

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 tannic acid^[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 Au⁰ 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 HAuCl₄ 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 ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, $\text{Au} > 47.8\%$) 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. $18.2 \text{ M}\Omega \cdot \text{cm}$ 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 $400\text{--}2000 \text{ cm}^{-1}$ 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 $10 \mu\text{L}$ 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.

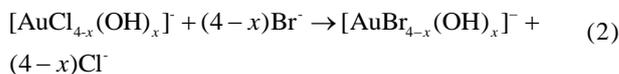
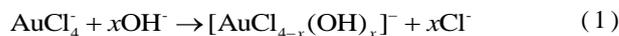
2 Results and Discussion

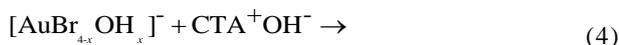
2.1 Formation of AuNPs

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 ($[\text{AuCl}_4]^-$) undergoes the hydrolysis reaction in water

to form six major species of the general form $[\text{AuCl}_{4-x}(\text{OH})_x]^-$ ($x=0\text{--}4$)^[12,13]. While the gold-halide complexes anions of the form $[\text{AuX}_4]^-$ ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$) with a decreased stability of the series ($\text{I} > \text{Br} > \text{Cl} \gg \text{F}$)^[14]. The exchange of Cl^- in $[\text{AuCl}_{4-x}(\text{OH})_x]^-$ ($x=0\text{--}4$) with Br^- takes place simultaneously. So $[\text{AuBr}_{4-x}(\text{OH})_x]^-$ and $[\text{AuCl}_{4-x}(\text{OH})_x]^-$ 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]. $[\text{AuBr}_2(\text{OH})_2]^-$, $[\text{AuBr}(\text{OH})_3]^-$, even $[\text{Au}(\text{OH})_4]^-$ will dominate in the solution for higher pH value. And then the ligands of OH^- in CTAOH and OH^- ligands in $[\text{AuBr}_{4-x}(\text{OH})_x]^-$ 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 ($(\text{CH}_2)_n$, $n > 4$) 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 $\text{CH}_3\text{-N}^+$ 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 $\alpha\text{-CH}_2$ and $\beta\text{-CH}_2$ 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.





2.2 Analysis of UV-Vis spectroscopy

A slight precipitate phenomenon is noticed during the colloidal aging. After three months aging, no further sedimentation of the colloids could be observed with naked eyes, which implies the colloidal solutions reach a relatively stable state. Before analysis of spectral performance, the solutions were shaken evenly. Then, the aged gold colloid was characterized by UV-Vis spectrometer at room temperature. UV-Vis spectra (Fig.2) show gold colloids obtained by [CTAB]=5 mmol/L and [HAuCl₄]=0.25 mmol/L with adding 600 μL of 1 mol/L NaOH, in 10 h, 24 h and three-month aged state. The colloids prepared after 10 and 24 h have the same surface plasma resonance (SPR) peaks at 522 nm (Fig.2). The Full width at half maximum (FWHM) of absorption lines is very similar to 64.5 and 69.5 nm. The two spectra of samples have an almost identical shape, representing the synthesis reaction is almost completed in about 10 h. The maximum absorption peak position shifts from 522 nm to 529 nm after three-month aging, while the FWHM changes noticeably and is broadened to 159 nm with the aged process. Indeed, it is well established that the bandwidth is inversely proportional to the diameter of the gold nanoparticle in the intrinsic size region (mean diameter smaller than 25 nm), indicating smaller size particles in aged colloid^[24]. This phenomenon is related to the size-dependent surface plasmon absorption in metal nanoparticles, which has been studied in detail by El-Sayed et al.^[24, 25], and also confirmed in the subsequent results of TEM observations in this study.

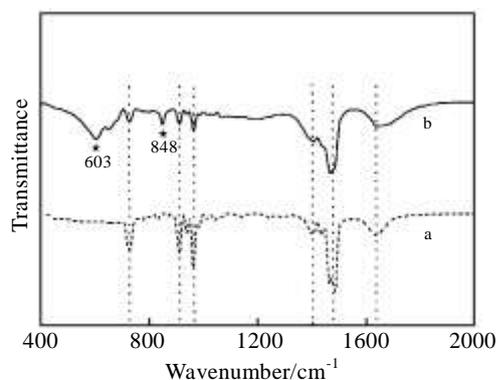


Fig.1 FTIR spectra of pure CTAB (a) and the nanoparticles capped by CTA-substitute (b)

Fig.3 and Fig. 4 show UV-Vis absorption spectra of gold colloids prepared by adding 150 and 25 μL of 1 mol/L NaOH to the CTAB and HAuCl₄ mixture solution, respectively. The plasmon absorption of all prepared colloids is clearly visible. The FWHM of the aged colloid by adding 150 μL of NaOH is also larger than that of colloid prepared after 10 and 24 h, which increases from 55 nm to 98 nm. And the maxima of the plasmon absorption for 10 h and 24 h synthesized colloidal solutions are observed at 522 nm, and gradually shift and increase to 535 nm for the aged sample (Fig.3). The broadening bandwidth implies that the diameter of AuNPs is also gradually decreased in the aging process, because the bandwidth is strongly size-dependent and inversely proportional to the diameter *R* of particles within the range of intrinsic size effects, approximately below *R*=25 nm for Ag or Au^[24,26,27]. Therefore, we can observe the broadening of adsorption peak in the aging gold colloids. These colloids are expected to obtain smaller particles, and the results are confirmed by the followed TEM images.

However, the AuNPs samples synthesized by adding 25 μL of NaOH show an entirely different aging process. In the UV-Vis spectra of the colloids a blue-shift occurs within the first 24 h, followed by a red shift in the period of aging. The peak position changes from 529.5 nm at 10 h to 526 nm at 24 h, and the position of aged colloid is located at 537.5 nm (Fig.4). It is suggested that the synthesis of nanoparticles is a slow process with adding small amounts of NaOH. The large particles (or aggregations) are formed at the first stage and decompose into small particles at the sequence stage. At the aging stage, the small particles grow slightly through the ripening process. The SPR bandwidth of gold nanoparticles increases from 88 nm to 121 nm. Besides, both aged colloids in Fig.3 and Fig.4 exhibit increase of absorption peak intensity, which means the increase of nanoparticle

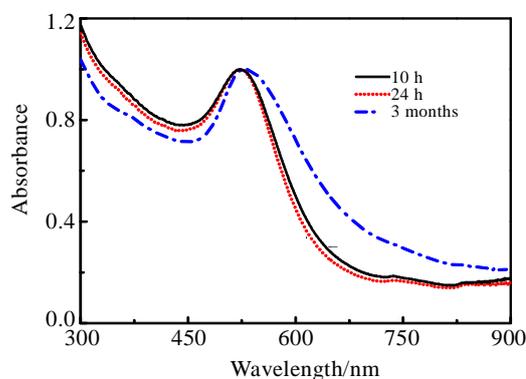


Fig.2 Normalized UV-Vis spectra of gold colloids obtained by [CTAB]=5 mmol/L and [HAuCl₄]=0.25 mmol/L with adding 600 μL of 1 mol/L NaOH, in 10 h, 24 h and three-month aged state

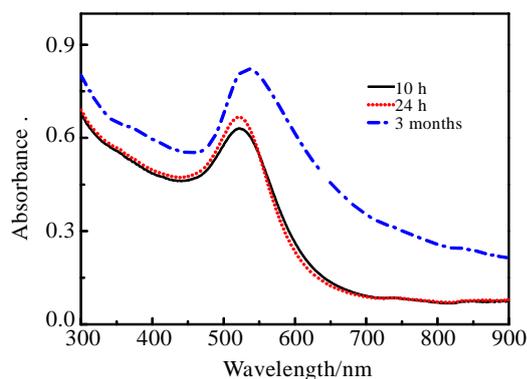


Fig.3 UV-Vis spectra of gold colloids obtained by [CTAB]=5 mmol/L and [HAuCl₄]=0.25 mmol/L with adding 150 μL of 1 mol/L NaOH, in 10 h, 24 h and three-month aged state

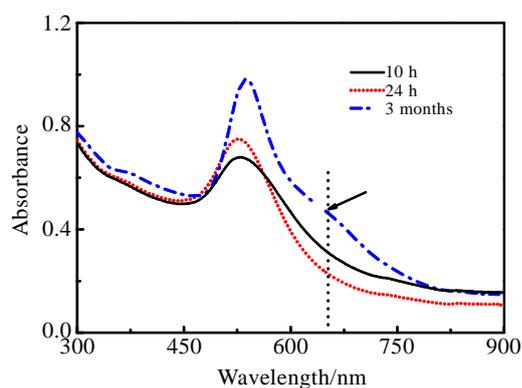


Fig.4 UV-Vis spectra of gold colloids obtained by [CTAB]=5 mmol/L and [HAuCl₄]=0.25 mmol/L with adding 25 μL of 1 mol/L NaOH, in 10 h, 24 h and three-month aged state

concentration^[28]. Meanwhile, a shoulder peak (marked by a dark arrow) at 650 nm is observed. This absorption spectrum indicated the presence of non-spherical nanoparticles in the aged colloidal solution. It may be explained by the TEM image of the aged sample.

2.3 TEM analysis

Fig.5 shows TEM images of three-month aged gold colloids and the inserted images are the fresh gold colloids. The fresh prepared AuNPs was discussed in detail in our previous report^[11]. As for the aged AuNPs, the diameter of the aged AuNPs prepared by adding 600 and 150 μL of NaOH is smaller than that of colloid prepared after 24 h (Fig.5a and 5b). As suggested above, the change of particle size leads to the broadening of

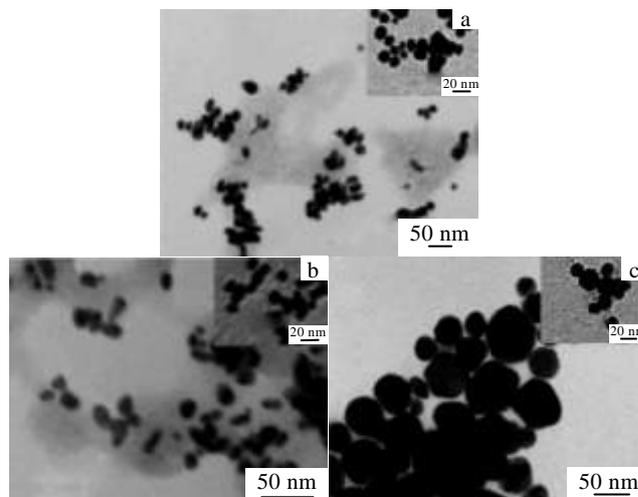


Fig.5 TEM images of aged gold nanoparticles colloids prepared with different amounts of NaOH the inserted are the fresh particles images: (a) 600 μL, (b) 150 μL, (c) 25 μL

plasmon absorption peak. The microscopic mechanisms of colloid aging cause smaller nanoparticles we can consult the earlier report about fabricating nanoparticles by a selective sedimentation of the colloids^[27]. Fig. 5c presents the size distribution of aged gold colloid by adding 25 μL of NaOH. This aged colloid contains more irregular particles and the diameter of AuNPs is increased to around 50 nm (a few over 60 nm). It is well known that the diameters of gold or silver nanoparticle are over 25 nm (extrinsic region), and the SPR bandwidth increases with increase in particle size^[29]. The result suggests that the large anisotropy nanoparticles gradually form during the aging process. In general, coarsening is governed by the growth of larger particles at the expense of smaller particles in the solution-phase synthesis^[30]. Hence, the growth of larger AuNPs is based on this ripening process and promotes the formation of faceted nanoparticles. These nanoparticles may be capable of causing surface enhancement of Raman signals and be used to SERS-active probe.

2.4 SERS activity

To investigate the SERS sensitivity of these aged colloids, the SERS spectra of MB were measured. For comparison, the normal Raman spectrum of 0.1 mol/L MB was also presented. Curves a, b and c in Fig.6 represent the surface-enhanced Raman spectra of aged colloids synthesized by adding 600, 150 and 25 μL of NaOH, respectively. All of the spectra exhibit similar shape,

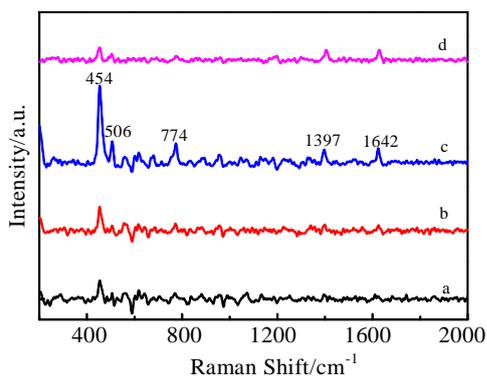


Fig.6 SERS spectra (integration time: 5 s) of MB molecules adsorbed on AuNPs with adding different amounts of NaOH: (a) 600 μL , (b) 150 μL , (c) 25 μL , and (d) Normal Raman spectrum (NRS) of 0.1 mol/L of MB solution (integration time: 20 s)

while the enhanced signal intensities are distinguished from each other. It is well known that SERS effect occurs because of the very strong electromagnetic fields and field gradients available in the so-called “hot spots” of the colloidal nanoparticle cluster^[31]. Hot spots are so important to SERS enhancement performance which are affected by the size, shape, composition, spacing and surface active-site of the nanoparticles. Simultaneously, the SERS signal intensities are proportional to the Raman cross section of the adsorbed molecule, the excitation laser intensity, and the number of molecules. In this paper, the size and shape of nanoparticles are the two major aspects to be considered. Fig.5 shows that the anisotropic and larger nanoparticles are synthesized by adding a fewer amount of NaOH. And it can be seen in Fig. 5c that the maximum diameter of the nanoparticles is about 64 nm. According to previous reports, the irregular metal nanoparticles can induce stronger SERS enhancement, and 60 nm colloidal Au particles can obtain the most intense SERS spectra signal in the size range of 20~100 nm^[32,33]. Hence, the aged gold colloid by adding 25 μL of NaOH achieves the largest enhancement effect. These frequencies and intensities of SERS bands are different from that of the normal Raman (curve d in Fig.6). And all the observed peaks are assigned. In normal Raman the most intense bands are observed at 453, 1405 and 1628 cm^{-1} due to C-S-C skeletal bending, C-N stretching and C-C stretching band, respectively. In SERS, the intense bands are obviously observed at 454, 506, 774, 1397 and 1621 cm^{-1} . The bands at 506 and 774 cm^{-1} are assigned to C-N-C skeletal bending and C-H out-of-plane bending,

respectively. The C-S-C skeletal bending, C-N stretching and C-C stretching band are shifted to 454, 1397 and 1621 cm^{-1} , respectively^[34, 35]. According to the “surface selection rules” for the interpretation of SERS data on the orientation of adsorbed molecule relation to the metal surface^[36], it is estimated that MB molecules adopt a parallel orientation on the gold nanoparticles surface. From this viewpoint, the relative intensities of bands at 454 and 506 cm^{-1} of all spectra are the largest.

3 Conclusions

- 1) Aged gold colloids are synthesized by alkaline HAuCl_4 and CTAB mixture solution.
- 2) Adding a small quantity of NaOH promotes the formation of irregular nanoparticles during the aging process. All the aged gold colloids show broadening of plasmon absorption peaks in UV-Vis spectra.
- 3) Additionally, the irregular nanoparticles of the aged colloid present enormous SERS activity and should be an ideal system for application in SERS probe and sensor.

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陈化胶体金的简便合成与光谱特性

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摘要: 描述了通过只添加氢氧化钠到氯金酸和十六烷基三甲基溴化铵混合液中合成陈化纳米金胶体, 并研究了该胶体的光谱特性。基于傅里叶红外光谱对纳米金的形成机理进行了分析并以紫外可见光谱和扫描电子显微镜表征了添加不同量的氢氧化钠而获得的陈化3 m的胶体金。同时获得了吸附于陈化了3 m的胶体金表面上的亚甲基蓝的表面增强拉曼光谱。结果表明, 陈化3 m的胶体金其紫外可见光谱具有宽的等离子吸收峰, 对这种宽化改变进行了解释分析。其透射电子显微镜分析表明在纳米金合成阶段, 添加不同量的氢氧化钠可影响纳米金大小, 同时不同量的氢氧化钠影响着胶体金的陈化过程并产生出形状依赖的陈化胶体金。表面增强拉曼光谱的增强特性不同证明了所形成的陈化胶体金的大小/形状依赖特征。因此, 我们期望着这种陈化胶体金能够在生化分析领域被得到开发应用。

关键词: 纳米金; 胶体; 陈化过程; 表面增强拉曼散射

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