A new approach for the formation of alloy nanoparticles: laser synthesis of gold–silver alloy from gold–silver colloidal mixtures†

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A new methodology has been developed to synthesize gold–silver alloy nanoparticles by laser irradiation of mixtures consisting of gold and silver nanoparticles.

Nanoscale materials have attracted a great deal of interest in scientific research and industrial applications, owing to their unique large surface-to-volume ratio and quantum size effect properties.[1] In principle, the preparations of metal nanometer-sized particles could be classified into two categories: physical and chemical techniques. Evaporation[2] or laser ablation[3] from metal bulk samples is utilized to generate nanoparticles in the physical methods whilst reduction of metal ions to neutral atoms, followed by metal growth is the common strategy in chemical syntheses, including conventional chemical (one- or two-phase systems),[4] photochemical,[5] sonochemical,[6] electrochemical[7] and radiolytic reductions.[8] In this report, a novel methodology is developed to fabricate gold–silver alloy nanoparticles, using laser irradiation of gold and silver colloidal solutions.

Nanocomposites, *i.e.* alloy and core–shell particles, are an attractive subject because of their composition-dependent optical and catalytic properties. To date, Papavassiliou has successfully prepared Au/Ag alloy particles *via.* evaporation of Au/Ag alloys.[2a] Kim and coworkers[4c] and El-Sayed and coworkers[4d] employed simultaneous reduction of gold and silver salts to form Au/Ag alloy nanoparticles of 4 nm and ≈ 18 nm diameter, respectively. Although Lis-Marzán *et al.* used a similar chemical method to synthesize gold–silver bimetallic colloids, the detailed structures of these remained ambiguous.[4b] It should be noted that the formation of alloy particles by co-reduction of different metal salts strongly relies on the reduction rates of the metal ions. A core–shell structure could be readily prepared through a heteronucleation process: the metal with the faster reduction forms the core and the other is the surrounding shell.

Recently, pulsed laser irradiation to nanorods or spherical particles was studied to unravel the photophysical properties of these particulates. The groups of El-Sayed and Koda suggested that the interaction between laser light and metal particles may lead to conformational changes *via* a melting process.[9] We have attempted to take advantage of this melting state, if present, to alloy a mixture containing two different kinds of metal particles under laser light irradiation. A gold–silver system was selected since both metals are miscible in the bulk phase, owing to very similar lattice constants.[10] Moreover, the UV–VIS absorption spectra of the Au/Ag bimetallic particles show a substantial difference between the alloy and a core–shell structure, which has been studied explicitly by experimental and theoretical measurements.[4b–d,11]

In this study, Au and Ag nanoparticles were prepared in aqueous solution following the methods employed by Natan and coworkers[12] and Lee and Meisel,[13] respectively. The mean diameters of the prepared colloids were 13.7 ± 0.8 nm for Au

and 16.8 ± 6.6 nm for Ag. Assuming that metal salts (HAuCl$_4$ and AgNO$_3$) are completely reduced into neutral metals completely, gold and silver colloids were mixed in molar ratios (Au∶Ag) of 1∶2, 1∶1 and 2∶1 (see ESI†).

Fig. 1 shows the UV–VIS absorption development of the 1∶1 molar ratio (Au∶Ag) colloidal suspensions before and after laser irradiation. Two distinct absorbance maxima at 396 and 519 nm, corresponding to Ag and Au plasmon bands, respectively, indicate segregated Ag and Au particles in the mixed suspension before exposure to laser light [Fig. 1(a)]. For solutions exposed to the laser [Fig. 1(b) and (c)] the absorption spectra changed as the irradiation time was increased. The Au surface plasmon band increases in magnitude and shifts to lower wavelength while the Ag plasmon band moves in the opposite direction with reduced intensity and absorption maximum. This variation in UV–VIS spectra clearly imply changes in the colloidal properties. Further irradiation [Fig. 1(d)], leads to a single absorption peak at 459 nm, located at an intermediate position between the Au and Ag plasmon bands. This surface plasmon band is likely due to the formation of the gold–silver alloy.[4c,d,11] Two plasmon bands (Au and Ag) would be expected if the colloids consisted of individual Au and Ag particles or of bimetallic composites with a core–shell structure.[11] A similar evolution in absorption spectra appeared in mixtures with Au∶Ag molar ratios of 1∶2 and 2∶1 (see ESI†). A linear relationship was obtained from the plot of the plasmon band position *vs.* the gold mole fraction, as shown in Fig. 2. Previous studies on Au/Ag alloy nanoparticles showed a linear red-shift in the position of the plasmon absorption with an increase in gold composition.[2a,4c,d,11] The final temperatures of the solutions rose by *ca.* 20 °C from room temperature (24 °C) after
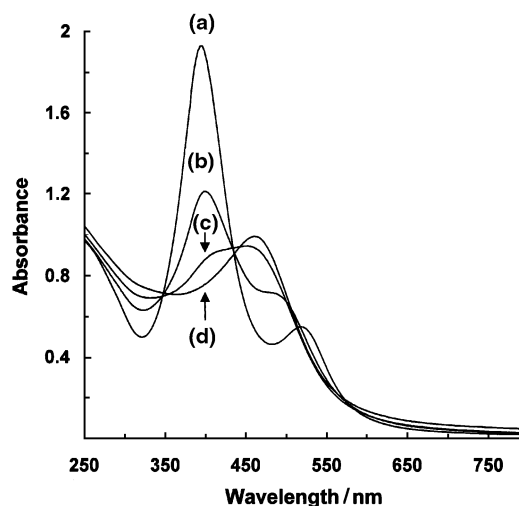

Fig. 1 Development of the UV-VIS absorption spectra of the 1∶1 molar ratio (Au∶Ag) colloidal suspension during irradiation using a pulsed laser, as a function of the exposure time: (a) 0 min, (b) 5 min, (c) 10 min, (d) 25 min. A 532 nm wavelength was utilized as light source and the laser intensity was maintained at 2.45 × 10² mJ pulse⁻¹.

Fig. 2 Absorption position of the surface plasmon maximum as a function of the gold mole fraction.

irradiation. We also found that a lower laser fluence required a longer irradiation time to form gold–silver alloys.

Fig. 3 displays the TEM images of the 1:1 molar ratio (Au:Ag) colloid suspension. The most striking feature is the formation of an interconnected network, as shown in Fig. 3(a). The network appearance can be readily observed at various stages, where two Au and Ag plasmon peaks appeared in the absorption spectra, in the course of colloidal mixture irradiation. On closer inspection of Fig. 3(a), the particles (indicated by arrows) seem to develop as ramification structures in a radial fashion and are interconnected with each other, leading to a network morphology. However, the shape changes back to spherical after the alloying process is complete [Fig. 3(b)]. According to the TEM images, the morphology changes in the alloy nanoparticle formation can be described as follows: spherical (initially prepared Au and Ag particles) → network structure → spherical (alloy particles). Fig. 3(b) indicates highly dispersed tiny gold–silver alloy nanoparticles. The average particle sizes are 4.9 ± 1.8 nm (molar ratio Au:Ag = 1:2), 4.9 ± 1.9 nm (molar ratio Au:Ag = 1:1), and 5.1 ± 2.1 nm (molar
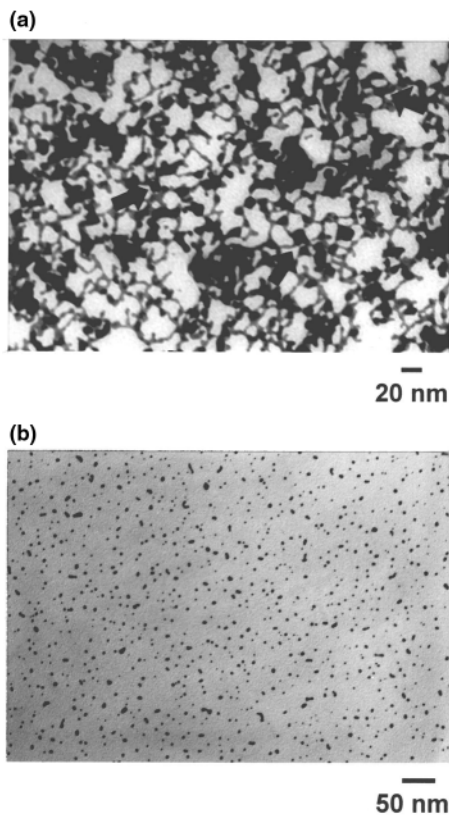

Fig. 3 TEM images of the 1:1 molar ratio (Au:Ag) colloidal suspensions after exposure to laser light for (a) 5 min and (b) 25 min.

ratio Au:Ag = 2:1). The minor variation in size is in contrast to the results of an increase in particle size when increasing the shell element amount in core–shell composites.[4b–d,11] The resulting alloy sizes are significantly less than those of the initially prepared Au and Ag colloids. In addition, the composition of the discrete bimetallic particles was analyzed using EDX. EDX measurements of selected particles, chosen at random, for molar ratio of 1:1 (Au:Ag) suspension, yielded the atomic ratios (Au:Ag): 49.1:50.9, 52.1:47.9, 47.2:52.8, 44.5:55.5 and 44.7:55.3. The compositions of the 1:2 and 2:1 molar ratios (Au:Ag) were also investigated using EDX analysis (see ESI†). Finally, from the viewpoint of their stability, the resulting alloy nanoparticles are preserved for at least one month with no sign of decay under aerobic conditions.

In summary, we have demonstrated that Au/Ag bimetallic particles, forming a mixture at the atomic level, can be synthesized *via* the methodology introduced here. It is expected that this strategy could be applied to prepare other binary systems. Although the original idea of this experiment is based on the melting state, leading to alloy particles, the detailed formation mechanism remains to be resolved. However, the intermediate morphology, as seen in Fig. 3(a), reveals that the particles (indicated by arrows) appear to show that the metals are at the melting stage. Studies of the compositions and structures of the irradiated colloidal mixtures as a function of irradiation time are in progress.

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