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ARTICLE

Facile Synthesis and Spectral Properties of Aged Gold Colloids

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Abstract: The present paper described the spectra properties of aged gold colloids, which were synthesized by only adding NaOH to the chloroauric acid and hexadecyl trimethyl ammonium bromide (CTAB) mixture solution. The formation mechanism for the gold nanoparticles (AuNPs) was discussed based on the Fourier transform infrared spectroscopy (FTIR) analysis. The gold colloids with different amounts of NaOH were aged for three months and then characterized by UV-Vis spectrometer and transmission electron microscopy (TEM). Moreover, surface-enhanced Raman scattering (SERS) spectra of methylene blue (MB) on the three months aged gold colloids were obtained. UV-Vis spectrometer showed the broadening of plasmon absorption peak of three months aged gold colloids. And an explanation for the broadening changes was provided in the as-prepared samples. TEM images demonstrate that the diameter and shape change of the AuNPs depend on addition difference NaOH at the stage of the synthesis, and the NaOH also affect the aging process. The corresponding SERS spectra on the aged three months gold colloid display the size/shape-dependent properties. Therefore, we expect that the aged colloidal gold will be developed and applied in biochemical analysis field.

Key words: gold nanoparticles; colloids; aging process; surface-enhanced raman scattering (SERS)

Gold nanoparticles (AuNPs) play important roles in many fields. For example, they have been widely exploited for use in surface enhanced Raman scattering (SERS)[1,2], imaging and sensing[3], biological probes[4], photothermal effects[5] and catalysis[6,7]. The extensively used procedures to prepare AuNPs in aqueous solutions were reduction of ionic gold by adding a reductant such as sodium citrate, sodium borohydride, ascorbic acid, and tannicacid[8]. Recently, synthesis of AuNPs without the use of extra reducing agents or templates have excited great interest among materials and chemical researchers. Zhou and co-workers[9] reported the synthesis of extremely stable size-controlled AuNPs in the presence of polyvinylpyrrolidone (PVP) without the use of extra reducing agent. Huang and co-workers[10] described a surfactant-promoted reductive route for the shape-controlled synthesis of gold nanostructures by hydrothermal treatment of chloroauric acid in the presence of the surfactant CTAB without using extra reducing agent. Since CTAB molecules promoted reduction of Au^{III} to Au^{0} involving in these researches need strict conditions, we can develop a simpler and more facile method to AuNPs synthesis and its scope of application could be further expanded by studying the optical properties.

Our group has published a paper on preparation and characterization of AuNPs without extra reducing agent by adding different amounts of NaOH to CTAB and $HAuCl_4$ mixture solution at room temperature[11]. Consequently, here we would like to study the spectra properties of aged gold colloids. The various spectra of colloidal solution were determined after aging for a period of three months. In addition, the aged gold colloids with adding different amounts of NaOH have been applied in SERS analysis with methylene blue (MB) as a probe molecule. The SERS

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spectra of MB acquired and indicated that enhancement effect of Au colloids has relation with size and shape. The aged colloidal gold could be explored and applied in the biochemical analysis field.

1 Experiment

Chloroauric acid ($HAuCl_4 \cdot 4H_2O$, Au>47.8%) was obtained from Shanghai Chemical Reagent Co., Ltd. Cetyl trimethyl ammonium bromide (CTAB, 99%) was supplied by Tianjin Kemiou Chemical Reagent Co. Ltd. Sodium hydroxide (NaOH, 96%) was purchased from Guangzhou Chemical Reagent Factory. All chemicals were of analytical reagent grade and used without further purification. 18.2 MΩ·cm E-pure water was used throughout the experiments. Then colloids were prepared according to the reported procedure[11]. Briefly, an amount of NaOH (1 mol/L) was added to 10 mL of CTAB and $HAuCl_4$ mixture solution with vigorous stirring. The mixed solution was continuously stirred for 24 h until the formation of light red solution. The morphologies and sizes of nanoparticles varied with changing the addition of the NaOH solution in the reaction system. All colloidal solutions were covered away from light and aged for three months at room temperature. Next, the AuNPs were collected for spectra analysis and characterization.

FT-IR spectra were recorded at room temperature using a Bruker Equinox 55 spectrometer equipped with a DTGS detector, operating in the spectral range 400~2000 cm^{-1} with a resolution of 4 cm^{-1}. The UV-Vis spectra of aged colloid solution were recorded using a UV–Vis spectrophotometer (SHIMADZU UV-2550) in a 1 cm optical path quartz cuvette. The size distribution and morphology of the nanoparticles were examined by TEM. TEM observations were carried out on a PHILIPS TECNAL-10 electron microscope operating at 100 kV. Raman spectra were recorded between 200 and 2000 cm^{-1} and used a 785 nm (40 mW) excitation Raman spectrometer (Advantage Raman Series, DeltaNu). Normal Raman measurements of 0.1 mol/L MB solution were carried out at room temperature and the accumulation time were 20 s. For SERS measurements, the sample was prepared by adding 10 μL of 50 mmol/L aqueous solution of MB to 1 mL aged gold colloid into a 1 mL glass cuvette. The measurements were started after MB and colloids were mixed uniformly in ambient environment with integration time of 5 s.

2 Results and Discussion

2.1 Formation of AuNPs

AuNPs were synthesized by a two-step procedure. The first step involves the reaction between OH^- and $AuCl_4^-$, Br^- and $AuCl_4^-$, and the second step involves the reduction of Au^{III} using CTAB molecular. Firstly, the chloroauric acid anion ($[AuCl_4]^-$) undergoes the hydrolysis reaction in water to form six major species of the general form $[AuCl_{4-x}(OH)_x]^-$ (x=0~4)[12,13]. While the gold-halide complexes anions of the form $[AuX_4]^-$ (X = F, Cl, Br, I) with a decreased stability of the series (I > Br > Cl >>F)[14]. The exchange of Cl^- in $[AuCl_{4-x}(OH)_x]^-$ (x=0~4) with Br^- takes place simultaneously. So $[AuBr_{4-x}(OH)_x]^-$ and $[AuCl_{4-x}(OH)_x]^-$ coexist in the $HAuCl_4$ and CTAB mixed aqueous solution (Eqs. 1 and 2)[11]. However, it is well-known that surfactant molecules self-assemble into aggregates in aqueous solution above the so-called critical micelle concentration (CMC). In this study, the CTAB concentration was 5 mmol/L, and the aggregates were generally spherical-like micelles[15,16]. Adding a certain amount of NaOH solution, the counterion Br^- in CTAB is replaced by nucleophilic OH^- and CTAB was thus transformed to cetyl trimethyl ammonium hydroxide (CTAOH) in second step (Eq.3)[17,18]. $[AuBr_2(OH)_2]^-$, $[AuBr(OH)_3]^-$, even $[Au(OH)_4]^-$ will dominate in the solution for higher pH value. And then the ligands of OH^- in CTAOH and OH^- ligands in $[AuBr_{4-x}(OH)_x]^-$ are bonded together in spherical-like micelles. The Au-O-CTA (substitute) complexes are formed by the dehydration reaction (Eq. 4), just like the growth unit model of oxide crystals proposed by Zhong et al.[19,20]. After this initial nucleation, the complexes function as seeds and increase with time until the formation of AuNPs. The entire process is in accordance with the nucleation-growth pathway[21]. Then, the colloidal gold solution was stood up for the stage of aging.

The CTA (substitute)-capped AuNPs was analyzed firstly by FTIR measurements. It can be seen from Fig.1 that the rocking mode of the methylene chain ($(CH_2)_n$, n > 4) is detected at 725 cm^{-1}, the C-N^+ stretching bands are found at 910 and 962 cm^{-1}, the asymmetric and symmetric C-H scissoring vibrations of CH_3-N^+ moiety is observed at 1405 and 1465 cm^{-1}, and the H-O-H bend mode is detected at 1639 cm^{-1}[11, 18, 22]. Those peaks are observed at both pure CTAB and CTA-capped AuNPs. The new bands of CTA-capped AuNPs at 603 and 848 cm^{-1} are considered as Au-O and N-O stretching vibrations[23], the protons at α-CH_2 and β-CH_2 methylene of CTA radical could be affected by the near-field effect or surface effect of AuNPs for the interaction of hydrophilic headgroups of CTAB molecules and AuNPs surface. The results are significantly different from the previous report [11]. But these analyses are more sufficient to convince the reaction of CTA-capped AuNPs synthesis than the previous ones. All of the reaction equations for the formation of AuNPs are as follows.

$$AuCl_4^- + xOH^- \rightarrow [AuCl_{4-x}(OH)_x]^- + xCl^- \quad (1)$$

$$[AuCl_{4-x}(OH)_x]^- + (4-x)Br^- \rightarrow [AuBr_{4-x}(OH)_x]^- + (4-x)Cl^- \quad (2)$$