Deposition of Silver Nanoparticles on Silica Spheres by Pretreatment Steps in Electroless Plating

Yoshio Kobayashi, Verónica Salgueiriño-Maceira, and Luis M. Liz-Marzán*

Departamento de Química Física, Universidade de Vigo, 36200 Vigo, Spain

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A new method was developed for the homogeneous deposition of silver nanoparticles on colloid silica spheres. The method does not make use of an external electron source, but of a chemical moiety adsorbed on the surface, which can easily get oxidized. The process is mainly performed in two steps: a first step in which the adsorption of Sn^{2+} ions occurs on the surface of the silica particles and a second step comprising the addition of Ag^+ ions, which are reduced and simultaneously adsorbed on the surface, while Sn^{2+} oxidizes to Sn^{4+}. The whole process can be repeated to obtain a denser coating on the surface.

Introduction

The assembly of nanoparticles of various nature as nanostructures is one of the more exciting challenges of modern colloid chemistry.[1] The properties of such nanostructures can be modulated not only through the nature of their constituting units but also through the distances between particles or the morphology of the whole system. A plethora of examples can be found, such as thin films,[2] colloid crystals and opals,[3] and mesoporous structures.[4] Recently, a number of reports have been published on the deposition on submicron colloid particles of nanoparticles such as magnetite,[5] quantum dots,[6] metals,[7,8] and vinyl polymer.[9] Because the nanoparticles are facing the outer surface of the substrate colloids, it should be possible to make use of the properties of the nanoparticles and/or their assemblies. Among the different types of nanoparticles widely used, metals are attracting a great deal of attention because of their special optical and electronic properties,[10] which depend on particle size. Organized structures of metal nanoparticles have been prepared on several substrates and for various applications, such as SERS,[11] nanoelectrode fabrication,[12] or modulation of optical properties.[13] Some of the techniques used to attach metal nanoparticles on particle substrates involve the use of bifunctional molecules, which can attach to both the substrate and the metal.[14,15] These methods have also been used to attach gold nanoparticles on silica colloid spheres[7] and even to form homogeneous metal shells.[7] In the present work we describe a simple method to deposit silver nanoparticles on silica spheres based on a common procedure to deposit metals on surfaces, which has recently been used for decoration of carbon nanotubes,[16,17] but has not been implemented on spherical colloids until now. The method consists of modifying the surface of the silica spheres with Sn^{2+} ions and then carrying out a redox reaction in which the Sn^{2+} ions are oxidized to Sn^{4+} and at the same time Ag^+ ions are reduced into metallic Ag, which stays attached on the silica surface in the form of nanometer-sized particles. This process is equivalent to the so-called “pretreatment steps” in electroless plating.[18]

Experimental Section

Materials. $SnCl_2$ (anhydrous), $AgNO_3$, trifluoroacetic acid, and NH_4OH (28%) were supplied by Aldrich and used as received. Tetraethoxysilane (TES), also from Aldrich, was

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(1) Fendler, J. H. *Nanoparticles and Nanostructured Films*; Wiley-VCH: Weinheim, 1998.

(2) Kotov, N. A.; Meldrum, F. C.; Fendler, J. H. *J. Phys. Chem.* **1994**, *98*, 8827; Kotov, N. A.; Fendler, J. H.; Dekany, I. *J. Phys. Chem.* **1995**, *99*, 13065; Schmitt, J.; Mächtle, P.; Eck, D.; Möhwald, H.; Helm, C. A. *Langmuir* **1999**, *15*, 3256; Aliev, F. G.; Correa-Duarte, M. A.; Mamedov, A.; Ostrander, J. W.; Giersig, M.; Liz-Marzán, L. M.; Kotov, N. A. *Adv. Mater.* **1999**, *11*, 1006.

(3) van Blaaderen, A.; Ruel, R.; Wiltzius, P. *Nature* **1997**, *385*, 321; Mayoral, R.; Requena, J.; Moya, J. S.; López, C.; Cintas, A.; Míguez, H.; Meseguer, F.; Vázquez, L.; Holgado, M.; Blanco, A. *Adv. Mater.* **1997**, *9*, 257; Park, S. H.; Qin, D.; Xia, Y. *Adv. Mater.* **1998**, *10*, 1028; Alejandro-Arellano, M.; Blanco, A.; Ung, T.; Mulvaney, P.; Liz-Marzán, L. M. *Pure Appl. Chem.* **2000**, *72*, 257.

(4) Imhof, A.; Pine, D. J. *Nature* **1998**, *389*, 948; Bertone, J. F.; Jiang, P.; Hwang, K. S.; Mittleman, D. M.; Colvin, V. L. *Phys. Rev. Lett.* **1999**, *83*, 300.

(5) Caruso, F.; Susha, A. S.; Giersig, M.; Möhwald, H. *Adv. Mater.* **1999**, *11*, 950.

(6) Rogach, A.; Susha, A.; Caruso, F.; Sukhorukov, G. Kornowski, A.; Kershaw, S.; Möhwald, H.; Eychmüller, A.; Weller, H. *Adv. Mater.* **2000**, *12*, 333.

(7) Westcott, S. L.; Oldenburg, S. J.; Randall, L.; Halas, N. J. *Langmuir* **1998**, *14*, 5396; Oldenburg, S. J.; Averitt, R. D.; Westcott, S. L.; Halas, N. J. *Chem. Phys. Lett.* **1998**, *288*, 243.

(8) Dokoutchaev, A.; James, J. T.; Koene, S. C.; Pathak, S.; Prakash, G. K. S.; Thompson, M. E. *Chem. Mater.* **1999**, *11*, 2389; Mayer, A. B. R.; Grebner, W.; Wannemacher, R. *J. Phys. Chem. B* **2000**, *104*, 7278.

(9) Percy, M. J.; Barthet, C.; Lobb, J. C.; Khan, M. A.; Lascelles, S. F.; Vamvakaki, M.; Armes, S. P. *Langmuir* **2000**, *16*, 6913.

(10) Henglein, A. *J. Phys. Chem.* **1993**, *97*, 5457; Mulvaney, P. *Langmuir* **1996**, *12*, 788.

(11) Freeman, R. G.; Grabar, K. C.; Allison, K. J.; Bright, R. M.; Davis, J. A.; Guthrie, A. P.; Hommer, M. B.; Jackson, M. A.; Smith, P. C.; Walter, D. G.; Natan, M. J. *Science* **1995**, *267*, 1629.

(12) Penner, R. M.; Martin, C. R. *Anal. Chem.* **1987**, *59*, 2625.

(13) Ung, T.; Liz-Marzán, L. M.; Mulvaney, P. *J. Phys. Chem. B*, in press.

(14) Nakanishi, T.; Ohtani, B.; Uosaki, K. *J. Phys. Chem. B* **1998**, *102*, 1571.

(15) Hu, K.; Brust, M.; Bard, A. J. *Chem. Mater.* **1998**, *10*, 1160.

(16) Li, Q. Q.; Fan, S. S.; Han, W. Q.; Sun, C. H.; Liang, W. S. *Jpn. J. Appl. Phys.* **1997**, *36*, L501.

(17) Ang, L.-M.; Hor, T. S. A.; Xu, G.-Q.; Tung, C.; Zhao, S.; Wang, J. L. S. *Chem. Mater.* **1999**, *11*, 2115−2118.

(18) Mallory, G. O., Hajdu, J. B., Eds. *Electroless Plating: Fundamentals and Applications*; American Electroplaters and Surface Finishers Society: Orlando, Fl, 1990; Chapter 1, pp 1−55.

10.1021/cm001240g CCC: $20.00

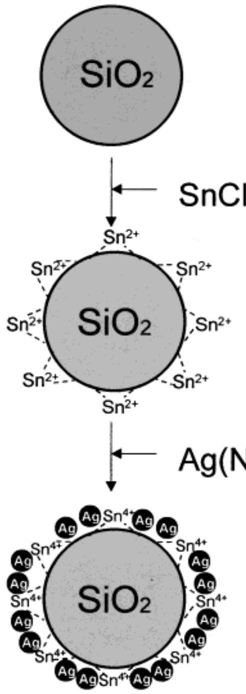

Figure 1. Sketch of surface reactions produced during the formation of silver nanoparticles on colloidal silica spheres.

distilled before use. In all preparations absolute ethanol (Scharlab) and Milli-Q water were used.

Preparation. Monodispersed colloidal silica particles were prepared by the well-known Stöber method,[19] which comprises the base-catalyzed hydrolysis of TES in water−ethanol mixtures. More specifically, aqueous ammonia, 11.9 mL, and ethanol, 88.1 mL, were mixed in an Erlenmeyer flask. This solution was placed in a water bath at 20 °C under stirring. Then, 3.6 mL of TES was added quickly under vigorous stirring. Gentle stirring was continued for at least 15 h to ensure that the reaction was complete. These preparation conditions resulted in a particle size of 223 ± 15 nm. The solvent was then exchanged by centrifuging at 3000 rpm for 30 min, removing the supernatant and adding 50% (v/v) methanol/water. This procedure was repeated a second time to complete the solvent exchange. To 1 mL of the silica colloid in water/methanol, with a silica concentration of 1.1 wt %, was added 9 mL of a solution of $SnCl_2$ (0.029 M) and CF_3COOH (0.072 M) in a 50% (v/v) methanol/water mixture. This resulted in deposition of the "sensitizer" (Sn^{2+}) onto colloid surfaces (*SiO_2@Sn^{2+}*). Forty-five minutes later, the colloid was washed twice, centrifuging at 3000 rpm for 30 min, removing supernatant, and adding water. To 1 mL of the colloid was added 9 mL of an aqueous solution of ammonical $AgNO_3$ (0.039 M). This resulted in the deposition of Ag nanoparticles on the colloid surfaces (*SiO_2@Ag-1*). After 5 min, the colloid was cleaned again using centrifugation and redispersion in water. For the second Ag deposition, the same procedures were performed (*SiO_2@Ag-2*).

Characterization. Transmission electron microscopy (TEM) was performed with a Philips CM20 microscope operating at 200 kV. UV−visible spectra were recorded on a Hewlett-Packard HP8453A diode-array spectrophotometer, using quartz cuvettes with 1-mm optical path length. X-ray photoelectron spectra (XPS) were measured at an angle of 0° using a VG EscaLab 220-IXL system. As an X-ray source, the Al Kα line was used, with a spectrophotometer step energy of 1486.92 and 0.1-eV resolution. Atomic force microscopy (AFM) was measured with a TOPOMETRIX Discoverer-Explorer unit, operating with a 1-μm scanner.

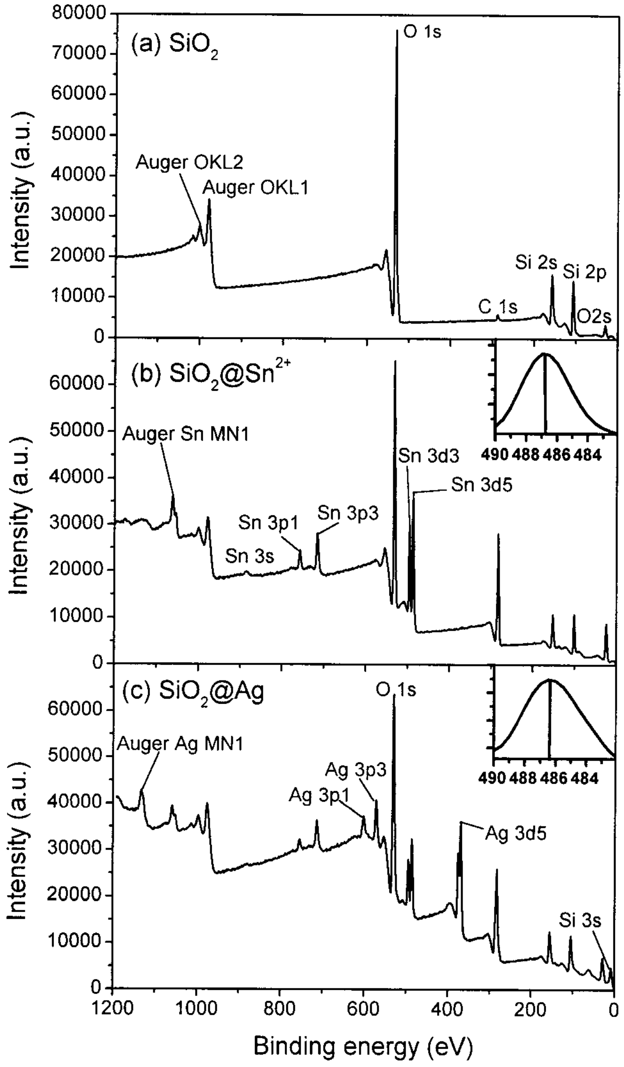

Figure 2. XPS spectra of silica spheres during the successive deposition steps. For each step, only the new peaks are labeled. The insets in b and c show an enlargement of the Sn $3d_5$ peaks for identification of the Sn oxidation state.

Results and Discussion

The technique for electroless metal plating[18] is based on the use of a chemical reducing agent that permits the reduction of the metal from solution on the surface of the substrate. For this process, the surface needs not be electronically conducting, while the kinetics of electron transfer should be slow enough to avoid the reduction of the metal ions and nucleation in solution. The surface acts then as a catalyst to ensure that reduction only takes place on the surface, so that the metal remains attached. In general, metal nanoparticles such as Ag or Pd need to be deposited as a catalyst on surfaces in advance (the pretreatment steps). The procedure used for the present work is similar to that used by Menon and Martin[20] on the pores of filtration membranes. The two basic steps involved are sketched in Figure 1. First, Sn^{2+} ions adsorb on the surface of the spherical silica particles. After removal of the excess Sn^{2+} ions from solution through several consecutive centrifugation/redispersion steps, ammonical $AgNO_3$ is

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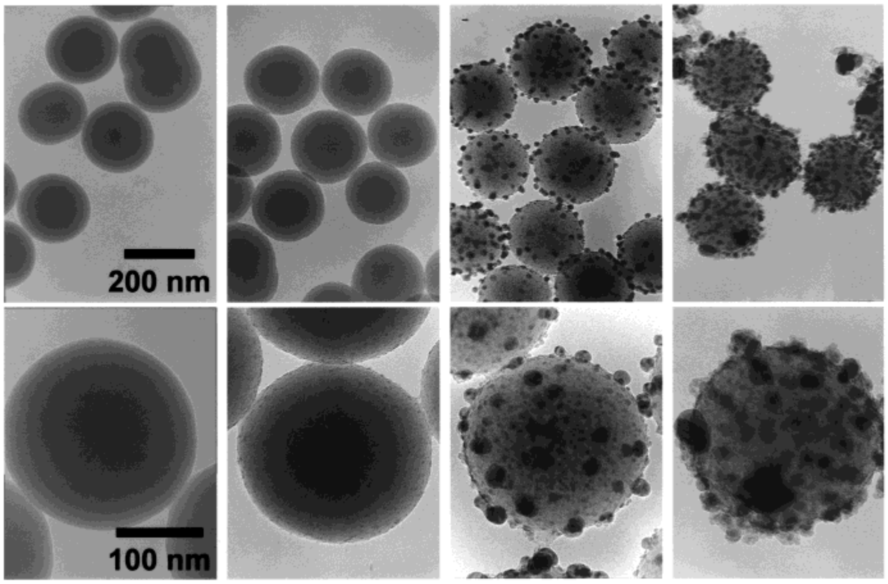
(19) Stöber, W.; Fink, A.; Bohn, E. *J. Colloid Interface Sci.* **1968**, *26*, 62.

(20) Menon, V. P.; Martin, C. R. *Anal. Chem.* **1995**, *67*, 1920.



(a) SiO_2 (b) $SiO_2@Sn^{2+}$ (c) $SiO_2@Ag$-1 (d) $SiO_2@Ag$-2

Figure 3. TEM micrographs of silica spheres during the successive deposition steps. Upper and lower photos were taken at lower and higher magnifications, respectively. Scale bars correspond to all four photos in each row.

added to the solution so that a redox reaction occurs involving the oxidation of surface Sn^{2+} to Sn^{4+} and reduction of Ag^+ to Ag^0.

The first step is performed by simple addition of 0.029 M of $SnCl_2$ and 0.072 M of trifluoroacetic acid in 50% (v/v) methanol/water solution. Trifluoroacetic acid acts here as a surfactant to facilitate the dissolution of $SnCl_2$. The adsorption of Sn^{2+} ions on the surface takes place through electrostatic interaction with the negatively charged silica surface. After this first step, the colloid remained milky white, indicating that Sn^{2+} does not have any effect on the optical properties of the colloid. The presence of adsorbed tin ions on the particle surface was confirmed by XPS, as shown in Figure 2. The basic difference between Figure 2a and 2b is the presence of Sn peaks, even after thorough cleaning of the system. The oxidation state of the tin ions on the surface can be estimated from the precise peak position of the 3d peaks. According to the literature, the $3d_5$ peak for Sn^{2+} should be placed around 486.7 eV[21] and that for Sn^{4+} should be around 486.5 eV,[21] which is very close and therefore hard to distinguish, while the zerovalent, metallic Sn is assigned to 484.9 eV.[22] The peak position for the $3d_5$ transition measured from a close-up of Figure 2b was found to be 486.8 eV, which basically coincides with the assignment for Sn^{2+}, and it definitely excludes Sn^0.

Figure 3 shows representative TEM micrographs from each step of the process. After adsorption of Sn^{2+} ions, the only visible difference is the presence of tiny darker dots on the silica surface. These may just indicate a slight increase in electron density due to the presence of the metal ions.

Once the particle surface has been homogeneously modified, the addition of a silver salt leads to the selective redox reaction on the surface. This process has also been confirmed by XPS measurements. For this sample, the Sn $3d_5$ peak is located at 486.4 eV. Although, as mentioned above, it is difficult to distinguish between Sn^{2+} and Sn^{4+}, this peak position seems to indicate that the oxidation of Sn^{2+} has indeed taken place and some Sn^{4+} ions are still adsorbed on the surface. Again, it is clear that no metallic Sn is present. With regard to silver, Ley et al.[23] assigned the Ag $3d_5$ peak for the metal to 368.5 eV, while for Ag^{2+} it is assigned to 367.2 and for Ag^+ to 367.6 eV.[21] In our sample (Figure 2c), the Ag $3d_5$ peak is centered at 368.9 eV, which is close to the literature value for Ag^0.

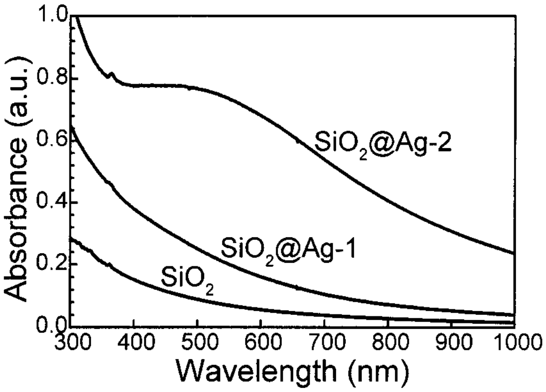


Figure 4. UV–vis absorption spectra of silica colloids during the successive deposition steps. The silver plasmon band is only visible after the second deposition.

The morphology of these nanoparticles comprises a myriad of individual, remarkably monodisperse silver nanoparticles with a diameter of 21.9 ± 2.4 nm uniformly distributed on the surface of the silica spheres, which was additionally confirmed by TEM (Figure 3c). The formation of metallic silver upon addition of Ag ions was also reflected in a color change to dark yellow.[10]

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(21) Briggs, D.; Seah, M. P. *Pratical Surface Analysis*, 2nd ed.; John Wiley & Sons: New York, 1993; Vol. 1.

(22) Barr, T. L. *J. Phys. Chem.* **1978**, *82*, 1801.

(23) Ley, L.; Cardona, M.; Baer, Y.; Campagna, M.; Grobman, W. D.; Hochst, H.; Hufner, S.; Koch, E. E.; Kunz, C.; Pollak, R. A.; Steigner, P.; Wertheim, G. K. *Topics in Applied Physics*; Ley, L., Cardona, M., Eds.; Springer-Verlag: Berlin, 1979; Vol. 27.

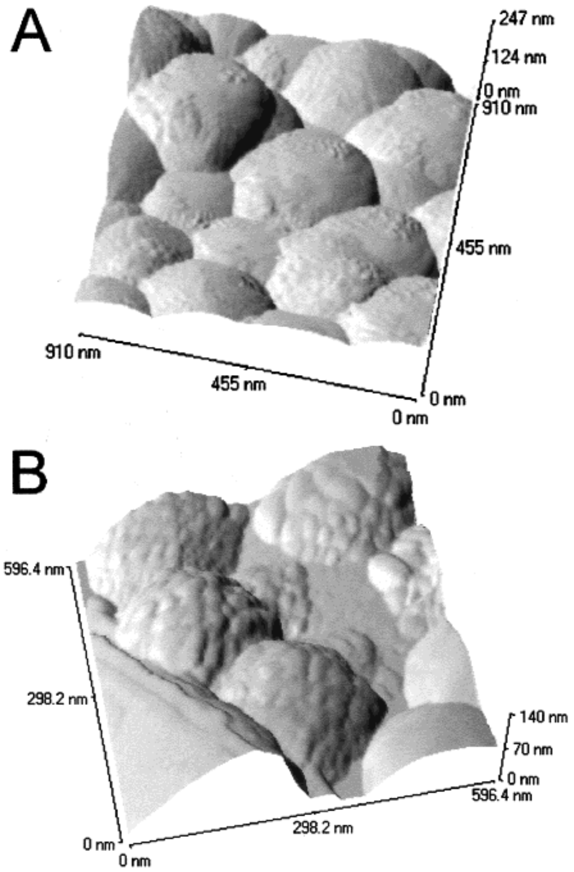

Figure 5. Three-dimensional representation of AFM images showing the surface roughness after the first (A) and second (B) deposition steps.

Figure 4 shows the UV−visible spectra of the silica colloids before and after silver deposition. Although an absorption peak that is attributed to the surface plasmon resonance is generally observed at around 400 nm in Ag nanoparticles, no remarkable peaks were found for the SiO_2@Ag-1 colloid. Obviously, the Ag surface plasmon band is screened by the strong scattering from the silica colloid.

To deposit a larger amount of Ag nanoparticles, a second coating step was carried out by repetition of the same steps involved in the first coating. TEM (Figure 3d) shows that the surface coverage by Ag nanoparticles was increased, either through the formation of new, small particles or through the growth of previously existing Ag nanoparticles. The Ag particle size ranges in this sample from 13.3 to 60.0 nm. In this case, opposite to the first step, a small amount of Ag particles were also observed away from the silica surfaces, which might be the result of detachment from the silica particles after deposition.

A comparison of the roughness of the particle surface, indicating the degree of coverage by the metal particles, was performed by AFM. Representative images are shown in Figure 5, where it can clearly be observed that after a second silver deposition the surface is more homogeneously covered than after a single deposition step. An estimate of the silver particle size from the AFM images basically coincides with that obtained from TEM.

In the UV−vis absorption spectrum, a broad peak was observed, which was centered around 500 nm, that is, clearly red-shifted with respect to the usual surface plasmon peak position of Ag nanoparticles. Such a red shift is partly attributed to the formation of larger particles (see Figure 3), but mainly to the interaction between neighboring particles, which was shown before to promote both red-shift and broadening of the plasmon bands for thin films on flat substrates[13,24] and also for gold nanoparticles deposited on silica spheres.[7]

Conclusions

It was demonstrated that electroless deposition is a suitable technique for the uniform deposition of Ag nanoparticles on the surface of silica colloid spheres. We have shown that the reduction of Ag^+ ions occurs selectively at the silica surface and the reduction occurs in a uniform manner, therefore producing rather monodisperse metal nanoparticles. The amount of silver deposited on the silica surface can be controlled through the number of coating steps, though we have been unable to obtain a complete metallic shell. This work opens up new possibilities for the deposition of other metals such as gold, which will be reported elsewhere.

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(24) Grabar, K. C.; Allison, K. J.; Baker, B. E.; Bright, R. M.; Brown, K. R.; Freeman, R. G.; Fox, A. P.; Keating, C. D.; Musick, M. D.; Natan, M. J. *Langmuir* **1996**, *12*, 2353.