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Journal of Colloid and Interface Science 309 (2007) 94–98
JOURNAL OF Colloid and Interface Science
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Gram-scale synthesis of aqueous gold colloids stabilized by various ligands

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Received 1 November 2006; accepted 14 December 2006

Available online 3 January 2007

Abstract

We have developed a method for the large-scale synthesis of gold nanoparticles (Au NPs) in an aqueous medium stabilized by various water-soluble ligands. Significantly, the narrow size-distribution of the particles is achieved without employing size-selective procedures. The versatility of the procedure is demonstrated for the preparation of three colloidal systems stabilized by different ligands. Transmission electron microscopy (TEM), ζ-potential measurements and UV–vis spectroscopy are used to characterize the three colloidal systems.

Keywords: Gold nanoparticles; Synthesis; Aqueous medium

1. Introduction

Many applications of gold nanoparticles (Au NPs) require their solubility in an aqueous medium and their stabilization by molecules with various functional groups. Water soluble Au NPs find applications as immunolabeling agents in cytochemistry [1] and as probes in various biomolecule detection schemes [2]. High quality metal NPs in non-aqueous solvents can be prepared by various methods and stabilized by different ligands [3]. In contrast, the reported synthetic methods for metal NPs in an aqueous medium are much less versatile, limited to the use of small number of ligands and require complicated size-selective procedures. The main reason is the electrostatic stabilization that prevails in an aqueous medium leading to the necessity of using different synthetic protocols compared to non-aqueous solvents. The most widely used method for synthesis of metal colloids (mainly Au and Ag) in an aqueous medium is the citrate reduction of metal salts [4]. Such colloids are electrostatically stabilized meaning that the particles are surrounded by an electrical double layer due to adsorbed citrate and chloride anions and the cations attracted to them. An increase of the ionic strength of the medium compresses the double layer and shortens the range of repulsion leading to an irreversible aggregation of the particles [5].

Aqueous Au colloids are usually prepared by a direct synthesis or phase transfer from a non-aqueous medium. Various ligands have been tested for the direct Au NP stabilization in an aqueous medium, such as tiopronin (*N*-2-mercaptopropionyl-glycine) [6], coenzyme A [6], cysteine [7], thionicotineamide [8], mercaptosuccinic acid [9], 4-hydroxyphenol [10], sodium 3-mercaptopropionate [11], glutathione [12], cyclodextrines [13], and polymers [14]. The phase transfer of metallic clusters from an organic solvent to an aqueous medium was first reported by Schmid et al. [15]. Gittins and Caruso [17] proposed an efficient method for a complete transfer of Au NPs from an organic to an aqueous medium using 4-*N*,*N*-dimethylaminopyridine (DMAP) as a phase transfer agent [16]. Dodecylamine-functionalized Au NPs in an organic solvent were transferred to an aqueous medium by a cationic surfactant forming interdigitated bilayers with the dodecylamine molecules on the particle surface.

The development of a method that allows a gram-scale preparation of aqueous metal NPs stabilized by various ligands would be of a major practical interest. Herein, we describe a method for synthesis of gram-scale quantities of aqueous Au NPs using the solvated metal atom dispersion (SMAD) technique. The SMAD method involves vaporization of a metal under vacuum and co-deposition of the atoms with the va-

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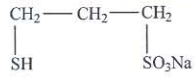
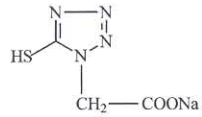
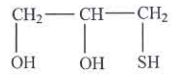
0021-9797/$ – see front matter
doi:10.1016/j.jcis.2006.12.064

Table 1
Water soluble ligands used for the stabilization of Au NPs prepared by the SMAD method in an aqueous medium and the outcome of the experiment in each case. Digestive ripening was carried out for 90 min at reflux under argon atmosphere

Water-soluble ligand	Formula	Outcome	
		'As-prepared' colloid (after acetone evaporation)	After digestive ripening
Sodium 3-mercapto-1-propanesulfonate		Dark brown colloid	Destabilizes upon heating. Stable upon ripening at room T
5-Mercapto-1-tetrazoleacetic acid sodium salt		Orange/red colloid	Destabilizes upon heating. Stable upon ripening at room T
3-Mercapto-1,2-propanediol		Dark brown colloid	Stable purple colloid

pors of a solvent on the walls of a reactor cooled to liquid nitrogen temperature (77 K). Nucleation and growth of the NPs take place during the warm-up stage. The SMAD technique allows synthesis of large amounts of colloidal solutions and obviates the need for any purification procedures. The SMAD method was initially used as a very efficient route to produce highly dispersed metal nanoparticles in an active form [18]. Such materials were not monodisperse but they turned out to be extremely active in many catalytic schemes due to the high degree of dispersion and the lack of stabilizing ligands on their surface [19]. In 2002, we reported the development of a greatly modified SMAD process which utilized a novel combination of solvents and stabilizing ligands, at controlled times and temperatures [20]. The modified SMAD method in combination with the digestive ripening procedure (reflux of the colloid in an excess stabilizing ligand) allowed the preparation of gram-scale quantities of various ligand-stabilized metal (Au, Ag, Cu) NPs with a narrow size distribution in non-aqueous solvents only [20,21]. In the present study, we have extended the capabilities of the SMAD method to synthesize gram-scale quantities of Au NPs in an aqueous medium stabilized by different ligands. Three water-soluble thiol-containing molecules are used as stabilizing ligands, namely sodium 3-mercapto-1-propanesulfonate, 5-mercapto-1-tetrazoleacetic acid sodium salt and 3-mercapto-1,2-propanediol (Table 1). Importantly, the final Au NPs are with a narrow size-distribution without carrying size-selective procedures. We characterize the aqueous Au colloids by transmission electron microscopy (TEM), ζ-potential measurements and UV–vis spectroscopy.

2. Materials and methods

2.1. Preparation of Au–acetone–water–ligand colloid

A stationary reactor described in [18,20] was used for the synthesis of the Au–acetone–water–ligand colloid. Acetone was obtained from Fisher. Acetone was dried over molecular sieve (200 mesh) and degassed five times by the standard freeze-thaw procedure. Ultrapure 18.2 MΩ Millipore water was used throughout the whole experiment. All ligands were purchased from Aldrich and used as received. All glassware was rigorously cleaned first with aqua regia (3 parts HCl, 1 part HNO_3), followed by soaking for 2 h in a base bath (saturated solution of NaOH in 2-propanol) and finally copiously washed with water. *Caution:* both aqua regia and the base bath can cause severe burns and should be handled with care wearing the proper protective clothing and goggles.

Typically, a W–Al_2O_3 crucible was assembled in the SMAD reactor and the whole system was pumped down. This was followed by a step-wise heating of the crucible and the pressure was allowed to reach 4×10^{-3} Torr at each heating step. The crucible was heated to red in about half an hour, then the heating was decreased and the whole reactor was left under vacuum overnight while the crucible was gently heated. This process ensured no contamination of the crucible. After overnight, the reactor was filled with air and the crucible was charged with ~0.1–0.35 g Au metal. At the same time, the desired amount of the ligand (the molar ratio of ligand to Au is ~30:1) was dissolved in 40 mL degassed (by boiling) water and placed in the bottom of the reactor chamber together with a stirring bar. Degassed acetone in a Schlenk tube was attached to the SMAD reactor. The whole system was evacuated and a liquid nitrogen filled Dewar placed around the vessel. The ligand and water were frozen in this way in the bottom of the reactor. When the vacuum reached 4×10^{-3} Torr, Au vapor and acetone (60–80 mL) were co-deposited over a period of 3–4 h. During this time, the pressure was maintained at about 4×10^{-3} Torr. The frozen matrix had a deep red color at the end of the deposition. After the process was complete the liquid nitrogen Dewar was removed and the matrix allowed to warm slowly over a period of ~1 h. During the warm-up process argon gas was allowed to fill the reactor system. Upon melting, the Au–acetone matrix mixed with the water/ligand solution. When the water/ligand solution started to melt, stirring was commenced and the whole solution was agitated for another 45 min. The as-prepared Au–acetone–water–ligand colloid was syphoned under argon into a Schlenk tube.

2.2. Preparation of Au–water–ligand colloid

The Schlenk tube containing the as-prepared Au–acetone–water–ligand colloid was connected to a vacuum line and the acetone was evaporated until a constant 1×10^{-2} Torr pressure was reached (the more volatile acetone was removed along with some of the water). At this time, the Au–water–ligand colloid was diluted to 60–80 mL by the addition of 18.2 MΩ water. Thus, the total volume of the final Au–water–ligand colloid was 60–80 mL containing 0.1–0.35 g of Au.

2.3. Reflux (digestive ripening)

The digestive ripening procedure generally involves heating or refluxing of a Au–solvent–ligand colloid for 90 min under argon atmosphere [20]. For the aqueous systems described here, the digestive ripening step destabilized the colloids when an ionic ligand was used (Table 1). The destabilization of electrostatically stabilized colloidal solutions upon heating is a well-known phenomenon [5].

2.4. Experimental techniques

Transmission electron microscopy (TEM) was performed with a Philips CM 100 operating at 100 kV or with JEM-2010 (JEOL, Japan) at 200 kV accelerating voltage. Samples for TEM were prepared by placing 10 μL drops of the aqueous gold colloids on formvar carbon-coated grids (300 mesh, Electron Microscopy Sciences). After 1–2 min waiting, the excess colloid was removed from the grid by touching with a filter paper.

UV–vis spectra were collected on a Cary 500 Scan spectrophotometer (Varian).

ζ-Potential measurements were performed on a Beckman Coulter, Delsa 440SX ζ-potential analyzer. The measurements were taken by four different lasers set up at various angles (8.9°, 17.6°, 26.3°, 35.2°) through the center of the channel. The reported data was averaged from the similar values obtained by the four lasers and was taken at the 0.16 mm vertical position of the channel. All measurements were performed in the presence of 5×10^{-3} M NaCl.

3. Results and discussion

Preliminary attempts to prepare stable Au colloids using water as a direct solvent in the SMAD process turned out to be unsuccessful. These results are in agreement with the fact that water does not efficiently solvate the metal atoms and clusters rapidly form during the warm-up stage leading to the eventual destabilization of the colloid. Acetone is known to strongly solvate the surface of Au NPs prepared by the SMAD process [18–20]. This fact was the motivation to use acetone as an initial solvent during the SMAD procedure providing preliminary stabilization of the Au particles. A flow diagram of the major synthetic steps is presented in Fig. 1. Upon acetone removal, the thiol-containing ligands provide the stabilization of the Au colloids and ensure the dispersity of the Au NPs in

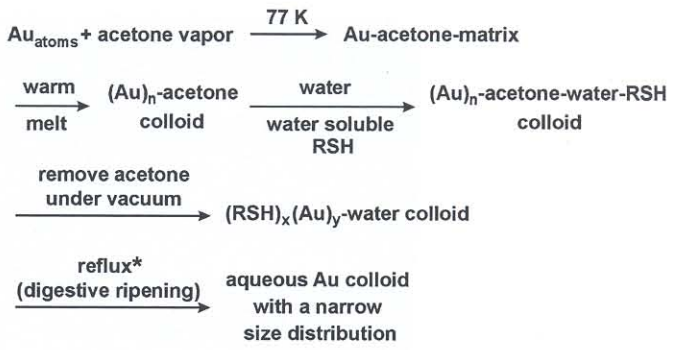


Fig. 1. Synthesis of aqueous Au colloids by the SMAD method.

the aqueous medium. Below, we present the TEM, ζ-potential and UV–vis studies of the Au colloids stabilized by the three water-soluble thiols. The conclusions of the TEM studies are based on the thorough examination of several samples and a representative TEM image is shown in each case. Additional TEM micrographs are provided in the supporting information. In each case, the UV–vis spectra are taken both in the absence of NaCl and in 0.01 M NaCl to validate that the colloids retain their characteristics at the salt concentration used for the ζ-potential measurements (Section 2).

3.1. Au NPs stabilized by sodium 3-mercapto-1-propanesulfonate

The Au NPs stabilized by sodium 3-mercapto-1-propanesulfonate are nearly monodisperse with an average size of 4.2 ± 0.5 nm. A representative TEM image of the particles and the corresponding histogram are shown in Figs. 2A and 2B, respectively. Note that the remarkable narrow size distribution in an aqueous medium is achieved without carrying size-selective procedures. Digestive ripening of the colloids at a reflux leads to their destabilization as expected for aqueous colloids stabilized by ionic molecules [5]. The Au colloids are brown with an absence of a distinctive plasmon absorption peak (Fig. 2C). The absence of a plasmon band was also observed by others in the case of Au nanoparticles in an aqueous medium stabilized by polymers [14b] and other molecules such as tiopronin [6a] and sodium 3-mercaptopropionate [11]. The dumping of the surface plasmon absorption could also result from a strong coordination of the thiol group to the Au surface [11]. The ζ-potential measurements indicate that the Au NPs functionalized with sodium 3-mercapto-1-propanesulfonate are negatively charged with an average ζ-potential value of −23 mV.

3.2. Au NPs stabilized by 5-mercapto-1-tetrazoleacetic acid sodium salt

The Au NPs stabilized by 5-mercapto-1-tetrazoleacetic sodium salt have an average size of 3.4 ± 0.6 nm and a narrow size distribution without size-selective procedures. The representative TEM images in Fig. 3A and Fig. 3S (supporting information) show the uniform shape and size of the Au NPs. The as-

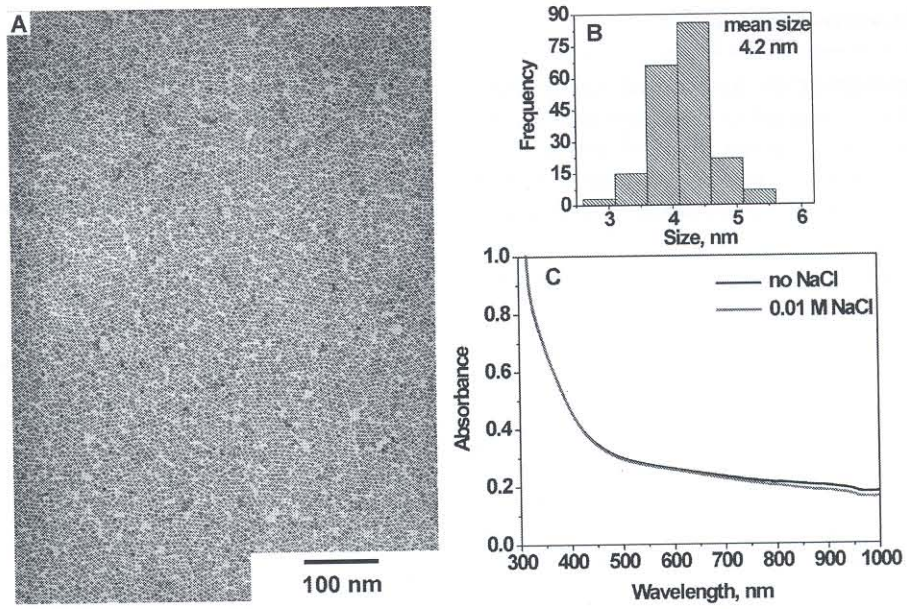


Fig. 2. (A) Representative TEM micrograph and (B) the corresponding histogram from measurement of 200 NPs stabilized by sodium 3-mercapto-1-propanesulfonate. (C) UV–vis spectra at different NaCl concentrations.

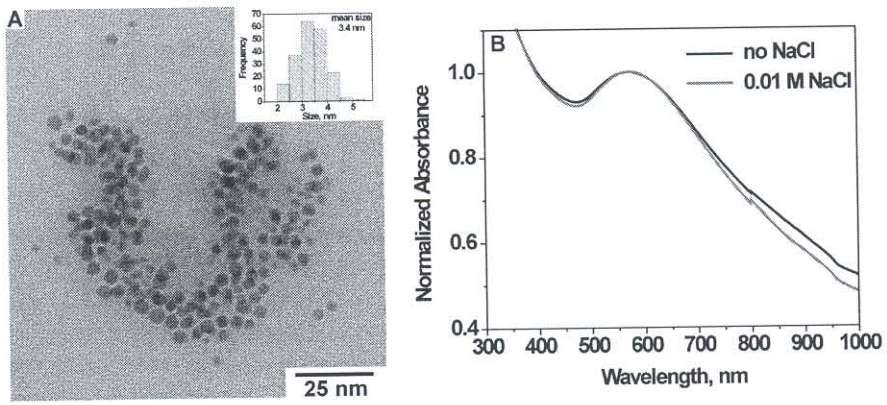


Fig. 3. (A) Representative TEM micrograph and the corresponding histogram (inset) of Au NPs stabilized by 5-mercapto-1-tetrazoleacetic acid sodium salt. The histogram is based on measurement of 200 Au NPs from (A) and Fig. 3S (supporting information). (B) UV–vis spectra at different NaCl concentrations.

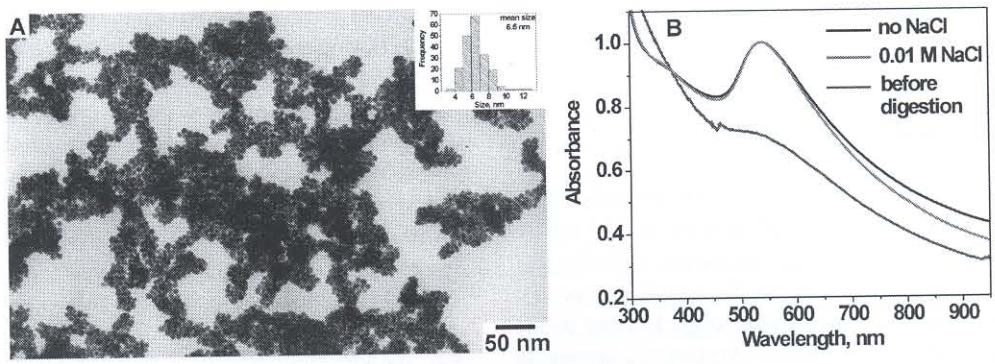


Fig. 4. (A) Representative TEM micrograph and the corresponding histogram (inset) from measurement of 200 Au NPs stabilized by 3-mercapto-1,2-propanediol. (B) UV–vis spectra before digestive ripening and at different NaCl concentrations after digestive ripening.

prepared Au colloids have an orange/red color with a distinctive plasmon absorption band at 570 nm (Fig. 3B). The stability of the colloids is retained at room temperature for several months. The Au colloids stabilized by 5-mercapto-1-tetrazoleacetic sodium salt are destabilized upon reflux similarly to the particles stabilized by sodium 3-mercapto-1-propanesulfonate. The Au colloids are negatively charged with an average ζ-potential value of -20 mV.

3.3. Au NPs stabilized by 3-mercapto-1,2-propanediol

The Au NPs stabilized by 3-mercapto-1,2-propanediol have a spherical shape (Fig. 4A) and an average diameter of 6.6 ± 1.3 nm without employment of size-selective procedures. The close proximity of the Au NPs visible from the TEM image in Fig. 4A and all other studied by TEM samples is most probably due to the formation of hydrogen bonds between the –OH groups of the stabilizing ligand. Importantly, the Au colloids are stable for months without noticeable aggregation. A noticeable feature of this system is the drastic improvement of the particles size and shape during digestive ripening. Note that 3-mercapto-1,2-propanediol is not an ionic compound compared to the other two ligands investigated in this study. UV–vis spectra recorded before and after the digestive ripening of the Au colloid in the presence of 3-mercapto-1,2-propanediol (Fig. 4B) also support the evolution of the particles during the ripening step. The as-prepared colloid does not show any specific absorption features, while the ripened colloid has a well-defined plasmon peak at 540 nm. The result is the first demonstration of the ability of the digestive ripening procedure to drastically improve the size and shape of colloids in an aqueous medium [3h,3i]. The Au colloids are negatively charged with an average ζ-potential value of -35 mV.

4. Summary

In conclusion, we have developed a method for the gram-scale synthesis of Au NPs in an aqueous medium using a metal vaporization technique. This method allows the functionalization of the NPs with various water-soluble ligands. The Au NPs are characterized with a narrow size-distribution without carrying size-selective procedures. The reported procedure can be extended for the synthesis of other metal NPs in an aqueous medium using the proper stabilizing molecules.

Acknowledgments

We acknowledge the National Science Foundation for financial support and V. Zaikovski (Boreskov Institute of Catalysis) for help with selected TEM images.

Supporting information available

The online version of this article contains additional representative TEM images of the aqueous Au colloids.

Please visit DOI: 10.1016/j.jcis.2006.12.064.

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