Plasma resonance ultraviolet absorption spectroscopy of gold nanorods

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Abstract. Au nanorods were prepared by seed growth method. Based on the local surface plasmon resonance (SPR) absorption spectra of gold nanoparticles, the formation and growth kinetics of gold nanorods were observed and studied in real time. The effects of temperature and reaction time on the growth process of gold nanorods were emphatically investigated. It was found that the shift of SPR UV-vis absorption peak was closely related to the experimental conditions. The influence factors and mechanism of SPR absorption peak shift are discussed. It is concluded that the moving direction of SPR peak is the result of the competition of particle size and charge transfer.

1. Introduction

Gold nanostructures have attracted much attention due to their unique physical and chemical properties. Due to size effect, surface effect, quantum size effect and quantum tunneling effect [1], metal nanoparticles have unique physical and chemical properties [2]. The macrostructure of gold nanorods is divided into two parts: transverse and longitudinal. The transverse surface plasmon resonance absorption peak (TSPR) and longitudinal surface plasmon resonance (LSPR) are shown in the UV Vis absorption spectrum. The ratio of length to diameter of absorption peak is the ratio of absorbance values of longitudinal and transverse parts [3]. Because the length diameter ratio, short diameter, long diameter and distribution range of gold nanorods can be adjusted, they have important application value in optical materials [4], electrochemical sensors, photochemical sensors [5], biosensors [1], biomedical imaging [6], cancer diagnosis and treatment [7], drug delivery [8] and medicine [9].

For most metals, such as tin, mercury, lead, cadmium, indium and so on, the LSPR spectrum peaks are located in the ultraviolet region, so the nanoparticles have no obvious color, and these metal nanoparticles are easy to be oxidized, so it is difficult to study the surface plasmon resonance (SPR) characteristics. However, gold and silver nanoparticles [10] are stable in air, and their LSPR frequency is usually in the visible region, which is suitable for in-depth research in biological analysis [11], optical sensing and physical optics.

Gold nanorods were synthesized by photochemical method [12]. The reaction process was accelerated by irradiation reaction solution containing gold precursor, surfactant and mild reducing agent. The effects of irradiation parameters on the morphology of gold nanorods were studied by UV Vis absorption spectroscopy and transmission electron microscopy. In particular, a wide range of gold nanorods can be prepared by controlling the ultraviolet irradiance (irradiation power per unit area) and
irradiation time [13]. With the increase of irradiation power, the length and diameter of gold nanorods decrease, resulting in smaller gold nanorods. With the decrease of the size of the two axes, the aspect ratio of the gold nanorods increases. Gold nanorods have two plasmon resonance (SPR) Absorption band: transverse SPR absorption peak and longitudinal SPR absorption peak, in which the position of longitudinal SPR absorption peak can be gradually red shifted with the increase of length diameter ratio. The tunability of SPR makes gold nanorod be a good SERS substrate, because according to the electromagnetic field enhancement mechanism of SERS, when the excitation and SPR resonance can maximize the enhancement function of single nanoparticles [14] The purpose of this paper is to study the change of SPR with the change of absorption spectrum.

2. Experimental part

2.1 experimental reagents and instruments

Main reagents: cetyltrimethylammonium bromide, chloroauric acid, sodium borohydride, silver nitrate, hydrochloric acid, ascorbic acid and water used in the experiment are all deionized water.

Main instruments: constant temperature magnetic stirrer, centrifuge, spectrometer, electron microscope, magneton immersed in aqua regia (HNO₃ and HCl, volume ratio 1:3), glass container immersed in alkaline solution, and the inner wall was cleaned with deionized water for many times.

2.2 Preparation of gold seed solution

Au nanorods were synthesized by seed growth method [15,16]. Take a 50 mL small beaker, measure 10 mL of deionized water in a measuring cylinder, use an electronic balance to weigh 0.3644 g CTAB into the small beaker, put the magneton gently, stir in the water bath on the magnetic stirrer, constant 27 °C, 350 r / min, fully mix and stir to prepare the solution.

Figure. 1 flow chart of seed solution preparation

0.0015132 g sodium borohydride solid powder was weighed and transferred to a 4mL centrifugal tube, and deionized water was added to the volume quickly to prepare 0.01 mol/L sodium borohydride solution; 20 mL and 10 mmol/L chloroauric acid solution were prepared in advance and put into the refrigerator for standby. After full melting, the solution is clear and transparent. Stop stirring. Use a pipette gun to quickly take out 250 uL chloroauric acid solution and 600 uL sodium borohydride solution to add to CTAB solution. The color of the solution turns yellow brown. Adjust the rotating speed to 150 r/min. seal the beaker with plastic film . After stirring for one hour, stop stirring and stand for two hours to get the yellow brown gold seed solution for standby. Flow chart  is as follows in Figure 1.

2.3 preparation of gold growth environment solution

100 mL of deionized water and 3.644 g CTAB were added into a 300 mL beaker, gently put the magneton into the beaker, stirred in the water bath on the magnetic stirrer, constant 27 °C, 350 r/min, fully mixed to prepare Au growth solution [17]. Transfer 0.0068 g silver nitrate solid powder into 4 mL centrifuge tube, and quickly add deionized water to constant volume to prepare 10 mmol/L silver nitrate solution, 0.0704 g ascorbic acid solid powder and transfer it to 4 mL centrifuge tube, add deionized water to constant volume quickly to prepare 0.1 mol/L ascorbic acid solution; using pipette gun to suck 507 uL, 37% hydrochloric acid into 4 mL centrifuge tube, and quickly add deionized water to make up 0.1 mol/L ascorbic acid solution. Add deionized water to constant volume and prepare 1 mmol / L hydrochloric acid solution. After CTAB in the beaker is completely melted, the solution is clear and transparent. Use a pipette gun to suck out 5 mL of chloroauric acid (the solution
turns yellow), 1mL of silver nitrate, 2 mL of hydrochloric acid, 800 uL of ascorbic acid (the yellow solution turns colorless immediately) and 240 uL of gold seed solution prepared in the first step (the color of the solution turns blue and purple). The gun head should be replaced every time the liquid is aspirated to prevent contamination of the liquid Stir at constant temperature for 2 hours. Put the final solution into a 50 mL centrifuge tube (6-8 centrifuge tubes, about 40 mL liquid) and centrifuge for 12 min at the speed of 8000 r/min. the supernatant of the first centrifugation is poured into a beaker, and the centrifuged sediment is transferred to a 5 mL centrifuge tube. The supernatant of the above centrifugation continues to be centrifuged, and the supernatant is poured into the waste liquid barrel, and the precipitate is transferred to a 5 mL centrifuge tube. This was repeated twice. The 5 mL centrifuge tube was separated by adding water, the supernatant was poured into the waste tank, and the precipitate was washed and centrifuged, and repeated for 3 times. Remove the impurities such as CTAB, seal the product and paste the note for use.

Figure. 2 configuration process flow chart of growth solution

Five groups were measured in parallel experiment. The control variable method was used to change the temperature (27 ℃, 30 ℃, 35 ℃, 40 ℃, 45 ℃), and other conditions were taken as dependent variables and remained unchanged. We can see with the naked eye that the higher the temperature, the darker the color. Flow chart is as follows in Figure2.

3. Discussion and analysis

In the early stage, the gold nanorod solution was sampled every five minutes, 1mL each time, for two hours; in the later stage, every 10 minutes, 1mL of gold nanorod solution was determined. In the experiment, the sample was moved to the sample pool and deionized water was used as the base layer, and the baseline remained unchanged during the test [3]. After comparing the five groups of experiments, it was found that the curve trend was basically the same, and the UV visible absorption was basically the same It can be reflected in the spectrogram, such as the UV-Vis absorption spectrum of reaction at 45 ℃ for 150 min, and the scanning range is 400 nm-900 nm. The transverse and longitudinal plasma resonance absorption peaks at 514 nm and 779 nm, respectively. Moreover, the longitudinal plasmon resonance absorption peak is "thin tip", and the length diameter ratio is about 2.524, which indicates that the gold nanorods have high yield and uniform particle size [3]. The UV Vis Spectrum Figure 3 is shown below.

Figure. 3 UV Vis spectroscopic analysis of gold nanorods

The average size and shape of the nanoparticles were characterized by TEM. The TEM images of at least 100 nanorods were measured with images, and the size distribution of the nanorods was obtained. The gold nanorods basically kept a relatively uniform shape and became short rods. It can be seen from the figure that with the increase of temperature, the shape of gold nanorods will gradually change
from rod like to spherical particles [2]. It can be inferred that the growth process of gold nanorods by CTAB seed growth method is basically uniform [1]. TEM spectrum analysis is as follows in Figure 4.

HAuCl₄ in the solution is instantaneously reduced to a large number of Au atoms under the action of strong reducing agent NaBH₄. Au atoms combine rapidly to form Au Au bonds with low energy. With the continuous combination of Au, gold nano baseball is gradually formed. Due to the existence of a large number of CTAB in the solution, the hydrophilic end of CTAB is bound to the gold nanoball and evenly distributed on the surface of the nanospheres. At the same time, because CTAB is distributed on the nanospheres, it can effectively prevent the collision between the nanospheres to form nanoparticles, and the Au atom can smoothly combine with the nanospheres through the CTAB molecular gap. Therefore, the nanospheres continue to grow and the size is about 3 nm.

The weak reducing agent in the growth solution can reduce HAuCl₄ to form Au atoms. After adding gold seeds, the crystal nucleus is provided. Au atoms can easily pass through the CTAB bimolecular layer on the surface of gold seeds and combine with gold seeds. Due to the slow reduction of Au atoms, after the Au atoms contact with the gold seeds, they first form ellipses arranged tightly, and the ctabs at the front and two ends are open. Au atoms continue to combine with gold seeds from both ends to form gold nanorods [3].

As shown in Figure 5, a, b, c, d and e are the gold nanorods synthesized at 27 °C, 30 °C, 35 °C, 40 °C and 45 °C, respectively. It can be seen from the figure that there are two directions of surface plasmon resonance absorption peaks of gold nanorods. The transverse plasma resonance absorption peaks of five kinds of gold nanorods are at 514 nm. However, the longitudinal plasma resonance absorption peaks of five kinds of gold nanorods are at 884 nm, 868 nm, 868 nm, 779 nm and 779 nm respectively. With the increase of temperature, the longitudinal plasma resonance of gold nanorods is observed The blue shift of the absorption peak occurs [1], and the absorbance gradually decreases, indicating that the number of gold nanorods decreases [2]. As the higher the position of the longitudinal absorption peak of the gold nanorods, the aspect ratio of the gold nanorods increases, which is independent of the size and length of the gold nanorods [3]. It can be
concluded that the aspect ratio of the five kinds of gold nanorods decreases with the increase of temperature in a certain range. Because the transverse absorption peaks of the five gold nanorods are all the same, the broadband of the five gold nanorods prepared is the same [1]. Therefore, we can adjust the temperature and control the length of gold nanorods.

Figure 6 shows the UV absorption spectra of the samples at 27 °C for 5 min, 60 min, 120 min and 150 min, respectively. It can be seen from the figure that with the reaction going on, the longer the reaction time, the more obvious the peak value. From 5 min, no gold nanorod was formed. From 150 min, the transverse peak appeared at 510 nm, and the longitudinal peak appeared at 893 nm. The aspect ratio was 4.105.

Figure 7 shows the UV absorption spectra of the samples at 45 °C for 5 min, 60 min, 120 min and 150 min, respectively. It can be seen from the figure that with the reaction going on, the longer the reaction time, the more obvious the peak value. From 5 min, no gold nanorod was formed, no longitudinal and transverse peak was found. The transverse peak appeared at 514 nm, and the longitudinal peak appeared at 779 nm. The aspect ratio was 2.524.
Figure 8 shows the variation of transverse and longitudinal characteristic absorption peaks with time during the growth of gold nanorods at 45 °C. It can be clearly seen from the figure that the transverse characteristic absorption peak has no obvious change, and the longitudinal absorption peak has a blue shift.

4. Conclusion
Gold nanorods with different aspect ratios were prepared by seed growth method at different temperatures. The prepared gold nanorods were observed by ultraviolet visible spectrophotometer and transmission electron microscope. Gold nanorods with different aspect ratios were prepared by a simple and efficient seed growth method. The yield of gold nanorods was over 90% by UV visible spectroscopy and TEM characterization. The results show that the gold nanorods have high consistency, uniform size and morphology. The effects of temperature and reaction time on the size of gold nanorods were discussed. We can control the size of gold nanorods simply and efficiently by adjusting the temperature change.

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