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The thermal stability mechanism of gold nanorods in aqueous solution

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ABSTRACT

Gold nanorods were prepared by seed-mediated growth method and were kept inaqueous solution between 45 and 105 °C. It was found that the longitudinal absorption peak of the gold nanorods obviously moved to a shorter wavelength between 60 and 90 °Cand this blue shift phenomenon disappeared after aperiod of time. In this paper, based on the theories of the liquid-like shell, combining the rule that the metal Gibbs free energy changes with temperature, the heat induced deformed mechanism has been studied and especially why the gold nanorods can be stably kept in aqueous solution at high temperature has been analyzed.

1. Introduction

The absorption spectrum of gold nanorods have two peaks corresponding to the surface plasmon resonance, and the position of the longitudinal surface plasmon resonance(LSPR) absorption peak is tunable from visible to near-infrared. Gold nanorods can be applied in many fields, such as biomedicine, information storage, sensing and anti-counterfeit [1–3]. For example, gold nanorods with different aspect ratios can be used as molecular probe, because of dependence of their longitudinal absorption peak positions on the environmental refractive index [1,2]; gold nanorods can also be used in preparing large capacity data storage disc because their absorption intensity is different for light with different wavelength and polarization direction [3]. In these applications, the thermal stability of gold nanorods should be very high, because any perceivable shape change of gold nanorods will change their optical properties [4–6].

In high temperatures, the particles shape will change, resulting in significant shifts of the longitudinal resonance absorption peak [7–11]. Hristina Petrova et al. [12] deposited gold nanorods on a glass slide, and heated the sample in a standard laboratory oven. All nanorods transformed into spheres within an hour at 250 °C. While some nanorods maintained in rod shape if the temperatures is lower than 250 °C, even for the case of heating time near 20 h. They indicated that the structural changes arise from the surface melting. S Karim et al. [13] found that Au nanowires on SiO_2 wafer pieces develop radial fluctuations already at 300 °C and decay completely into linear rows of spheres at 500 °Cdue to capillary or so-called Rayleigh instability. However, the Au nanoparticles used in the experiments described above were put on the substrate which increases the stability against Rayleigh decay as compared to free-standing rods.

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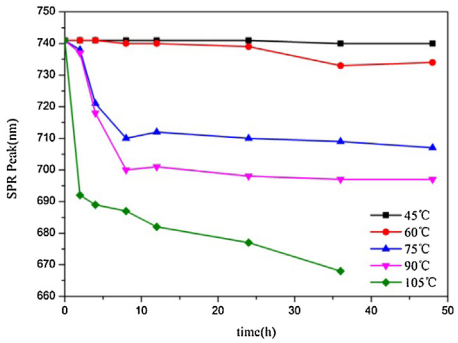

Fig. 1. Temporal evolution of the LSPR absorption peak of the gold nanorods.

AL-Sayed et al. [14] have prepared gold nanorods in micelles via electrochemical method, and immersed the sample into the thermostat bath at 130 °C, after about 30 min, no further changes have been observed and the maximum blue shift was 60 nm. V. Canpean et al. [15] used a thermal cell to heat gold nanorods in water solution between 25 and 90 °C. They found that rod-shaped nanoparticles transformed into spheres. The surface melting was considered to be the main mechanism for the reshaping of the AuNRs under thermal treatment. Renxian Zou et al. [16] heated the gold nanorods solution in a clean three-neck flask to 95 °C. They found that the movement of the longitudinal absorption peak finally stopped after 5 h, and most of the particles still kept in rod-like shape. The deformation of gold nanorods in high temperature solution was thought to be caused by the Ostwald ripening or the surface melting. Although the phenomena that gold nanorods can be dispersed in solution stably under a certain temperature are not difficult to be observed [17,18], seldom explanations were carried out on the reason why blue shifts of the LSPR absorption peak stop under a certain temperature after a period of thermal treatment.

In this paper, we report the effect of thermal treatment on gold nanorods in aqueous solution. The gold nanorods were kept for different hours (2 h, 4 h, 8 h, 12 h, 24 h, 36 h, 48 h) in a drying oven at different temperatures (45 °C, 60 °C, 75 °C, 90 °C, 105 °C). The thermal deformation mechanism of gold nanorods was interpreted based on the change of Gibbs free energy with temperature.

2. Experimental details

Gold nanorods were synthesized by employing the seed-mediated growth method [19]. Firstly, Au seeds were prepared at room temperature: 0.25 mL of 0.01M $HAuCl_4 \cdot 3H_2O$ was added into 7.5 mL of a 0.10 M CTAB solution, then 0.60 mL of 0.01 M $NaBH_4$ solution was added. The mixture was kept in a water bath at 25 °C for 2 h. Gold nanorods were also prepared at room temperature: 4.75 mL of 0.10 M CTAB, 0.200 mL of 0.01 M $HAuCl_4 \cdot 3H_2O$, 0.030 mL of 0.01 M $AgNO_3$, and 0.032 mL of 0.10 M AA solutions were added in order. Finally, 0.010 mL of seed solution was added, and kept in a water bath at 25 °C for at least 3 h.

The prepared gold nanorods were dispersed in deionized water and heated at five temperatures ranging from 45 to 105 °C. The treating time is between 2 and 48 h. TEM images and UV–vis absorption spectrum were used to analyze the shape of the gold nanorods.

3. Results and discussions

As shown in Fig. 1, the LSPR absorption peak of the gold nanorods had no obvious change in 48 h at 45 °C. While, the LSPR absorption peaks continually shifted to shorter wavelengths at 105 °C. At temperatures ranging from 60 to 90 °C, the LSPR absorption peaks of the gold nanorods shifted toward shorter wavelengths only in the beginning. After a period of time, the blue shift gradually stopped. This phenomenon indicates that gold nanorods can exist stably in aqueous solution after a certain degree of deformation at temperatures ranging from 60 to 90 °C.

The blue shift started after different time of thermal treatment between 60 and 90 °C. At 60 °C, the blue shift occurred after 24 h of heating. While at 70 and 90 °C, the blue shift was obvious after 2 h of heating. The blue shift speeds are higher at higher temperatures and the final values of the longitudinal absorption peaks varied depending on the temperature and time. Under 48 h of heating treatments with temperatures of 45 °C, 60 °C, 75 °C and 90 °C, the absorption peaks of the LSPR were 742 nm, 734 nm, 707 nm, 697 nm respectively.

As shown in Fig. 2, the longitudinal absorption peaks of the gold nanorods were 737 nm, 718 nm, 701 nm, 700 nm, 698 nm, 697 nm, 697 nm at 90 °C, corresponding to seven heat treatment time (2 h, 4 h, 8 h, 12 h, 24 h, 36 h, 48 h) respectively. The blue shift occurred more quickly in the first 8 h. After 8 h of thermal treatment the blue shift tended to stop. In addition, no significant variation were observed on the shape and the peak width of the longitudinal absorption band at different times of thermal treatment, so the gold nanorods can be considered as uniformly deformed.