

Modulation of Localized Surface Plasmons and SERS Response in Gold Dumbbells through Silver Coating

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In this work, we describe the modulation of localized surface plasmons in gold dumbbell-like nanoparticles through step-wise silver coating. We analyse and compare the experimental and calculated optical response of the obtained nanoparticles. Additionally, we discuss on the near-field distributions and their relevance in surface-enhanced Raman scattering (SERS) and demonstrate the improved efficiency of these bimetallic nanoparticles as SERS substrates.

Gold dumbbells were formed through seeded growth of preformed nanorods (average aspect ratio ~ 4), by reduction of HAuCl_4 with ascorbic acid in the presence of hexadecyltrimethylammonium bromide (CTAB), AgNO_3 and small amounts of iodide ions. The selective tip growth leads to a controlled red-shift of the longitudinal surface plasmon resonance of the nanorods.¹ The as-prepared Au dumbbells were coated with silver in an aqueous solution containing CTAB, AgNO_3 , NaOH and ascorbic acid.² Opposite to tip growth, deposition of the silver shell caused the longitudinal plasmon band to significantly blue-shift, but additionally a new plasmon band arose and its intensity increased with reaction time and silver salt concentration.

Characterization of the samples performed with transmission (TEM and HRTEM) and scanning transmission electron microscopy (X-ray spectrometer coupled to a STEM) showed that conformal growth is only obtained for rather low silver concentration, whereas for intermediate and high silver salt concentration, the final nanoparticles have rod-like and/or irregular faceted morphologies as a consequence of anisotropic silver growth (Figure 1).

The experimental UV-visible spectra were analyzed and compared with simulations based on the boundary element method (BEM),^{3,4} which allows numerical resolution of Maxwell's equations in frequency space. Since HRTEM images showed well-defined interfaces between the two metals, each metal was described in simulations by tabulated dielectric functions that depend only on the frequency of light applying the local approximation. Calculations of the extinction cross section and near-field maps were carried out for gold dumbbells and Au@Ag core-shell nanoparticles of different morphologies. Additionally, assignment of transverse and longitudinal plasmon modes was achieved by simulating the extinction cross sections for incident light with different polarizations and comparing these data with experimental spectra from measurements on aligned nanorods.

Finally, we carried out average SERS on the dilute colloids using 1-naphthalenethiol (1NAT) as a Raman active probe and compared the efficiency between the bimetallic Au@Ag with those of the starting nanoparticles (AuNRs and AuDBs). The results for the different samples upon excitation with two visible lasers are depicted in Figure 2.

References

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Figures

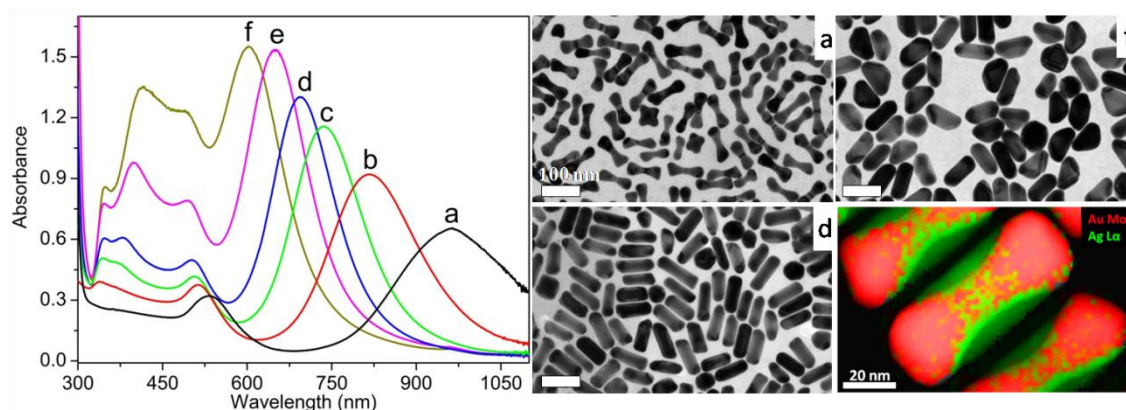


Figure 1. Left: UV-visible spectra of Au dumbbells (a) and bimetallic NPs grown with increasing $[Ag^+]/[Au^0]$ molar ratios from b to f. Right: Representative TEM images corresponding to samples a, d and f (scale bars: 100nm) and STEM-XEDS elemental map of sample d.

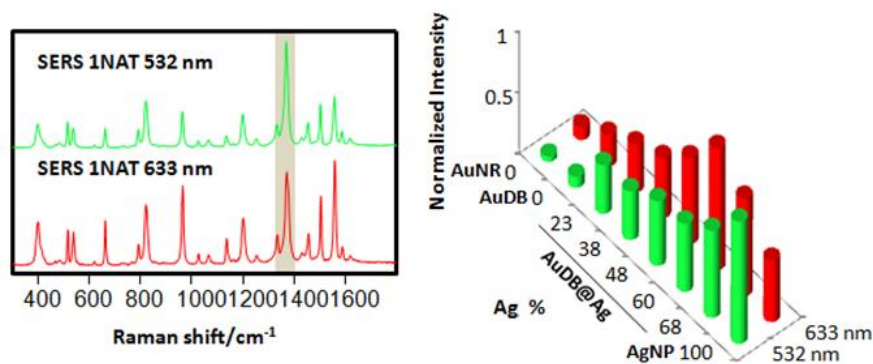


Figure 2. Left: Average SERS spectra of 1NAT on AuDB@Ag, acquired in solution with green and a red laser lines. Right: Intensities of the ring stretching (1368 cm⁻¹) band as a function of silver molar percentage in the particles (AuNR and AuDB: 0%; AuDB@Ag b, c, d, e: 23, 38, 48, 60, 68%, respectively; Ag-citrate: 100%).