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Preparation and characterization of gold nanoparticles using ascorbic acid as reducing agent in reverse micelles

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Abstract In this study, well-dispersed gold nanoparticles were prepared by the reduction of $HAuCl_4$ in sodium bis (2-ethylhexyl)sulfosuccinate/isooctane reverse micelles system using ascorbic acid as reducing agent. The properties of the obtained nanoparticles were characterized with transmission electron microscopy, X-ray diffraction, thermogravimetric analysis, and UV–vis absorption spectrophotometer. Due to its high water solubility, biodegradability, and low toxicity, ascorbic acid could be used as a benign naturally available reducing agent to synthesize gold nanoparticles.

Introduction

Nanoparticles of metals have attracted worldwide research interests during the recent years, and the preparation and characterization of those particles with nanometer-sized dimensions have become an important aspect of materials research [1]. The extremely small size, large surface-to-volume ratio, and the increased surface activity of those nanoparticles have made them applicable to a widespread range of chemical and physical aspects [2]. Gold nanoparticles have widely been paid attention due to their application potential in catalysis, electrical conductivity, optical properties etc. [3]. These applications are strongly dependent on the size and shape of the gold nanoparticles. Therefore, the synthesis of controlled size of nanoparticles could be potentially important for these applications [4]. In order to prepare high monodispersity and controlled size nanoparticles, an important issue is to achieve protection of the particles, which avoid aggregation without disturbing the desired properties, when dealing with those particles [5]. As for the preparation of gold nanoparticles, many synthetic methods have been developed to form and to stabilize gold nanoparticles among which reverse micelles are one of the appropriate methods undoubtedly [6].

As an influential part of organism, ascorbic acid is a vitamin participating in several biochemical reactions among which antioxidant effect is its one of the best-known biological functions [7]. Due to its high water solubility, biodegradability, and low toxicity compared with other chemical reducing agent such as $NaBH_4$, ascorbic acid was used as reducing agent to synthesize metal nanoparticles. There have been a few reports about the reduction of metallic ions to be metal nanoparticles using ascorbic acid as weakly reducing reagent in aqueous solution. For example, Varma et al. reported that bimetallic nanoparticles with a core-shell structure have been synthesized in aqueous solution by using benign naturally available antioxidant ascorbic acid. Products form in a few seconds to afford different shapes and sizes through utilized various core and shell materials. Au–Cu core-shell structure formed regular spherical particles and the scope of particle size was in the range of 5–50 nm. Their investigated results indicated that the synthetical core-shell particles structure exhibited well degree of surface coverage and the morphology of the particles is uniform through using ascorbic acid [8, 9]. But preparation of gold nanoparticles in microemulsion system using ascorbic acid is not that well reported in previously literature.

In this research, we proposed the bioreducing agent, ascorbic acid, to synthesize the gold nanoparticles in

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reverse micelles without the addition and introduction of other reducing reagents and protective reagents. Reverse micelles are used as microreactors to form different size of gold nanoparticles because water pool makes this reaction system particularly favorable for the synthesis of nanoparticles and the water pool can be turned by changing the water content [10]. The gold nanoparticles dispersed in this system have a high colloidal stability and a narrow size distribution, and the production obtained are characterized by UV–visible absorption spectrum, X-ray diffraction (XRD), thermogravimetric analysis (TGA), transmission electron microscopy (TEM).

Experimental section

Materials

Sodium bis (2-ethylhexyl)-sulfosuccinate (AOT) was obtained from Acros Orgamics. Isooctane was purchased from Fisher. Chloroauricacid ($HAuCl_4$) was supplied by Aldrich. Ascorbic acid was the guaranteed reagent of Shantou Guanghua chemical reagent corporation. All reagents were used as received without further purification. All solutions were prepared with redistilled water.

The mixed reverse micellar solutions were prepared by injecting the required amounts of the corresponding $HAuCl_4$ aqueous solution into an isooctane solution of AOT, and then were used for the preparation of nanoparticles.

Preparation of gold nanoparticles

Gold nanoparticles were prepared as following: 0.5 M AOT/isooctane reverse micelle was prepared using 0.4631 g AOT and 2 ml isooctane mixed solution and stirred vigorously for 10 min until the solution was transparent without turbidity. About 45 μL 20 mmol/L $HAuCl_4$ aqueous solution and 180 μL redistilled water were introduced into AOT/isooctane reverse micelle system, respectively. Subsequently, 45 μL 0.1 mol/L ascorbic acid aqueous solutions were added dropwise into microemulsion system under vigorous stirring [11]. The molar ratio of water/surfactant ratio (ω_0) was 15. The system was reacted 24 h thoroughly at room temperature under magnetic stirring and aim to make the reaction complete (Scheme 1). Then, ethanol or acetone was introduced into the reverse micelle system include gold particles, this mixture solution was stirred for 5 min in order to centrifuge gold nanoparticles and deposit, the procedure was repeated several times. The resulting precipitate was used for further characterization.

Characterization

Transmission electron microscope was used for the physical characteristics of the gold nanoparticles obtained. Sample for TEM was prepared by placing a drop of gold solution of ultrasonically dispersed products on a copper grid and then dried at room temperature. TEM images were performed using JEM-1200EX operated at an accelerating voltage of 120 kV.

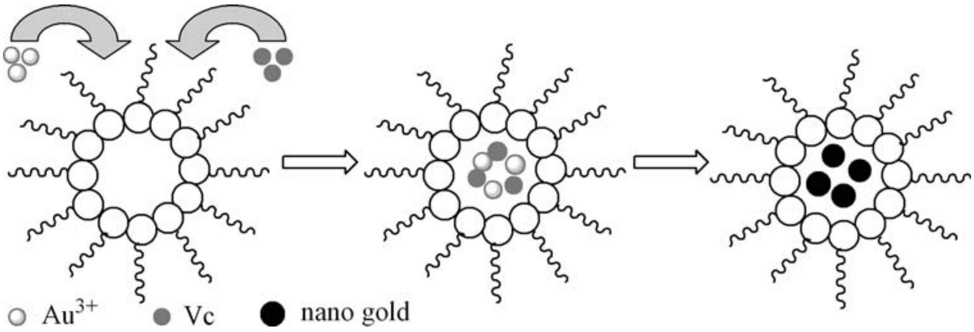
X-ray diffraction analysis of gold nanoparticles were carried on a Phillips X′pert PW 3040/60 instrument at room temperature operating at 40 KV and a current of 40 mA using Cu K α radiation ($\lambda = 0.154178$ nm).

The weight loss behavior of the sample was studied by TGA analysis in the temperature range 30–700 °C at the heating rate of 10 °C/min in N_2 atmosphere.

UV–visible absorption spectra were performed using a commercial TU-1810 spectrophotometer at room temperature with 1 cm optical path length.

Results and discussions

AOT is an interesting surfactant for obtaining reverse micelles due to its compact structure and thermodynamic stability [12, 13]. According to this method, gold nanoparticles were prepared by the reduction of $HAuCl_4$ in this reverse micelle system using ascorbic acid as the reducing agent and different sizes of gold nanoparticles were



Scheme 1 The synthesis procedure of gold nanoparticles in AOT/isooctane reverse micelles

obtained by changing the water/surfactant ratio. The color of microemulsion system was observed from transparent to shallow purple slowly, and the color changes depending on the concentrations of $HAuCl_4$ aqueous solution used. It means that the reduction of total ionic Au^{3+} to atomic Au^0 is accomplished, and thereby gold nanoparticles were formed. The reaction equation of this system is as follow:

$$2[AuCl_4]^- + 3C_6H_8O_6 = 2Au + 8[Cl]^- + 3C_6H_6O_6 + 6[H]^+.$$

In this reaction process, ascorbic acid was converted to gluconic acid, which has non-biological activity; meanwhile, this reaction is an irreversible process. Two important functions were concluded by introducing excessive ascorbic acid solution. First, the reaction of ionic Au^{3+} to atomic Au^0 is completed. Second, it increases the degree of reaction supersaturation and accelerates the speed of formative gold nanoparticles core.

Figure 1 illustrates the examples of TEM micrograph for gold samples prepared as described in the experimental section [14]. The surface morphology of the particles is nearly spherical and the average size of resulting particles is about 5–10 nm. The histogram also indicates that particles between 7 and 8 nm are the dominant distribution according to the statistics results of 213 particles. It clearly indicates that the samples display high disperses and homogeneously prepared via this method [15]. From the micrographs of samples, it can be concluded that AOT/isooctane reverse micelles provide not only as an ideal method for the preparation of metal nanoparticles but also as a favorable stabilizer for metal particles, to prevent further growth and precipitation of nanoparticles core. In fact, some larger particles observed by TEM should be due to the reason of extraction and redispersion process in water after the reaction was completed.

Figure 2 shows the X-ray diffraction patterns of prepared gold nanoparticles. First, the samples were processed at different temperature to decrease the interference from unevaporated water, oil phase, and residual surfactant. A drop-coated film of the sample on glass substrate was used for XRD measurements. The characteristic peaks corresponding to (111), (200), (220), (311) of Au are located at $2\theta = 38.29°$, 44.43°, 64.68°, and 77.62°, respectively. The result, very close to the literature data, indicates that the sample is composed of crystalline gold [16, 17]. As can be seen from Fig. 2, all the peaks become stronger and sharper with the temperature increasing [18]. The reason is that the interferential substance of microemulsion was removed and the crystallinity of gold was improved after the temperature increased. Meanwhile, no impurity peaks were detected, indicating that pure gold products were obtained though the present synthetic method.

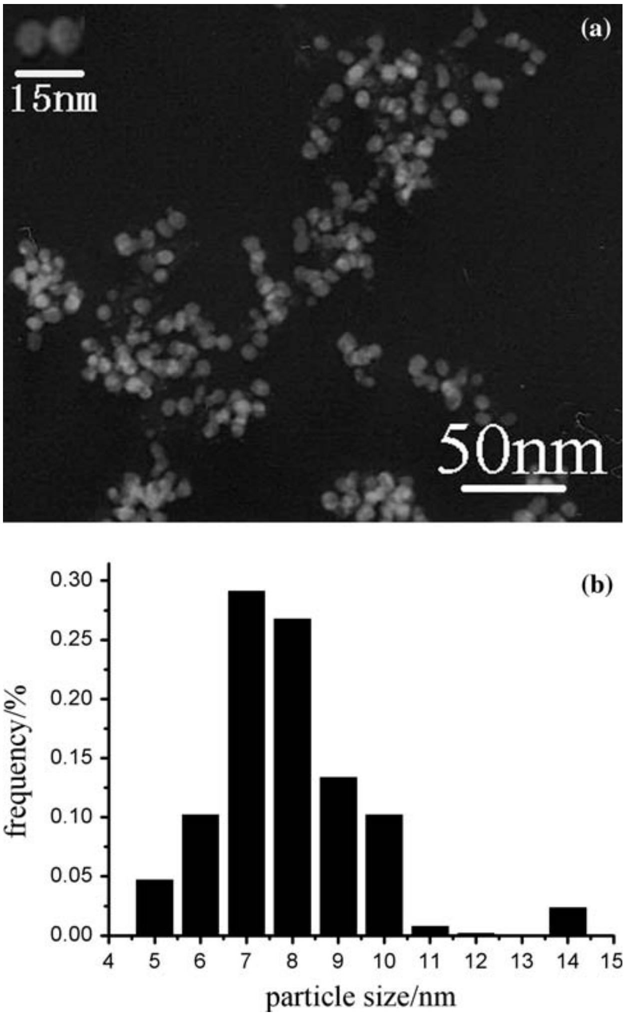


Fig. 1 TEM images of gold particles prepared in AOT reverse micelles and histogram of size distribution according to the statistics results of 213 particles. $[HAuCl_4] = 20 \times 10^{-3}$ M; [ascorbic acid] = 0.1 M; [AOT] = 0.5 M; $[\omega_0] = 15$

The formation of gold nanoparticles was detected by TGA and heated at the heating rate of 10 °C/min in N_2 atmosphere, and the result is shown in Fig. 3. Two peaks are observed in DTA curve. The first broad exothermic peak appears at 35–100 °C, and the second sharp endothermic peak appears at about 220–350 °C. The exothermic peak is due to the loss of oil phase and other solvents, the endothermic peak is considered due to the decomposition of AOT coat on the particles surface. From TG curve, the mass loss condition of the sample can be seen. There are two main mass loss at about 100 °C and 300 °C, respectively. In the temperature range 30–100 °C, the TG curve shows a gradual weight loss of about 5% and in the temperature range 240–300 °C, the TG curve shows a sharp weight loss of 66%. From this data, we can conclude that gold nanoparticles were synthesized in water pool that consists of surfactant AOT. It was difficult to remove the

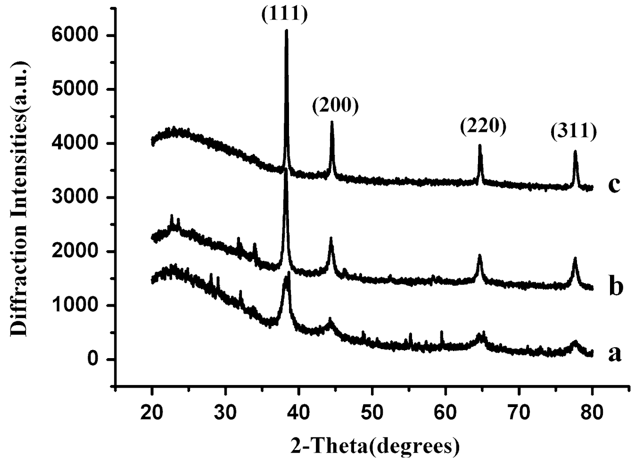


Fig. 2 XRD patterns of gold nanoparticles at different temperature: (a) 100 °C; (b) 200 °C; (c) 500 °C

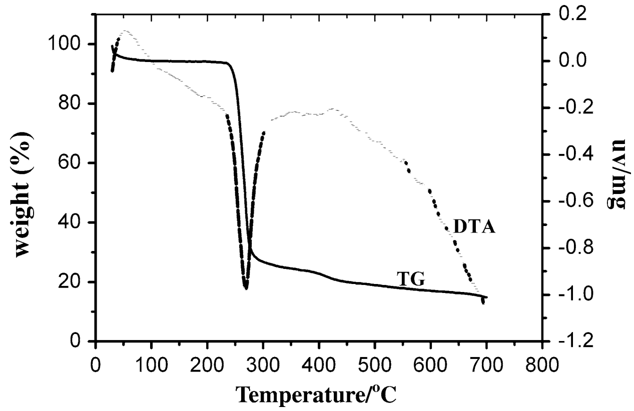


Fig. 3 TG and DTA curve of gold nanoparticles obtained in AOT/isooctane reverse micelles

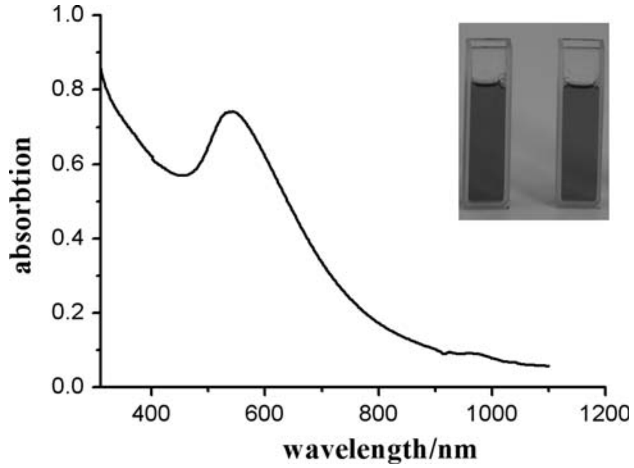


Fig. 4 UV–vis absorption spectra showing characteristic of supported gold nanoparticles. Inset: the color of prepared gold colloid solution

total surfactant coat on the particles surface through mechanical centrifugation. Therefore, the curve indicated that a mass loses because of the decomposition of surfactant coat on the particles surface when the temperature was elevated to 300 °C.

Some previous research reported UV–vis spectrophotometry as an effective method to monitor the evolution of metal species in the synthesis of metal particles [19, 20]. Figure 4 shows the UV–vis absorption spectrum of gold nanoparticles that were prepared with ascorbic acid reduction through reverse micelles. All UV–vis spectra were recorded at room temperature against the same reference sample. A strong absorption peak at approximately 540 nm indicates the formation of gold nanoparticles. It is worthwhile mentioning that $HAuCl_4$ can be reduced to form gold nanoparticles though ascorbic acid, because we have not introduced other reducing reagents in the mix solution. However, a second weak peak can also be seen in the near-IR wavelength in the range of 900–1000 nm, this unexpected result was similar to the shown in Fig. 1, and it indicated that slight aggregation of particles exist in water solution due to the reason of extraction and redispersion process in water after the reaction was completed. The aggregation cannot totally be prevented by the absorption of AOT molecules. Inset shows the color of the as-formed solution and the shallow purple also indicates the formation of gold nanoparticles. At the same time, transparent solution reflects that the size distribution of the nanoparticles is narrow and also indicates that the particles can remain well separated from each other.

It is known that ω_0 value as a size determining important parameter of microemulsion exhibit the considerable effect on the particles synthesis. The optical properties such as the absorption peak position are related to the size of the particles. Figure 5 shows the absorption spectra obtained

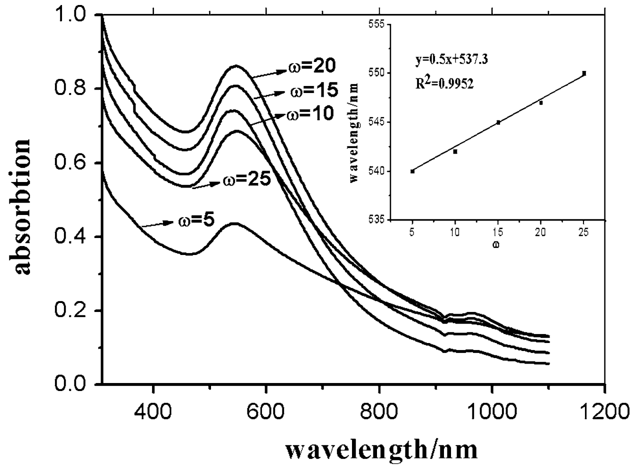


Fig. 5 Comparison of UV–vis spectra with different ω_0 values, and effect of ω_0 on the absorption peak position (inset) in the gold colloids

for gold particles using different water/surfactant ratio. With the increase of $\omega_{0,}$ the synthesis of gold nanoparticles showed different λmax at 540, 542, 545, 547, and 550 nm, respectively, as shown in Fig. 5 (inset). This result indicates that different size of gold nanoparticles was obtained as well as the red shift in surface plasmon absorption peak to vary with increase of gold diameter. It has been well established that the maximum wavelength of nanoparticles strongly depends on size and shape, so this directly corresponds to a shift of the absorption peak, where large gold particle sizes will cause an absorption peak shift to longer wavelengths, lower frequency, and lower energies [21–23].

Conclusion

In summary, the gold nanoparticles were produced directly and simply by reduction of Au(III) with ascorbic acid in AOT/isooctane reversed micelle, which controlled the size of particles. The simple formation mechanism of different size gold particles in this synthesis is considered that water pool with various ω_0 value forms a stable coat on the particles surface, which stops the particle's growth. TEM, XRD, TGA, and UV characterization suggest that gold nanoparticles can be obtained.

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