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Selective structure changes of core–shell gold–silver nanoparticles by laser irradiation: homogeneisation *vs.* silver removal

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A method involving laser irradiation is shown to lead to selective modification of core–shell gold–silver nanoparticles.

In recent years, a large range of preparations have been proposed for the design of novel metallic nanoparticles. For both uncoated and passivated metallic nanoparticles like thioalkane or thionicotinamide-coated gold nanoparticles,[1,2] numerous chemical or physical procedures for their preparation have been published and compared,[3–6] in particular with respect to the size and shape distributions.[7] For spherical nanoparticles, a strong emphasis has always been given to the diameter of the particles and the width of the distribution around the mean diameter. These properties are usually assessed by UV–VIS absorption spectroscopy and Transmission Electron Microscopy (TEM). Routinely, particles with diameters between 5 and 25 nm with a standard deviation between 1 and 2 nm are reported. One general aim is to reduce even further the standard deviation of the size distribution since many physical properties of the particles are size dependent. This is true for the wavelength corresponding to the maximum of the absorption spectrum of the particles in solution and also for the hyperpolarisability of the particles.[8,9]

The control of the size distribution is not very efficient during nanoparticle formation when the metal salt reduction technique is used. However, this is probably the most widely used technique although it does not yield a very narrow distribution. Subsequent size separation processes are therefore required.[10] The search for a convenient way to narrow the size distribution for monodisperse aqueous solutions of nanoparticles is thus required and recently laser irradiation has been proposed with the report of both size reduction and shape changes of metal particles in solution.[2,11–13] Nevertheless, the physical mechanisms at work have not been fully elucidated although melting, photoejection of electrons and fragmentation have been observed depending on the laser irradiation conditions. In this work, we report the laser irradiation of core-shell gold–silver nanoparticles with a diameter *ca.* 23.4 nm and their subsequent changes for different laser fluences when pulses with a 5 ns duration at a 532 nm wavelength are used.

Silver coated gold nanoparticles were prepared by reduction of a gold tetrachloroaurate salt containing 10 mg of gold in 190 mL of water made up to 200 mL with 10 mL of a 38.8 mM sodium citrate solution.[14] The ruby red coloured solution was then cooled down to room temperature before being boiled again. Near the boiling point, silver nitrate was added to 60 mL of the gold solution in aliquots of 200 μL with the amount of silver adjusted to the desired mole fraction with respect to gold. The stoichiometric equivalents of citrate were added after each silver addition to ensure the complete reduction of the silver ions. Here we present the results for a solution with a mole fraction of gold of 0.60 although other ratios can be obtained by this preparation method. The size distribution of the solution was characterized by TEM on a Philips CM20 transmission electron microscope and UV–VIS absorbance spectra were recorded with a Varian 1E UV–VIS spectrophotometer. For the TEM measurements, a drop of the solution was deposited on a copper grid on a carbon film and dried under a N_2 atmosphere in a glove box. The size distribution was then deduced from the measurements of the diameter of 200 particles from 6 different batches. The average diameter measured was 23.4 nm with a standard deviation of 1.4 nm. The laser irradiation was performed with a nanosecond Continuum Minilite II Nd^{3+}–YAG laser, delivering pulses at a repetition rate of 10 Hz at 532 nm. The cross section of the irradiation beam was controlled with a 10 cm focal lens and measured to be 0.125 cm^2 at the entrance of the cell. At energies varying between 12 and 2 mJ per pulse, this corresponds to fluences between 96 and 16 mJ cm^{-2}, respectively. In all experiments, the nanoparticle solutions were used directly as prepared without further additions of others species such as oxidising agents. The volume of the aqueous solution of nanoparticles was maintained at 1.5 mL in a quartz cell. Irradiation times were varied but the results presented here all correspond to irradiation times of 60 minutes. The UV–VIS absorbance of the initial orange coloured solution of the nanoparticles consisting of a gold core with a silver outer-shell is presented in Fig. 1. The absorbance of the core–shell nanoparticle exhibits two surface plasmon resonances at 410 and 502 nm characteristic of this bimetallic phase system. It is important to realise though that one cannot attribute a particular band to the surface plasmon excitation of one single metal phase only. Indeed, from a Mie theory calculation for such a core–shell system, one calculates the absorption cross-section of the core–shell particle altogether. It can however be noticed that the absorption cross-section is always dominated by the gold core absorption at all wavelengths.[15] From the TEM measurements, no rod shaped particles were observed and therefore the particles are assumed spherical hereafter.

Upon 60 minutes of irradiation of the sample with 532 nm light at a high fluence of 96 mJ cm^{-2}, the UV–VIS absorbance spectrum is substantially modified, now presenting only one surface plasmon excitation located at 510 nm, see Fig. 2, which

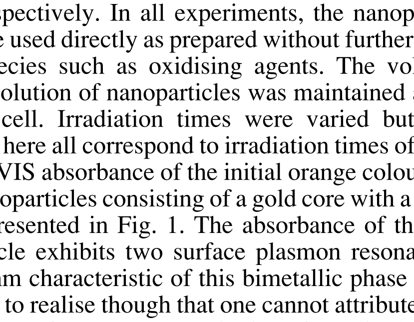

Fig. 1 UV–VIS spectra for Au 0.6 Ag 0.4 core–shell nanoparticles of different morphologies: mixed core–shell (solid line), homogeneous (dashed line) particles. The spectrum of pure gold is also given (dotted line).

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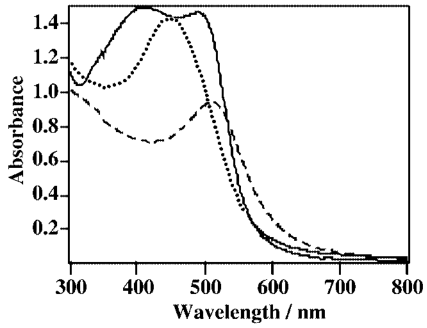

Fig. 2 Absorption spectra of Ag coated Au nanoparticles after irradiation with different fluences for 60 min: no irradiation (solid line), irradiation at low fluence (dotted line) and at high fluence (dashed line).

is a value very close to the position of the surface plasmon band for pure gold particles. From the TEM measurements of the irradiated samples, it appears that particles with diameters larger than 15 nm are not observed anymore whereas the number of particles with a diameter between 3 and 15 nm increased. When the solution is irradiated during an equal amount of time with a lower fluence of 16 mJ cm^{-2}, the absorbance spectrum is different with a single surface plasmon band observed located at a wavelength of 455 nm, see Fig. 2. This is the exact location of the surface plasmon band excitation for a mixed gold–silver nanoparticle with the same mole fraction of 0.6 for gold. Such a homogeneous particle can be produced by the simultaneous reduction by citrate of a mixed salt of sodium tetrachloroaurate and silver nitrate with an initial mole fraction of gold of 0.6. From the TEM measurements, the diameter of the particles ranged between 3 and 17 nm and no particles with a diameter larger than 17 nm were observed. These results at low fluence have recently been observed by Hodak *et al.*[16] The origin of the difference in the resulting UV–VIS absorbance spectra after irradiation is the result of the competition between two dominant processes: surface oxidation and melting. At low fluences with an irradiation wavelength of 532 nm, the absorption is preferentially localised into the gold core because of the smaller absorptivity of silver compared to the gold at this wavelength.[17] The plasmon excitation is the dominant process leading to a rapid phonon excitation through electron–phonon coupling in less than 1 ps and thermal relaxation within the nanosecond pulse duration by phonon–phonon coupling. This process induces the melting of the particle since internal temperatures reached are above the melting temperature for gold, the bulk value of which is 1339 K. However, this phenomenon occurs on a very short timescale since phonon–phonon equilibration with the surrounding medium is complete within 100 ps.[18] The internal diffusion process involving the mixing of the gold internal core and the outer silver shell must then be rapid, with a timescale of the same order of magnitude of 100 ps. It is likely that complete homogeneity is only obtained after a number of pulses.[16] In contrast, at high fluences, the process is different leading to the removal of the silver layer. Absorption of more than one photon is a process known to occur.[12] At high fluences with a wavelength of 532 nm, the process of the absorption of at least two photons, or an energy of more than 4.64 eV, a value above that of the work function of silver equal to 4.3 eV, induces the photooxidation of silver. The redox reaction is similar to an electrochemical anodic dissolution of silver ($E^0_{\mathrm{Ag^+/Ag}}$) concomitant with the reduction of the electrolyte. The gold inner shell is not affected by photooxidation as the work function of gold is higher (5.2 eV). The process of evaporation of atoms of both silver or gold is highly unlikely from a physical statistics point of view and thus the successive absorption of photons with time intervals greater than 100 ps cannot be regarded as a dominant channel of relaxation. No pure silver particles were observed in solution after irradiation as seen from the absence of any plasmon band excitation around 400 nm. The silver cations formed therefore by photooxidation are not reduced again in solution to form silver nanoparticles.

The irradiation fluence was observed to change the shape as well as the diameter of the nanoparticles. This work demonstrates the possibility of the use of laser irradiation as a tool to selectively change the morphology of core–shell gold–silver nanoparticles.

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Notes and references

1 M. Brust, J. Fink, D. Bethell, D. J. Schiffrin and C. Kiely, *J. Chem. Soc., Chem. Commun.*, 1995, 1655.
2 H. Fujiwara, S. Yanagida and P. V. Kamat, *J. Phys. Chem. B*, 1999, **103**, 2589.
3 J. Turkevich, P. J. Stevenson and J. Hillier, *Discuss. Faraday Soc.*, 1951, **11**, 55.
4 J. H. Fendler, *Chem. Rev.*, 1987, **87**, 877.
5 L. Rodriguez-Sanchez, M. C. Blanco and M. A. Lopez-Quintela, *J. Phys. Chem. B*, 2000, **104**, 9683.
6 F. Mafune, J. Kohno, Y. Takeda, T. Kondow and H. Sawabe, *J. Phys. Chem. B*, 2000, **104**, 9111.
7 Y. Yu, S. Chang, C. Lee and C. R. C. Wang, *J. Phys. Chem. B*, 1997, **101**, 6661.
8 U. Kreibig and M. Vollmer, in *Optical Properties of Metal Clusters*, Springer, Berlin, 1995.
9 P. Galletto, P. F. Brevet, H. H. Girault, R. Antoine and M. Broyer, *Chem. Commun.*, 1999, 581.
10 T. G. Schaaf, M. N. Shafigullin, J. T. Khoury, I. Vezmar, R. L. Whetten, W. G. Cullen and P. N. First, *J. Phys. Chem. B*, 1997, **101**, 7885.
11 A. Takami, H. Kurita and S. Koda, *J. Phys. Chem. B*, 1999, **103**, 1226.
12 P. V. Kamat, M. Flumiani and G. V. Hartland, *J. Phys. Chem. B*, 1998, **102**, 3123.
13 S. Link, C. Burda, B. Nikoobakht and M. A. El-Sayed, *J. Phys. Chem. B*, 2000, **104**, 6152.
14 R. G. Freeman, M. B. Hommer, K. C. Grabar, M. A. Jackson and M. J. Natan, *J. Phys. Chem.*, 1996, **100**, 718.
15 C. F. Bohren and D. R. Huffman, in *Absorption and Scattering of Light by Small Particles*, Wiley, New York, 1983.
16 J. H. Hodak, A. Henglein, M. Giersieg and G. V. Hartland, *J. Phys. Chem.*, 2000, **104**, 11 708.
17 A. M. Prokhorov, V. I. Konov, I. Ursu and I. N. Mihailescu, *Laser Heating of Metals*, Adam Hilger, 1990.
18 T. S. Ahmadi, S. L. Logunov and M. A. El-Sayed, *J. Phys. Chem.*, 1996, **100**, 8053.