An investigation of binary surfactant in the synthesis of gold nanorods

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Abstract. The method by using hexadecyltrimethylammonium bromide (CTAB) and sodium oleate (NaOL) as binary surfactant mixture to synthesize high quality gold nanorods (AuNRs) has been one of the most widely used methods in this field. But the specific influence on the obtained AuNRs of these two surfactants has not been systematically studied in previous works. Here, we carry out series of experiments and characterized the results. By using the UV-VIR spectrophotometer and transmission electron microscope, we found the higher CTAB concentrations will lead to the larger aspect ratios of the obtained AuNRs. In addition, the final products under this method are more sensitive to the NaOL concentration.

1. Introduction
Gold nanorods have drawn great attention in the past 20 years for the special optical property and size tunability. Due to the localized surface plasmon resonance (LSPR) effect, the electrons on AuNRs surface interact with certain wavelengths of electromagnetic waves from 600 nm to the near-infrared region, causing an extinction of the corresponding electromagnetic waves and forming a thermal effect. It has been put into applications in SERS,[1-3] biomedicine,[4-6] and biological sensing.[7-8] As the LSPR effect is directly related to the aspect ratio of AuNRs, synthesis and tuning have always played an important role. A significant breakthrough in the development of such method for growing AuNRs was carried out by El-Sayed et al.,[9] Au³⁺ was fast reduced by sodium borohydride and turned into gold nanoparticles (~ 2 nm in size) as seeds which provide a template for slow overgrowth and catalyse the reaction in an aqueous CTAB solution. Surfactant CTAB is introduced in this process as stabilizer and enhanced the anisotropic growth.[10] After the mild reduction of Au³⁺ in the growth solution by ascorbic acid, Au⁰ directionally grow onto the seeds. This seed-mediated method greatly improved the yield and shape monodispersity of the obtained AuNRs. By the further developments of many researchers including Murray,[11] Murphy,[12] and Liz-Marzán[13] groups, seed-mediated growth of AuNRs has been greatly improved.

One of the most widely used synthesis methods of AuNRs was proposed in 2013 by Ye et al. [11] They introduced NaOL as another surfactant, successfully dropped the surfactants concentration (cCTAB + cNaOL) to nearly 45 mM as well as maintaining both high monodispersity and tunability. However, the binary surfactant concentration was fixed in 37 mM, 47 mM of CTAB and 8 mM, 11
mM of NaOL. The influence of the binary surfactant has not been systematically studied in the above work.

In this work, we studied this synthesis method in different angle in order to figure out the influence of the binary surfactant in the synthesis process. AuNRs were synthesized under different concentration combinations of binary surfactant, and characterized by the UV-vis spectroscopy and transmission electron microscopy (TEM). We discussed the effect caused by single variety of CTAB and NaOL when other parameters were fixed.

2. Materials and Methods

2.1. Synthesis of AuNRs samples

Seed solution: 0.25 mL of 10 mM HAuCl₄ was added to 10 mL 0.1 M CTAB solution. Then the 0.6 mL of 10 mM NaBH₄ (freshly prepared with cold water) was added, under the vigorous stirring. The colour of the solution changed from yellow to brownish yellow. The seed solution was aged at 30 ℃ for 30 min before use.

The growth solution was prepared by adding 2.5 mL of 0.1 M CTAB in a 40 mL scintillation vial. Then, 0.037 g of NaOL was dissolved in 21.25 mL of warm water (45-50 ℃) in the same scintillation vial. When the solution cooled down to 30 ℃, 0.9 mL of 4 mM AgNO₃ solution was added. The mixture was kept undisturbed at 30 ℃ for 15 min after which 10 mL of 0.25 mM HAuCl₄ was added. The solution became colourless after 90 min of stirring. To adjust the pH, 0.3 mL of HCl (37 wt.% in water) was added. 0.075 mL of 64 mM ascorbic acid and 0.04 mL of seed solution was added after 15 min. Finally, the resultant solution was left undisturbed at 30 ℃ for 12 h to growth. The final CTAB concentration is 0.01 M. The experimental parameters were listed at Tables 1.

2.2. Characterization

Optical extinction spectra were recorded with a UV-1900i Spectrophotometer (SHIMADZU, Japan) with a 10-mm optical path. Transmission electron microscopy (TEM) images were obtained with a HT-7700 microscope (HITACHI, JAPAN) operating at 100 kV. The particle sizes of the AuNRs were measured from TEM images, whereby >100 particles were measured for each sample.

3. Results and Discussion

Table 1. Reaction conditions and LSPR peaks of AuNRs synthesized under different CTAB/NaOL concentrations. The volume of final solution is 25 mL.

| CTAB (M) | NaOL (M) | HCl (mL) | AgNO₃ (mM) | Seed (mL) | LSPR Peak (nm) | Figure Number |
|----------|----------|----------|------------|-----------|----------------|---------------|
| 0.037    | 0.002    | 0.105    | 0.144      | 0.04      | 1018           | Fig. 1e black |
| 0.037    | 0.004    | 0.105    | 0.144      | 0.04      | 1058           | Fig. 1e red   |
| 0.037    | 0.006    | 0.105    | 0.144      | 0.04      | 1062           | Fig. 1e blue  |
| 0.037    | 0.008    | 0.105    | 0.144      | 0.04      | 873            | Fig. 1e green |
| 0.037    | 0.0010   | 0.105    | 0.144      | 0.04      | 685            | Fig. 1e purple|
| 0.037    | 0.0012   | 0.105    | 0.144      | 0.04      | -              | Fig. 1e brown |
| 0.010    | 0.005    | 0.3      | 0.144      | 0.04      | 690            | Fig. 1f black |
| 0.012    | 0.005    | 0.3      | 0.144      | 0.04      | 729            | Fig. 1f red   |
| 0.014    | 0.005    | 0.3      | 0.144      | 0.04      | 805            | Fig. 1f blue  |
| 0.016    | 0.005    | 0.3      | 0.144      | 0.04      | 893            | Fig. 1f green |
| 0.018    | 0.005    | 0.3      | 0.144      | 0.04      | 992            | Fig. 1f purple|
| 0.010    | 0.008    | 0.3      | 0.144      | 0.04      | 655            | Fig. 1e       |
Figure 1. Characterization of AuNRs synthesized under different concentrations of CTAB/NaOL. (a) TEM image of AuNRs synthesized under 10 mM CTAB and 5 mM NaOL (black spectrum in 1f); (b) TEM image of AuNRs synthesized under 12 mM CTAB and 5 mM NaOL (red spectrum in 1f); (c) TEM image of the obtained Au impurities in AuNRs synthesis process. (d) Optical image of the AuNRs samples shown in figure 1f; (e) Extinction spectra of AuNRs synthesized under 2 – 12 mM NaOL when other parameters were fixed. (f): Normalized extinction spectra of AuNRs synthesized under 10 – 18 mM CTAB when other parameters were fixed. The reaction conditions and LSPR peaks were listed in Table 1.

Figure 1 showed a series of characterization of AuNRs synthesized under different concentrations of CTAB/NaOL. All the amounts of corresponding chemicals were listed in Table 1. It can be observed from Figure 1a and 1b that although the surfactants concentrations ($c_{\text{CTAB}} + c_{\text{NaOL}} = 15$ mM and 17 mM) were very low, by adding more HCl, high quality AuNRs can still be obtained. Figure 1c showed the impurities of AuNRs synthesized under 0.010 M CTAB and 0.008 M NaOL. When we only changed the concentration of NaOL (0.005 M vs. 0.008 M), the shape impurities increased and we failed to obtain high quality AuNRs. Figure 1d showed the optical image of AuNRs samples synthesized under the increase of NaOL concentration. The aspect ratio of AuNRs got larger with the increasing of CTAB concentration. We also carried out a series of experiments when all amounts of reactants were fixed except NaOL. The results were shown in figure 1e. But there were no obvious trends of LSPR peaks of AuNRs samples synthesized under the increase of NaOL concentration.
4. Conclusions
In conclusion, we have given the results of the influence on the obtained AuNRs under this binary surfactant method. This is an area that has not been systematically studied by former works. TEM images showed that the CTAB concentration does affect the aspect ratios of the obtained AuNRs. The increase of CTAB concentration leads to the red-shift of LSPR peak and the increase of aspect ratios of the products. These results may due to the CTAB, which produce an stabilizing power to the \{100\} facets of AuNRs, when the CTAB concentration increases, the growing speed of \{100\} facets of AuNRs gets lower, leads to the increase of the aspect ratios.[10] Moreover, the spectra show that the qualities of the obtained AuNRs are more sensitive to the NaOL concentration. We are surprised to found that the surfactants concentration $c_{\text{CTAB}} + c_{\text{NaOL}}$ can dropped to 15 mM while maintaining the monodispersity and purity of the obtained AuNRs. What can’t be ignored is the NaOL concentration should be kept neither too high or low. One possible explanation is that the quality or the final products is more sensitive to the pH. After all, these results finally bring us some valuable questions that why we need to dropped the NaOL concentration to 5 mM instead of keeping it at the best concentration (8 mM) which has been used in former work. [11]

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