



Research paper

Heat-induced morphological transformation of gold nanodumbbells in ionic surfactant solutions

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ABSTRACT

The thermal stability of gold nanodumbbells (NDs) is studied in aqueous solution of ionic surfactants. It is found in aqueous solution of cetyltrimethylammonium bromide that the blue-shift of longitudinal surface plasmon resonance band of gold NDs occurs at 75 °C and the new gold nanorods (NRs) with shortened aspect ratio are formed at the same time. The aspect ratio of the generated gold NRs gradually decreases and finally approaches ~ 1.7 after repeated processing. Similarly, the same results are also obtained in aqueous solution of sodium dodecyl sulfate at room temperature. Mechanism is proposed for the shape transformation of gold NDs.

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1. Introduction

Among the metal nanoparticles (NPs) that have been studied in detail [1], the synthesis of gold NPs and NRs is established at the early stage of nanomaterials [2,3]. These NPs and NRs could be easily prepared by the wet methods in the presence of the protecting molecules such as thiols, polymers and surfactants [4–6]. And they are also particularly interesting starting nanomaterials for the formation of both gold NPs and NRs-based entities. For example, many bimetallic core-shell nanostructures with gold cores are frequently employed as catalysts to promote their catalytic activities [7,8]. On the other hand, when metallic NPs are exposed to an electromagnetic wave, the oscillation of the free electrons in their surfaces occurs and results in the peculiar phenomenon called surface plasmon resonance (SPR). The frequency of the SPR band strongly depends on the aspect ratios (ARs) of gold NRs and the geometry of gold NPs. And it has been demonstrated in many works that the shape of gold NRs could be modified to tune the frequencies of their SPR bands [9–11]. When these NPs are coated with silver to produce Au-Ag core-shell NPs with their characteristic SPR bands blue shifted in the ultraviolet and visible regions. In particular, the particular property has been successfully applied to surface enhanced Raman spectroscopy (SERS) detection with a higher enhanced sensitivity and dye-sensitized solar cells (DSSC) with an enhanced light-harvesting efficiency [12,13].

The preparation of gold NRs is mostly achieved in aqueous micellar solution of cationic surfactants. It has been known that cetyltrimethylammonium bromide (CTAB) is a stabilizing reagent and plays an important role in inhibiting the isotropic growth of gold atoms on gold nano-seeds in the growth solution [3]. At the same time, other reagents such as silver ions and co-factor are essential to adjust the anisotropic reduction reaction of Au ions, and to promote the formation of gold NRs in a one-dimensional direction. In general, the ARs of gold NRs could be controlled in visible and near-infrared regions by the different methods reported in the literatures [3,14,15]. But, the final ARs highly depend on the actual reaction conditions involved [16–19]. Therefore, it is useful to develop the synthetic method that the ARs could be subsequently fine-tuned in demand after gold NRs have been prepared. In the previous work, we show that gold NRs could be changed into gold NDs with extended ARs in the reaction of Au ions and ascorbic acid (AA) [20]. In this Letter, we further report the investigation in the stability of gold NDs in the ionic surfactant solution of CTAB at 75 °C and sodium dodecyl sulfate (SDS) at room temperature (RT), respectively. In contrast to cationic CTAB, SDS is a typical anionic surfactant and is widely used in the gel electrophoresis of protein separation [21]. Our results reveal that gold NDs could be transformed back into gold NRs with smaller ARs in comparison with the original gold NRs and NDs. Moreover, the new ARs of gold NRs could be continuously fine-tuned to ~ 1.7 after repeated processing. Repeated cycles lead to a controlled tuning of AR. At the same time, there is a consistent increase in the sizes of both the long and short ends of gold NR. Our studies suggest that

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the occurrence of morphological transformation of gold NDs is related to the protecting ability of the surfactant molecule in the heating process.

2. Materials and methods

2.1. Chemicals

Sodium borohydride was purchased from Alfa Aesar. All other reagents were obtained from Acros. All the chemicals were used as received.

2.2. Characterization

Optical characterization was carried out by UV/Vis spectroscopy with a Hitachi U-3900 spectrophotometer. Transmission electron microscopy (TEM) images obtained were obtained on a JEOL JEM-2100F microscope operating at 200 kV.

2.3. Synthesis of gold nanorods and nanodumbbells

For gold NRs with AR \sim 2.6, they were prepared by a modified method published by Liz-Marzán and coworkers [14]. 5 mL of 0.25 mM HAuCl₄ and 0.1 M CTAB was mixed with 0.3 mL ice-cold 0.01 M NaBH₄. The solution was then stirred at RT. The gold particles were formed and used as seeds in the following growth solution after 3 h. For growth solutions, 4.5 mg of 5-bromosalicylic acid was first dissolved in 2.5 mL of 0.1 M CTAB. And 1.5 mL of 0.3 mM AgNO₃ was added to the above solution. After stirring for 15 min at RT, 1 mL of 2.5 mM HAuCl₄ (HA) was added to the mixture. After 3 h, 12 μ L of 0.1 M AA was added under vigorous stirring, followed by 80 μ L of gold seed solution. The mixture was stirred overnight at RT. Finally, the reaction solution was centrifuged at 8000 RPM for 20 min and the supernatant was discharged. The residue was diluted to give a 10 mL Au NR-containing solution of 5 mM CTAB. After that, 31.1 μ L of 79 mM AA was added to the above 5 mL Au NR-containing solution. 13.8 μ L of 25.4 mM HA was subsequently added 10 min later. After 1 h, Au NDs were formed in the reaction mixture. Both Au NRs and NDs were then analyzed for collecting absorption spectra and TEM images.

For gold NRs with AR \sim 3.8, they were prepared by a modified method published by El-Sayed and coworkers [6]. 5 mL of 0.25 mM HA and 0.1 M CTAB was mixed with 300 μ L ice-cold 10 mM NaBH₄. The resulting mixture was then stirred at room temperature. After 3 h, the gold particles were formed and used as seeds for the synthesis of gold NRs. 5 mL of 0.5 mM HA and 0.1 M CTAB was mixed with 50 μ L of 10 mM AgNO₃, followed by the addition of AA (32 μ L, 0.1 M) and the above gold seed solution (10 μ L). After being stirred at RT for 17 h, the solution was centrifuged at 8000 RPM for 20 min. The supernatant was discarded and the NR-containing solution was diluted with 1 mL of 5 mM CTAB. Then, the sample was used to prepare gold NDs via the same procedure as described above.

2.4. Transformation of gold nanodumbbells

- (1) Heating in CTAB solutions: the Au NDs prepared in Section 2.3 was first centrifuged and the supernatant was discharged. The residue was diluted to give a 25 mL Au ND-containing solution of 5 mM CTAB. Then, the above 5 mL Au ND-containing solution was heated on a hot plate at 75 °C for 1.5 hrs. After that, the absorption spectrum of the final reaction solution was recorded and the image of Au NPs in the solution was obtained by TEM. For multicycle heating reaction, this process comprises a simple repetition of the previous procedures: the formation of Au NDs from

Au NRs and the subsequent heating at the same condition. UV-vis absorption spectra and the images of Au NPs were taken between each run after purification.

- (2) RT in SDS solutions: the Au NDs prepared in Section 2.3 was first centrifuged and the supernatant was discharged. The residue was diluted to give a 1 mL Au ND-containing solution of 5 mM CTAB. Then, the above 1 mL Au ND-containing solution was slowly added with stirring to 5 mL of 20 mM SDS in 50 min at RT. After 30 min, the stirring was stopped and the mixture was centrifuged again and the supernatant was discharged. The residue was diluted to give a 1.5 mL Au ND-containing solution of 20 mM SDS. After the same procedure again, the solution was left undisturbed at RT overnight. After that, some precipitate in the solution was discharged. The residue was diluted to give a 5 mL Au NP-containing solution of 20 mM SDS. The absorption spectrum of the reaction solution was recorded and the image of Au NPs in the solution was obtained by TEM. For multicycle reaction, Au NRs in SDS solution was first transferred to the CTAB solution. The procedure of the transfer is similar to the above and the only difference is the use of 100 mM CTAB instead of 20 mM SDS. Finally, Au NRs are dispersed in 5 mL of 5 mM CTAB and ready for the preparation of Au NDs as described in Section 2.3.

2.5. Chemical modification and assembly of gold nanodumbbells

100 μ L of 10 mM cysteine was added to 5 mL Au ND-containing solution of 5 mM CTAB prepared in Section 2.3. (1) Transformation: after 10 min, the solution is heated at 75 °C as described in Section 2.4. (2) Assembly: after 30 min, the solution was mixed with 100 μ L of 100 mM HCl. The pH of the final solution is near 3. UV-vis absorption spectra and the images of Au NDs were taken after 1 h.

3. Results and discussion

Fig. 1a is the UV/Vis absorption spectrum of gold NRs formed in the growth reaction. The absorption peak at 664 nm is assigned to the longitudinal SPR band of gold NRs (dash line). Their lengths and diameter, measured by the TEM images as shown in Fig. 1b, are about 49.7 ± 7.0 nm and 19.0 ± 1.3 nm, respectively. The AR is \sim 2.6. And the high-resolution TEM image of a gold NR revealed the lattice spacing \sim 0.205 nm, corresponding to the spacing of (1 0 0) plane of face-centered cubic structure of gold. And it was also confirmed by the fast Fourier transform (FFT) pattern. The results are the same as those reported in the literatures [22,23]. Gold NRs subsequently reacted with AA and HA to produce gold NDs. It is apparent that a red-shift of longitudinal SPR band appears and the intensity of absorption band at 682 nm increase (solid line, Fig. 1a). The TEM image in Fig. 1c shows the formation of gold NDs with a higher AR \sim 2.9. The average diameter of gold NDs between the tips is 53.4 ± 5.6 nm and became longer than that of gold NRs, but their length (18.6 ± 1.4 nm) in the middle almost remained constant as before. The data shown in Fig. 1 are reminiscent of the results we reported earlier in the synthesis of gold NDs with AR \sim 4.2 [20]. Next, the thermal stability of the prepared gold NDs was studied in the CTAB solution by heating them at 75 °C for 1.5 h. Fig. 2 is the UV/Vis absorption spectrum of gold NDs before (dash line) and after (solid line) heating in the CTAB solution. Particularly noteworthy is the presence of the blue-shift of longitudinal SPR band at 634 nm, suggesting the occurrence of the decrease in ARs. It is also confirmed by the TEM image in the inset of Fig. 2 that the original gold NDs were transformed into the new gold NRs (AR \sim 2.4) whose lengths and diameter are about

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