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Preparation of silver nanoparticles in solution from a silver salt by laser irradiation

J. P. Abid,*[a] A. W. Wark,[a] P. F. Brevet[b] and H. H. Girault[a]
[a] *Laboratoire d'Electrochimie, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland*
[b] *Laboratoire de Spectrométrie Ionique et Moléculaire, Université Claude Bernard Lyon 1, Bâtiment Alfred Kastler, UMR CNRS 5579, 43 Boulevard du 11 Novembre 1918, F-6922 Villeurbanne cedex, France. E-mail: jean-pierre.abid@epfl.ch*

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A new method is proposed for the fabrication of a well-defined size and shape distribution of silver nanoparticles in solution; the method employs direct laser irradiation of an aqueous solution containing a silver salt and a surfactant in the absence of reducing agents.

In recent years, there has been a surge of interest in the understanding and application of the unique optical, electronic and catalytic properties of nanoparticle materials.[1,2] The advancement of our comprehension of the physical and chemical properties of these materials largely rests on the preparation of well-defined nanoparticle distributions in terms of both size and shape. Depending on these parameters, new properties are observable for these materials such as melting temperature,[3] photoluminescence[4] and nonlinear optical properties.[5] This in turn requires a great deal of control over the size, structure and of the surface composition during the formation and growth processes. As a result, an important part of the research field is devoted to the development of simple and versatile methods to prepare size- and shape-selected samples. The wet preparation methods themselves range from synthesis by chemical reduction in solution or in reverse micelles[6] to the laser ablation of metal foils.[7] Among all the methods proposed, one of the simplest is the chemical reduction of a metal salt in an aqueous solution by citrate.[8] This reducing agent also acts as a stabilizer for the particles, preventing their rapid aggregation. Although the kinetics of the dual action of the citrate anions has yet to be fully elucidated, colloidal solutions of low dispersity are readily prepared with some control over the average size of the particles by adjusting the ratio of concentration of the citrate ion to that of the metal salt. The use of stronger reducing agents such as sodium borohydride is another way to extend the range of accessible sizes but control of the chemical reaction is difficult. More advanced preparations have now been proposed to synthesize functionalized particles starting from different metallic salts,[9] opening up a wider range of possibilities based on synthetic organic and inorganic chemistry.

A recent alternative to the chemical preparation of nanoparticles in solution is the direct use of lasers. Gold and silver nanoparticles have been produced by direct laser ablation of metal plates in a solution containing a suitable surfactant with pulsed nanosecond lasers delivering high energy pulses. This approach allows the formation of nanoparticles of a controlled size but with a significant polydispersity. Laser irradiation techniques have also been recently investigated as a powerful tool for the controlled reshaping and resizing of nanoparticles produced by chemical methods through melting and fragmentation mechanisms.[10,11]

The aim of this communication is to propose an alternative method for the preparation of metallic nanoparticles based on the laser irradiation of a metallic salt solution containing no reducing agent. The dependence on the particle growth was then investigated for different concentrations of surfactants introduced to the metal salt in solution. In all experiments, a volume of 3 mL of an aqueous solution of silver nitrate (concentrations ranging from 0.833 to 4.166 mM) was placed in a closed spectrophotometric cuvette (light path length of 1 cm) and irradiated by a focused laser beam in the presence of the surfactant sodium dodecyl sulfate (SDS). The laser beam was delivered by a Nd^{3+}-YAG laser pumped optical parametric oscillator (OPO) operating at 500 nm with a pulse duration of 6 ns and a repetition rate of 10 Hz. The average energy per pulse in all experiments was measured to be in the range of 12–14 mJ. The laser beam was focussed using a 150 mm focal lens with the focal point located within the cell. All the solutions were deaerated by bubbling pure nitrogen prior to illumination. During irradiation, the nucleation and the growth of the nanoparticles were followed by *in-situ* UV-vis absorption spectroscopy with a typical acquisition rate of 10 spectra s^{-1}. The cell holder was placed on a magnetic plate allowing a controlled convection of the solution. The UV-Vis and laser beams, and the magnetic stirrer were all located at different levels within the cell thus leading to a minimal effect on the noise level of the acquired spectra. Using a Philips CM20 transmission electron microscope, the size distribution of the prepared colloidal solutions were deduced. An initial experiment was performed involving the laser irradiation of an aqueous solution of 5 mM silver nitrate in the absence of any surfactant. After 30 min a broad absorption band ranging from 380 to 650 nm was observed to develop. The spectrum was similar to that obtained from a solution of silver nanoparticles prepared by the citrate reduction method indicative of a very large size and shape distribution. As expected, the final solution was not stable and rapidly precipitated once the irradiation was stopped.

Subsequent preparations were all performed in the presence of varying concentrations of SDS added to the silver nitrate solution. Over the concentration range studied, stable solutions of monodispersed silver particles were prepared which were characterised by a narrowing of the surface plasmon resonance absorption band around 410 nm as compared to a solution prepared by the wet chemical reduction of silver ions by citrate (see Fig. 1). Additionally, TEM measurements indicated that the samples prepared under irradiation retained a narrower

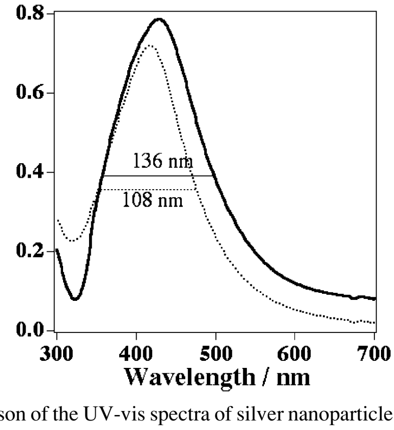

Fig. 1 Comparison of the UV-vis spectra of silver nanoparticles prepared by laser irradiation of a solution containing silver nitrate (0.833 mM) and sodium dodecyl sulfate (8.33 mM) (dotted line) with the classical Turkevich approach (solid line).

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standard deviation around the average size of the particles with a polydispersity of about 13% as compared to the conventional wet chemical reduction methods which yield an average diameter of about 35 nm with a polydispersity of 27% (see Fig. 2). Experiments were performed both above and below the critical micelle concentration (cmc), the value of which is 8.3 mM at 298 K for SDS, to investigate the effect of the micelles as well as the surfactant concentration on the growth rate. It was found that no significant change in the particle growth and formation was observed at and below the cmc in relation to the formation of micelles at the cmc apart from the general observed trends attributed to the overall increase of the SDS concentration.

The mechanism for the formation of silver nanoparticles by laser irradiation of the metal salt in the absence of any reducing agent occurs through the photolysis of water and the formation of radicals in the solution.[12] Indeed, near the focal point, which defines the reaction volume, the energy density is high enough for multiphoton processes to take place. With a three photon absorption process, the energy absorbed during the transition is in excess of 7 eV, a value above the 6.5 eV required for the photodecomposition of water leading to the production of e^-_{aq}, OH_{aq}, H_{aq} radicals.[13] Owing to the multiphotonic character of this first step, the efficiency is very low. In our case, the fraction of reduced silver ions is estimated to be 10–20% after a period of 60 min. Nevertheless, in the absence of stirring, a distinct gradient in color is observed away from the beam focal point. Other processes are also observed to occur such as bubble formation and heating effects. The solvated electron and the hydrogen radicals are potential reducing agents with redox potentials of $E_0(H_2O/e^-_{aq}) = -2.8$ V *vs.* SHE and $E_0(H^+/H) = -2.3$ V *vs.* SHE, respectively. Despite having a very short lifetime, these two species can therefore reduce the silver metal ions to their zero valence state through the following scheme:

$$Ag^+ + e^-_{aq} \rightarrow Ag^0 \tag{1a}$$

$$Ag^+ + H^\cdot \rightarrow Ag^0 + H^+ \tag{1b}$$

It can also be pointed out that the water photolysis reaction may also lead to the formation of hydroxyl radicals, which are potential oxidizing agents for Ag^+. At constant silver ion concentration, the pH of the reaction solution varied from 5.8 to a final value of 5.1. To investigate further the reduction process, the effect of a scavenger was studied. In the presence of an excess of 2-propanol, introduced into the reaction vessel at a concentration of 0.5 M, the rate of formation of silver particles decreased by a factor of about 25% as measured by the time required for the solution to reach a fixed absorbance. In the presence of 2-propanol, both the concentrations of hydrogen and hydroxyl radicals are reduced [eqn. (2)]:

$$(CH_3)_2CHOH + OH^\cdot, (H^\cdot) \rightarrow (CH_3)_2C^\cdot OH + H_2O, (H_2) \tag{2}$$

The rate of silver oxidation and reduction is also decreased. The radicals produced through eqn. (2) have a redox potential of only −1.8 V *vs.* SHE.

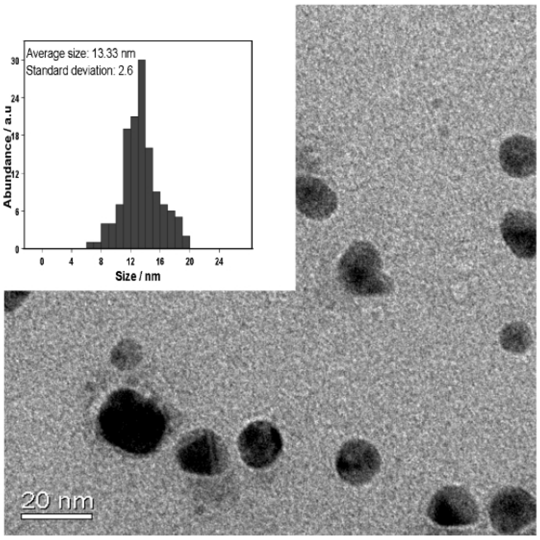

Fig. 2 TEM micrograph and size distribution of the nanoparticles prepared by irradiation of silver nitrate (0.833 M) and sodium dodecyl sulfate (8.33 mM).

The silver nuclei formed by water photolysis are able to grow through either addition of already reduced silver ions or by addition of silver ions followed by reduction. The formation of charged metallic nanoparticles has already been reported in the literature, especially for silver where small charged cluster ions, for example Ag_4^{2+}, are rather stable.[14] These charged particles exhibit an absorption band centred at 292 nm, which can be observed in Fig. 1. The growth reaction is in competition with the termination reaction, which is the adsorption of SDS anions onto the particles. It would be expected therefore, that any increase in the surfactant concentration with respect to the silver salt concentration would lead to a faster termination process leading to a smaller size distribution. For a concentration ratio $[SDS]/[AgNO_3]$ ranging from 0.2 to 40, the average size available was always limited between 13 and 16 nm but without any significant broadening of the distribution. Furthermore, since the reactions of nucleation, growth and termination occur under continuous laser irradiation, shape changes take place yielding spherical particles with no elongated or rod-shape particles. Such particle shapes are common in irradiated colloidal solutions.[15] This may explain the narrow standard deviation of the size distributions observed.

In conclusion, we report a novel method for the fabrication of small metallic nanoparticles with narrow size distributions as compared to wet chemical reduction preparations. The shapes of the particles are also exclusively spherical owing to the continuous irradiation of the solution. Other metals like gold and platinum have also been studied leading to similar conclusions. The mechanism of preparation is described as arising from the formation of radicals in the solution by multiphoton excitation, the termination of the growth of the particles being controlled by the concentration of SDS surfactant introduced in the solution initially.

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