Core–shell gold/silver nanoparticles: Synthesis and optical properties

Lu Lu, Gwendolyn Burkey, Ionel Halaciuga, Dan V. Goia *

Center for Advanced Materials Processing, Clarkson University, Potsdam, NY 13699-5814, USA

ARTICLE INFO

ABSTRACT

Highly dispersed gold–silver core–shell nanoparticles were synthesized in a two-step process. The stabilizer-free gold core particles with an average diameter of ∼30 nm were first precipitated by rapid reduction of $HAuCl_4$ with L-ascorbic acid. Thin continuous silver shells of variable thickness were subsequently obtained by reducing controlled amounts of silver nitrate added in the gold sol. The plasmon band of gold gradually blue-shifted and a peak characteristic for silver eventually emerged as the amount of deposited silver increased. A strong and well-defined silver absorption band was recorded when the Ag content exceeded 60 wt.%. It is shown that the concentration of Cl^- ions in the gold precursor solution plays a critical role in the stability of the bi-metallic sol and the structure of the deposited silver shell.

1. Introduction

Silver and gold nanoparticles have received considerable attention due to their unique optical properties [1–10]. Particularly, their localized surface plasmon resonance (LSPR) band is the basis for many applications in biosensors [4–13], photo-thermal cancer therapy [14–17], and surface-enhanced Raman scattering [18–23]. Combining these two metals in core–shell entities offers the possibility to tune the LSPR by changing both the size of the core and the thickness of the external shell. Since both metals have a face-centered cubic (fcc) crystal structure and similar lattice constants, the synthesis of gold–silver alloys or core–shell structures is quite facile [24–33]. Tsuji et al. [29] reported the preparation of Au–Ag core–shell nanostructures with different sizes and morphologies by growing silver layers onto Au seeds using a microwave mediated polyol reduction. Ma et al. [32] prepared cubic Au–Ag core–shell nanoparticles in aqueous medium by depositing silver with ascorbic acid on gold seeds prepared in the presence of different capping agents. The latter have been widely used in the preparation of Au–Ag core–shell nanostructures either to tailor the particle size/morphology or to improve dispersion stability. However, capping agents tend to interfere with the epitaxial deposition of silver atoms and the formation of continuous shells. For example, Tsuji et al. [29,30] showed that the morphology of resulting particles changed during the silver deposition due to selective adsorption of polyvinylpyrrolidone (PVP). Yu et al. [33] also reported that cetyltrimethylammonium bromide (CTAB)

inhibited the formation of a continuous compact silver shell on gold rod-like nanoparticles.

This study describes the deposition of continuous compact silver shells onto gold core nanoparticles, prepared by reducing tetrachloroauric (III) acid with ascorbic acid in the absence of a stabilizer. In this simple and convenient system, the thickness of silver shell can be controlled by adjusting the amount of silver nitrate added into the gold dispersion. A novel element in this work is the finding that the concentration of Cl^- ions, always present when using $[AuCl]_4^-$ species but never previously investigated, plays a critical role in the stability of the Au–Ag bi-metallic sols and the structure of the deposited silver shell.

2. Experimental

2.1. Materials

The tetrachloroauric acid solution ($HAuCl_4·HCl$, 23.11 wt.% Au, 5.97 wt.% excess HCl) was received from Umicore (South Plainfield/NJ), while the auric chloride crystals ($AuCl_3$, 64.4% Au) were purchased from Alfa Aesar (Ward Hill/MA). Silver nitrate crystals (Ames Goldsmith, Glens Falls/NY) and L-ascorbic acid crystals (Alfa Aesar, Ward Hill/MA) were used as received.

2.2. Solutions

The silver nitrate stock solution (2.4×10^{-3} mol dm^{-3} Ag) was prepared by dissolving 40 mg of $AgNO_3$ crystals in 100.0 cm^3 deionized (DI) water. An equal volume of reducing solution of L-ascorbic acid ($C_6H_8O_6$) with a concentration of 2.2×10^{-3} mol dm^{-3} was prepared by dissolving 40 mg of crystals in deionized water. Both solutions were always freshly prepared.

* Corresponding author.
E-mail address: goiadanv@clarkson.edu (D.V. Goia).

Table 1
Experimental conditions used for the preparation of Au–Ag core–shell nanoparticles.

	Silver nitrate solution (cm^3)	Ascorbic acid solution (cm^3)	Amount of Ag deposited (mg)	% Ag in the Au–Ag	Ag shell thickness (nm)
1	0.55	0.34	0.22	10	1.0
2	1.23	0.76	0.59	20	2.0
3	2.11	1.32	0.84	30	3.2
4	3.29	2.06	1.32	40	4.6
5	4.92	3.08	1.97	50	6.2
6	7.75	4.84	3.10	60	8.4

2.3. Preparation of stabilizer-free gold sols

The gold sols (100 cm^3) were prepared according to the protocol described previously by Goia et al. [34]. The resulting dispersions contained 1×10^{-4} mol dm^{-3} gold (or 1.97 mg/100 cm^3) in form of spherical nanoparticles with an average diameter of ~30 nm. The sols were next diluted to 150 cm^3 with DI water and kept at room temperature for at least 2 h before silver deposition to ensure the complete oxidation of excess ascorbic. To remove the excess Cl$^-$ ions resulting from the precipitation of gold, the sol was first placed in a dialyzing tube and then immersed in a vessel containing ~2000 cm^3 of deionized (DI) water. The water was replaced every 2 h until its conductivity remained unchanged.

2.4. Deposition of silver shell

Increasing volumes of silver nitrate stock solution were added to the gold dispersion followed by the rapid addition of the reducing solution. The volumes of silver nitrate and ascorbic acid stock solutions needed to obtain Au–Ag core–shell particles with increasing silver content (10–60 wt.%) are given in Table 1. The values of the shell thickness were estimated assuming that the average size of gold cores was ~30 nm and the deposited silver layer was uniform.

2.5. Characterization of Au–Ag core–shell nanoparticles and sols

The UV–Vis absorption spectra of gold and gold–silver sols were obtained without dilution using a Perkin-Elmer Lambda 35 spectrophotometer. The size, size distribution, and morphology of metallic nanoparticles were assessed by high resolution transmission electron microscopy (HRTEM), using a JEOL 2010 electron microscope. For this purpose, a drop of dispersion was placed on a carbon coated copper grid and the solvent was removed in vacuum. The same instrument was used to perform elemental mapping of the two metals.

3. Results and discussion

3.1. Preparation of gold nanoparticles

The characteristic red color of the gold sol and the narrow plasmon band in the UV–Vis spectrum (Fig. 1a) were clear indications that the dispersion of gold nanoparticles was effectively stabilized just by electrostatic repulsion. The HRTEM analysis (Fig. 1b) revealed the presence of reasonably uniform spherical gold nanoparticles. The histogram obtained from measuring 60 particles gave an average particle diameter of ~30 nm with a standard deviation of ±8 nm.

3.2. Deposition of Ag shell

As illustrated by the UV–Vis plots in Fig. 2 and the data summarized in Table 2, the plasmon band of gold cores shifts gradually from 523 nm (Au sol, black line), to 518 nm (10% Ag, red line), and 511 nm (20% Ag, green line) as the thickness of the Ag shell increases.

Starting at 30% Ag, a second absorption peak characteristic to silver emerges at 391 nm while the plasmon band of gold 'blue-shifts' further to 500 nm. As additional silver is deposited, the former peak grows in intensity and 'red-shifts' to 400 nm while the gold plasmon barely registers as a shoulder at ~500 nm.

The marked difference between the absorption profiles at 20% and 30% Ag indicates that a critical shell thickness that triggers electron oscillations characteristic for pure silver was exceeded. Assuming that the Ag coating is uniform and continuous, this threshold value is between 2.0 and 3.2 nm. The data also show that above a shell thickness of ~4 nm a distinct plasmon band of gold cores is not anymore observed. It is also noteworthy that the intensity of the Ag absorption peak (yellow curve) in the final Au–Ag core shell nanoparticles is much stronger (~4 times) than for the initial Au sol. The narrow absorption bands at all silver levels
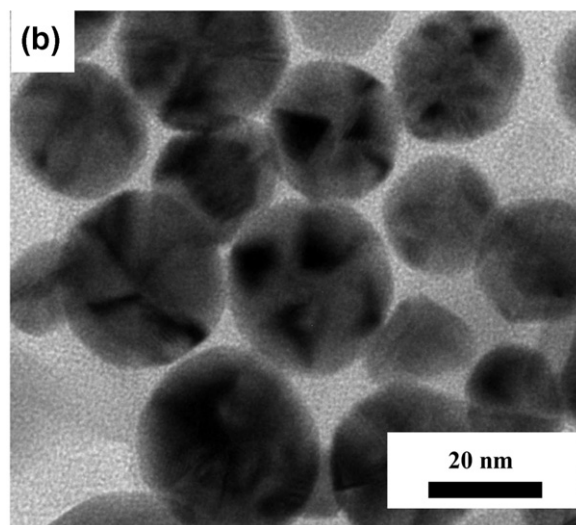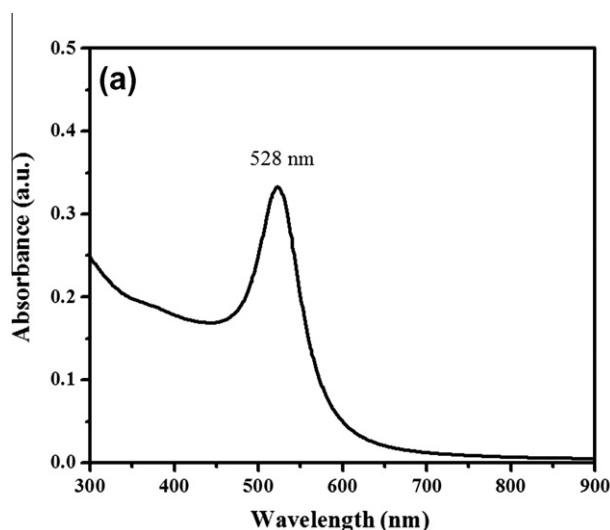

Fig. 1. (a) UV–Vis spectrum of the gold sol obtained by reducing HAuCl$_4$ with ascorbic acid at room temperature; (b) HRTEM images of the gold nanoparticles obtained.