ µl, $V_{seeds} = 40$ µl, $m_{CTAB} = 0.7288$ g, and pH = 1.6. And in the case of panel (b), $V_{HAuCl_4} = 2$ ml, $V_{AA} = 180$ µl, $V_{seeds} = 40$ µl, $m_{CTAB} = 0.7288$ g, and pH = 1.6.

Figure 2(b) shows the absorption spectra of Au nanorods synthesized in growth solutions with various concentrations of Ag ions. Without adding Ag^+ to growth solution, Au nanorods present high aspect ratio, yet the yield is quite low.[18] A trace amount of Ag^+ introduced into the process of growth which greatly changes the shape of nanorod and improves the yield.[19] Nikoobakht and El-Sayed[15] have indicated that CTAB are adsorbed onto face [110] in the development of growth, yet the charge density on Br^- results in mutual repulsion between neighboring headgroups of surfactant, which hampers the adsorption of CTAB onto gold surface. In the presence of Ag^+, Ag ions were considered as Ag–Br-surfactant via combining with Br ions from CTAB. Consequently, the charge density on Br^- is reduced, which enhances the adsorption of CTAB onto Au nanorods. This result causes the aspect ratio of gold nanorods to increase with the concentration of Ag ions increasing, however, what is similar to the behaviors of Au ions is that the further increase of Ag ions leads to the decrease of aspect ratio as shown in Fig. 2(b). It can also be explained by the ionic strength effect, which is observed for gold ions.[15]

As the reductant, ascorbic acid also controls the aspect ratio of the gold nanorod. The length of rods and aspect ratio of rods increase with increasing the concentration of AA. It is confirmed by the TEM topography and the absorption spectra in Fig. 3. Slight variation can be observed that the transverse plasma absorption peak shows broadening with a rather high quality of AA. The shape of gold nanorod looks like a dumbbell with a larger width on both ends of rod than in the middle. The inhomogeneity of width leads to the broadening of transverse peak.[20]

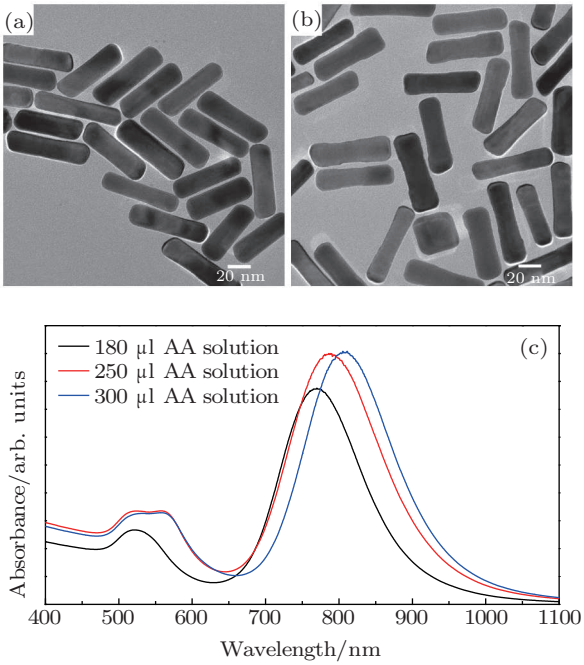


Fig. 3. (color online) (a) and (b) TEM micrographs and (c) absorption spectra of gold nanorods synthesized with adding ascorbic acid: (a) $V_{AA} = 250$ µl and (b) $V_{AA} = 300$ µl. (c) $V_{AA} = 180$ µl, 250 µl, and 300 µl. In all the cases, $V_{HAuCl_4} = 2$ ml, $V_{AgNO_3} = 0.5$ ml, $V_{seeds} = 40$ µl, $m_{CTAB} = 0.7288$ g, and pH = 1.6.

Figure 4 shows the TEM micrographs and absorption spectra of Au nanorods synthesized in growth solutions with $V_{HAuCl_4} = 2$ ml, $V_{AgNO_3} = 0.5$ ml, $V_{AA} = 180$ µl, $V_{seeds} = 40$ µl, pH = 1.6 and various quantities of CTAB. From the results of Figs. 4(a)–4(c), it follows that the aspect ratio of Au nanorod decreases as CTAB content increases. This result also shows that the yield of Au nanorods decreases simultaneously. In the formation process of gold nanorods, CTAB adsorbed onto Au nanorods ensures the formation of rod-like shape.[15] In fact, CTAB obstructs the reduction rate of Au ions by a factor of 100–1000. High concentration of CTAB lessened the supply of Au atoms to the development of nanorods. Hence, the aspect ratio of nanorod decreases as the concentration of CTAB increases.

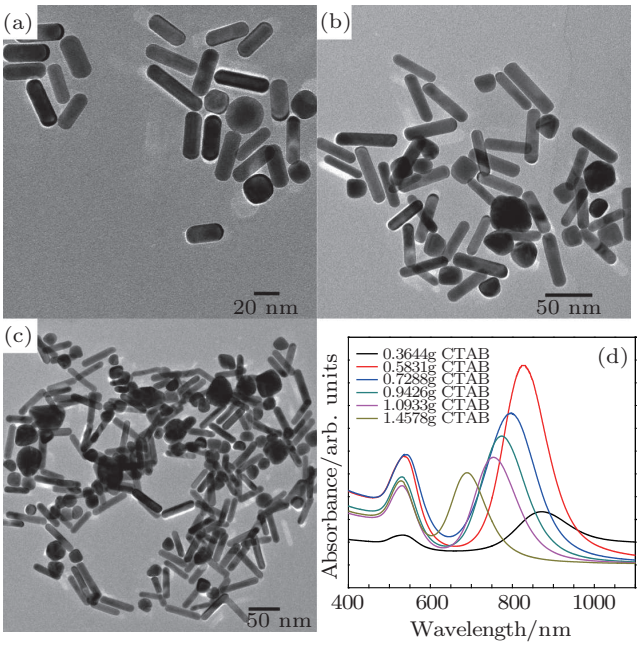


Fig. 4. (color online) (a)–(c) TEM micrographs and (d) absorption spectra of gold nanorods synthesized under additional quantities of CTAB, $m_{CTAB} = 1.0933$ g (a), 0.5831 g (b), and 0.3644 g (c), (d) absorption spectra. In all the cases, $V_{HAuCl_4} = 2$ ml, $V_{AgNO_3} = 0.5$ ml, V_{AA}=180 μl, $V_{seeds} = 40$ μl, and pH = 1.6.

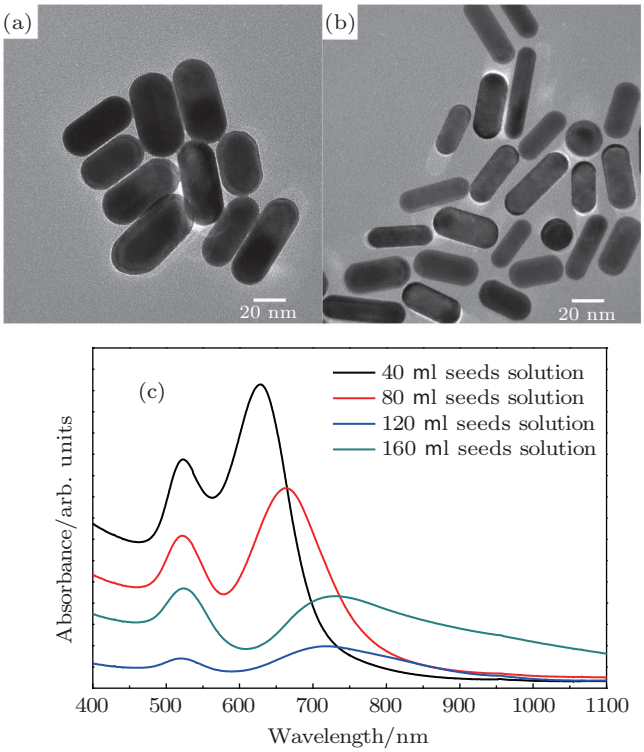


Fig. 5. (color online) (a) and (b) TEM micrographs of gold nanorods synthesized under additional quantities of $V_{seeds} = 40$ μl (a) and 80 μl (b) of seeds; (c) UV-visible absorption spectra of Au nanorods for different additional quantities of seeds. In all cases above, $V_{HAuCl_4} = 1$ ml, $V_{AgNO_3} = 0.25$ ml, $V_{AA} = 90$ μl, $m_{CTAB} = 03644$ g, pH = 1.6.

TEM micrographs and absorption spectra of Au nanorods synthesized for growth solution including various quantities of seeds are shown in Fig. 5. From Figs. 5(a) and 5(b) it follows that the length and width of Au nanorod both decrease with increasing the concentration of seeds. Figure 5(c) shows the absorption spectra of Au nanorods synthesized with adding various quantities of seeds. It reveals that the position of longitudinal peak shifts from 627 nm to 725 nm with the concentration of seed solution increasing from 40 μl to 180 μl. For a higher concentration of seeds under otherwise identical conditions of growth, the quality of Au distributed to each seed will decrease, yet the degree of reduction in width is greater than in length, which have been demonstrated by the previously reported results.[14,21] The results of the present study are in agreement with the previously reported results.[14,21]

3.3. Absorptions of Au nanorods with different aspect ratios studied by calculation and experiment

The various dimensions and shapes correspond to diverse absorption spectra, and the absorption peak of Au nanorods originates from the surface plasmon resonance, which have been reported by Huang *et al.*[16] According to the Gans theory,[22,23] the analytical expression for extinction coefficient γ of particles is given as

$$\gamma = \frac{2\pi NV\varepsilon_m^{3/2}}{3\lambda}\sum_j \frac{\left(1/p_j^2\right)\varepsilon_2}{\left(\varepsilon_1 + \frac{1-p_j}{p_j}\varepsilon_m\right)^2 + \varepsilon_2{}^2}, \quad (1)$$

where N is the number of particles per unit volume, V the volume of each particle, ε_m the dielectric constant of the surrounding medium, λ the wavelength of the light, and ε_1 and ε_2 are the real part and complex part of the gold dielectric function respectively, and P_j the depolarization factors for the three axes A (long axes), B, C of rod and expressed by the following equations:

$$P_A = \frac{1-e^2}{e^2}\left[\frac{1}{2e}\ln\left(\frac{1+e}{1-e}\right) - 1\right], \quad (2)$$

$$P_B = P_C = \frac{1-P_A}{2}, \quad (3)$$

$$e = \sqrt{1-\left(\frac{B}{A}\right)^2}, \quad (4)$$

the value of ε_m for water is 1.7689, the values of ε_1 and ε_2 for gold are cited from the reports by Johnsch and Chriaty.[24]

Figure 6 shows the TEM micrographs and the absorption spectra of the synthesized Au nanorods with various aspect ratios. Figures 6(a)–6(d) show the TEM micrographs of Au nanorods with aspect ratios ranging from 2.2 to 4.7. The simulated absorption spectra of Au nanorods by plotting from Eq. (2) for three different aspect ratios are shown in Fig. 6(e), showing that the increase in the aspect ratio leads to the longitudinal plasma band red-shift.[25] This result also demonstrates that the desired extinction coefficient can be tuned by controlling the aspect ratio of Au nanorod in a certain surrounding medium. Figure 6(f) shows the variations of absorption spectra of Au nanorods with aspect ratio in water, from

which it follows that in all plasma absorption spectra there appear two peaks, one is the transverse resonance absorption near 530-nm band and the other is the longitudinal resonance absorption between 600 nm and 900 nm which is sensitive to the aspect ratio, presenting a red-shifted trend with increasing aspect ratio. The simulation result is in agreement with the experimental result.

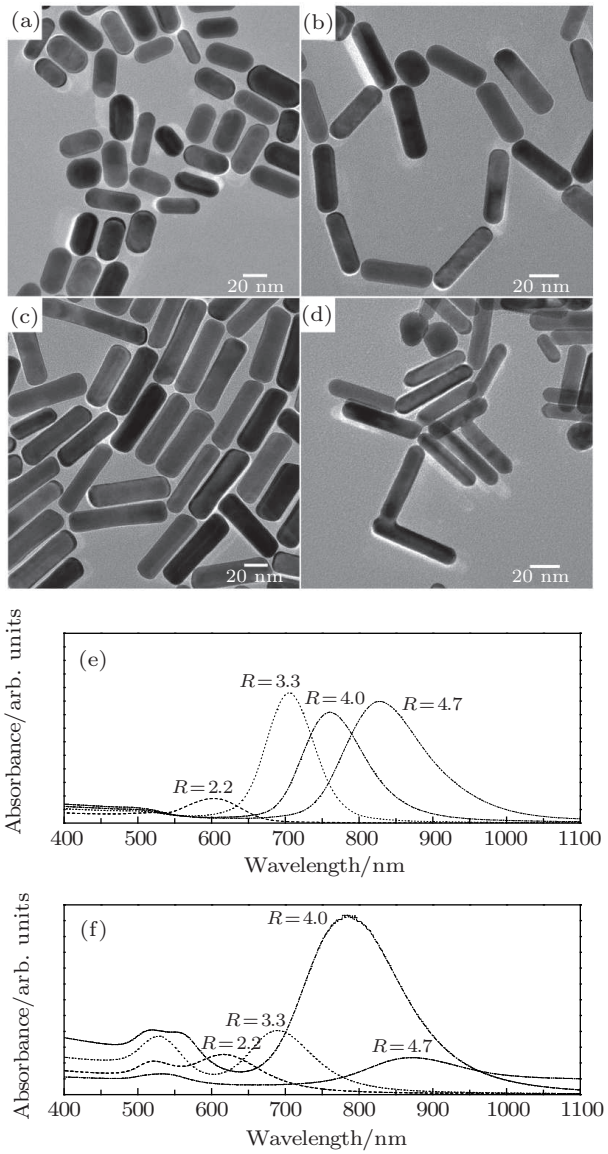


Fig. 6. (a)–(d) TEM microscope images of Au nanorods with aspect ratios of (a) 2.2, (b) 3.3, (c) 4.0, and (d) 4.8; (e) simulated spectra and (f) experimental spectra of Au nanorods with different aspect ratios.

4. Conclusions

The optical properties of Au nanorods synthesized at a lower pH growth solution are investigated by seed-media method. The results are summarized below.

(i) The longitudinal peak positions of Au nanorods present different shifting trends in the process of growth at various low pH values from 2.8 to 1.6.

(ii) Rigidly controlling the growth environment such as the concentration of Au ions, Ag ions, AA, CTAB and seeds makes it possible to synthesize gold nanorods with tunable aspect ratio at pH = 1.6.

(iii) The positions of longitudinal peaks shift between 600 nm and 900 nm with the aspect ratios of Au nanorods varying from 2.4 to 4.8, indicated by both the simulation results and the experimental results. The simulation results are in agreement with experimental results.

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