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Seed-mediated growth of large, monodisperse core–shell gold–silver nanoparticles with Ag-like optical properties

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Large, monodisperse core–shell Au–Ag nanoparticles with Ag-like optical properties have been prepared by the seeding growth method in micellar media.

Bimetallic gold–silver nanoparticles have received enormous attention due to their specific electronic, optical and catalytic properties that are distant from those of the corresponding monometal nanoparticles.[1–3] They are prospective substrates for surface-enhanced Raman spectroscopy (SERS). It is known that the Au surface shows a lower enhancement factor in the visible in comparison with that of Ag although Au colloids have many advantages with respect to easier preparation and high homogeneity in the dispersion of diameters. For this reason, many different preparation methods have been reported for synthesis of composite particles that combine desirable features of both Au and Ag.[4–10] For example, Ag-coated Au and Au-coated Ag colloidal particles were prepared by Sanchez-Cortes and coworkers[8] by deposition of Ag or Au through chemical reduction on Au or Ag seed colloid, respectively. Girault and coworkers[10] showed the possibility of the use of laser irradiation as a tool for selective modification of core–shell gold–silver nanoparticles. Moreover, Natan's group[4] prepared Ag-clad Au colloid monolayers by chemical and electrochemical Ag deposition. However, for the average particle diameter, $d > 25$ nm, the monodispersity of bimetallic Au–Ag nanoparticles becomes poor. As a result, these particles are of limited value for nanometer-scale architectures. A recent advance[4,11] involves the use of 'seeds' for preparing the larger nanoparticles. This method exhibits well the advantage in terms of monodispersity. In this communication, we describe a simple synthesis method of large core–shell Au–Ag nanoparticles. Preformed 12 nm Au seeds have been used to promote silver growth in cetyltrimethylammonium bromide (CTAB) solution by chemical reduction of a silver salt. We have been able to achieve reproducible preparation of larger core–shell Au–Ag nanoparticles. It was found that these large nanoparticles possess the monodispersity of gold with the optical properties of silver.

The 12 nm gold seeds were prepared by the citrate-reduction procedure of Frens.[12] A 100 ml solution containing 0.01 g $HAuCl_4 \cdot 3H_2O$ was heated to boiling, and then 3 ml of a 1% sodium citrate solution was added to the boiling solution. The solution was further boiled for 40 min and then left to cool to room temperature. From transmission electron microscopy (TEM) measurements, the average particle diameter obtained was 12 nm, with a standard deviation of 2 nm. The preparation of core–shell Au–Ag composite nanoparticles was as follows. Five sets of solutions (A, B, C, D, E) containing 0.5 ml of 10 mM $AgNO_3$, 1 ml of 100 mM ascorbic acid, and 20 ml of 50 mM CTAB were prepared. Afterwards, different amounts (2, 1, 0.5, 0.2, 0.1 ml) of the 12 nm seed solution were added, respectively, and then 0.1 ml 1M NaOH was added drop-by-drop to the above solutions while stirring. Within 1–10 min, a color change occurred varying from red to brown depending on the seed concentration, suggesting the formation of composite nanoparticles. Throughout the experiment, the temperature was maintained at room temperature. The size distribution of nanoparticles was characterized by TEM on a JEOL 2000-FX transmission electron microscope and UV–Vis absorption spectra were measured using a Perkin Elmer spectrophotometer (Lambda 7). Fourier transform (FT)-Raman spectra were recorded using a Bruker RFS 100/S model spectrophotometer. For surface-enhanced Raman scattering (SERS) measurements, the composite nanoparticles were separated from the surfactant by centrifugation at 4000 rpm for 10 min. Samples for TEM were prepared by placing a drop of the solution onto a carbon-coated copper grid, and allowing natural evaporation of the solvent.

Fig. 1 shows the UV–Vis absorption spectra of nanoparticles prepared by the reduction of $AgNO_3$ with ascorbic acid in the presence of the 12 nm seed solution, and including the spectrum of the seed solution itself. The concentration of the Au seed solution decreases from A to E. Evident from Fig. 1, in the presence of the seed solution, only a plasmon band appears between 420 and *ca.* 450 nm, which can be exclusively attributed to plasmon resonance of Ag particles. The plasmon band gradually red shifts as the seed concentration is decreased, suggesting the formation of larger average particle diameters as the seed concentration decreases. A similar result was also observed by Jana *et al.*[13] Moreover, the magnitude of the plasmon band of the nanoparticles varies with seed concentration; the lower absorbance for a low amount of seed suggests a relatively smaller population of larger particles compared with those of samples A, B and C. From the UV–Vis absorption spectra we can reasonably infer that the reduction of Ag salt alone occurs on the preformed Au core surface rather than forming more nucleation sites. As a result, the core–shell structure Au–Ag composite nanoparticles were formed, which has also been confirmed by comparing the experimental absorption spectra of core–shell Au–Ag nanoparticles and their calculated spectra according to the equation given by Bohren and Huffmann.[14] Thus, it is not surprising that the optical

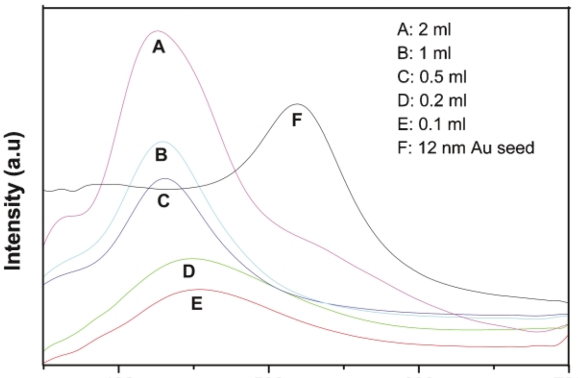

Fig. 1 UV–Vis spectra of Au–Ag composite nanoparticles prepared in the presence of different Au seed concentrations for samples A–E. F represents the spectrum of the 12 nm gold seeds.

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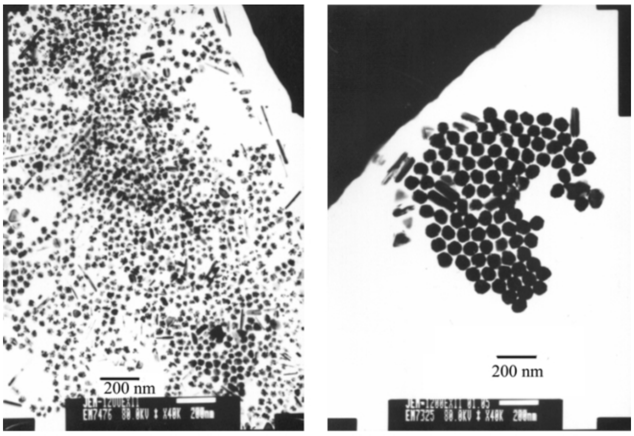

(a) (b)

Fig. 2 TEM images of the Au–Ag composite nanoparticles: (a) sample B, and (b) sample E.

properties of composite nanoparticles are dominated by the Ag shell, and the plasmon band of the composite nanoparticles red shifts when the Ag shell gradually becomes thicker as the seed concentration is decreased. Moreover, TEM analysis of composite nanoparticles was performed. Fig. 2 shows the TEM images of composite nanoparticles corresponding to B and E. Evident from the Fig. 2, these nanoparticles have good monodispersity and most of particles are spherical with a very small percentage of nanorods. The average size of the spherical particles for samples B and E was characterized by diameter to be 27 and 62 nm, respectively. The population of nanoparticles in sample B is evidently greater than that in sample E. No seed-sized (or smaller) particles are observed, suggesting that no additional nucleation events took place during the preparation of the composite nanoparticles. Interestingly, these larger nanoparticles for sample E are able to self-organize into a hexagonal close-packed array on the copper grid. These results further confirm our reasoning.

SERS is a useful probe of the resultant surface of composite nanoparticles.[4,8]Fig. 3 shows the surface-enhanced Raman spectra of rhodamine (R6G) absorbed on the composite nanoparticles at an excitation wavelength of 514.5 nm for samples A and C. As seen in Fig. 3, the increase of particle size obviously leads to the enhancement of SERS intensity. The marked peaks in the SERS spectra correspond to the Raman bands for R6G, suggesting that both kinds of nanoparticles are SERS-active using 514.5 nm excitation. According to earlier reports,[4,15] Au is SERS-inactive at the excitation wavelength 514.5 nm. This indicates that Ag atoms provide SERS-active sites on the Au surface, and composite nanoparticles obtained in the present study are highly efficient for surface-enhanced Raman scattering.

In summary, the interest in the present synthetic method is three-fold. First, it provides an alternative for the direct preparation of larger core–shell Au–Ag nanoparticles with improved monodispersity. Second, the structure, size and composition of the nanoparticles can be controlled by proper combination of the seed and initial reaction solution. Finally, since these composite nanoparticles possess the monodispersity of Au with the optical properties of Ag, they can be widely used as a substrate for surface-enhanced Raman scattering.

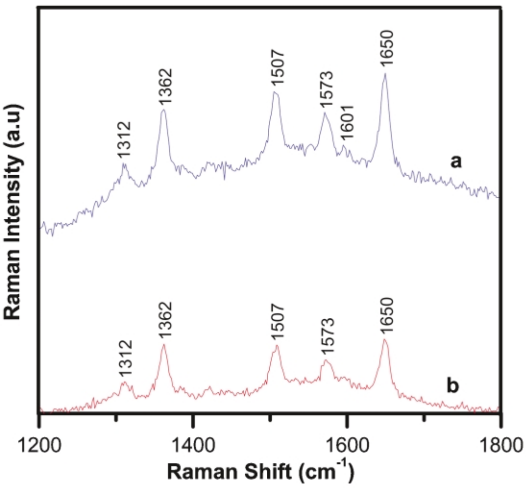

Fig. 3 SERS spectra of R6G absorbed on the Au–Ag composite nanoparticle: (a) sample E; (b) sample B. KCl was added at a concentration of 1 mM, and R6G was added at a concentration of 2 nM. Laser wavelength is 514.5 nm.

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