Silica-Coating and Hydrophobation of CTAB-Stabilized Gold Nanorods

Isabel Pastoriza-Santos,* Jorge Pérez-Juste,* and Luis M. Liz-Marzán

Departamento de Química Física, Universidade de Vigo, Vigo 36310, Spain

Received February 6, 2006
Revised Manuscript Received April 6, 2006

Size and shape control of metal nanoparticles has been the focus of continuous efforts during the past decades.[1−5] In particular, gold and silver nanoparticles have been intensely studied because of their characteristic size- and shape-dependent optical properties, which make them interesting for a wide variety of applications.[6−9] Recently, various wet chemical approaches have been developed for the synthesis of either spherical or anisometric metal nanoparticles.[4,10−12] The most-successful methods for size and shape control rely on the use of cationic surfactant cetyltrimethylammonium bromide (CTAB) as the "shape-inducing" agent. The synthesis of gold nanorods is, to date, the clearest example of size and shape control in aqueous surfactant solutions, leading in turn to a fine-tuning of the optical properties of the system in the visible and NIR spectral regions.[13−16] This particular micellar environment enhances nanoparticle stability under aggressive conditions, such as centrifugation, high ionic strength, etc., as compared to other aqueous synthetic protocols,[17] but such stability is conditioned to the presence of CTAB molecules in a narrow concentration range close to its critical micelle concentration. On the other hand, the strong binding of CTAB molecules to the gold surface makes surface hydrophobation difficult.[18] Only a couple of recent papers successfully deal with this issue of aiming to phase transfer into organic solvents, but this is achieved only under very strict experimental conditions.[19,20] Silica coating of gold nanorods appears as an attractive alternative for their manipulation and for providing enhanced colloidal stability. Although several procedures have been developed for silica-coating of colloidal particles,[21−23] the selection of a suitable method is mainly determined by the chemical affinity of the surface material for silica. While some materials such as magnetite,[24] titania,[25] zirconia,[26] or some clays[27] can be directly coated with silica, most materials require the presence of a polymer[22] or a silane coupling agent[21] on the surface. Silica-coating of citrate-stabilized gold nanoparticles has been achieved by means of two main protocols, that make use of surface priming with either a silane coupling agent[21] (aminopropyltrimethoxysilane, APS) or poly(vinylpyrrolidone) (PVP),[22] which not only facilitates transfer into ethanol but also promotes silica coating. However, for CTAB-stabilized gold nanoparticles, the strong binding of the surfactant to the gold nanoparticle surface makes its displacement by APS or MPS (the equivalent mercapto-silane) molecules difficult especially at the flat sides of the nanorods; displacement is more favorable at the tips, which has been exploited in several recently published end-to-end linkage protocols.[28−31] Although Murphy et al.[32] reported the use of MPS for the coating of high-aspect-ratio gold rods, we have found that for small aspect ratio nanorods, the reproducibility is poor and particle aggregation (again, preferentially through the tips) is usually observed during the sodium silicate addition step.[33,34] On the other hand, coating through PVP capping[22] has also been found to fail for these particles. CTAB-coated nanoparticles can indeed be transferred into ethanol upon functionalization with the slightly negatively charged polymer PVP;[35] however, controlled hydrolysis and condensation of TEOS on the nanoparticle surface could not be achieved, probably because the remaining CTAB monomers promote the formation of mesoporous silica.[36,37] Even when using 2-propanol as a solvent to favor growth over

* To whom correspondence should be addressed. Fax: 34 986812556. Tel: 34 986813813. E-mail: pastoriza@uvigo.es (I.P.-S.); juste@uvigo.es (J.P.-J.).

(1) Liz-Marzán, L. M. *Mater. Today* **2004**, *7*, 26.
(2) Kelly, K. L.; Coronado, E.; Zhao, L. L.; Schatz, G. C. *J. Phys. Chem. B.* **2003**, *107*, 668.
(3) Liz-Marzán, L. M. *Langmuir* **2006**, *22*, 32.
(4) Pérez-Juste, J.; Pastoriza-Santos, I.; Liz-Marzán, L. M.; Mulvaney, P. *Coord. Chem. Rev.* **2005**, *249*, 1870.
(5) Burda, C.; Chen, X.; Narayanan, R.; El-Sayed, M. A. *Chem. Rev.* **2005**, *105*, 1025.
(6) Haes, A. J.; Van Duyne, R. P. *J. Am. Chem. Soc*. **2002**, *124*, 10596.
(7) Dirix, Y.; Bastiaansen, C.; Caseri, W.; Smith, P. *Adv. Mater*. **1999**, *11*, 223.
(8) Wilson, O.; Wilson, G. J.; Mulvaney, P. *Adv. Mater.* **2002**, *14*, 1000.
(9) Pérez -Juste, J.; Rodríguez-González, B.; Mulvaney, P.; Liz-Marzán, L. M. *Adv. Funct. Mater.* **2005**, *15*, 1065.
(10) Pileni, M. P. *Nature Mater.* **2003**, *2*, 145.
(11) Sun, Y. G.; Xia, Y. N. *Analyst* **2003**, *128*, 686.
(12) Murphy, C. J.; Sau, T. K.; Gole, A. M.; Orendorff, C. J.; Gao, J.; Gou, L.; Hunyadi, S. E.; Li, T. J. *J. Phys. Chem. B* **2005**, *109*, 13857.
(13) Jana, N. R.; Gearheart, L.; Murphy, C. J. *J. Phys. Chem. B* **2001**, *105*, 4065.
(14) Nikoobakht, B.; El-Sayed, M. A. *Chem. Mater.* **2003**, *15*, 1957.
(15) Pérez-Juste, J.; Rodríguez-González, B.; Mulvaney, P.; Liz-Marzán, L. M. *Adv. Funct. Mater.* **2005**, *15*, 1065.
(16) Liu, M.; Guyot-Sionnest, P. *J. Phys. Chem. B* **2005**, *109*, 22192.
(17) Enustun, B. V.; Turkevich, J. *J. Am. Chem. Soc*. **1963**, *85*, 3317.
(18) Nikoobakht, B.; El-Sayed, M. A. *Langmuir* **2001**, *17*, 6368.
(19) Wei, G.-T.; Yang, Z.; Lee, C.-Y.; Yang, H.-Y.; Wang, C. R. *J. Am. Chem. Soc.* **2004**, *126*, 5036.
(20) Yang, J.; Wu, J.; Wu, Y.; Wang, J.; Chen, C. *Chem. Phys. Lett.* **2005**, *416*, 215.
(21) Liz-Marzán, L. M.; Giersig, M.; Mulvaney, P. *Langmuir* **1996**, *12*, 4329.
(22) Graf, C.; Vossen, D. L. J.; Imhof, A.; van Blaaderen, A. *Langmuir* **2003**, *19*, 6693.
(23) Liu, S.; Hang, M. *Adv. Funct. Mater*. **2005**, *15*, 961.
(24) Philipse, A. P.; van Bruggen, M. P. B.; Pathmamanoharan, C. *Langmuir* **1994**, *10*, 92.
(25) Bechger, L.; Koenderink, A. F.; Vos, W. L. *Langmuir* **2002**, *18*, 2444.
(26) Ryan, J. N.; Elimelech, M.; Baeseman, J. L.; Magelky, R. D. *Environ. Sci. Technol.* **2000**, *34*, 2000.
(27) Iler, R. K. U.S. Patent 2885366, 1959.
(28) Chang, J.-Y.; Wu, H.; Chen, H.; Ling, Y.-C.; Tan, W. *Chem. Commun.* **2005**, 1092.
(29) Caswell, K. K.; Wilson, J. N.; Bunz, U. H. F.; Murphy, C. J. *J. Am. Chem. Soc.* **2003**, *125*, 13914.
(30) Thomas, K. G.; Barazzouk, S.; Ipe, B. I.; Joseph, S. T. S.; Kamat, P. V. *J. Phys. Chem. B* **2004**, *108*, 13066.
(31) Sudeep, P. K.; Joseph, S. T. S.; Thomas, K. G. *J. Am. Chem. Soc.* **2005**, *127*, 6516.
(32) Obare, S. O.; Jana, N. R.; Murphy, C. J. *Nano Lett.* **2001**, *1*, 601.
(33) Chang, S.-S.; Shih, C.-W.; Chen, C.-D.; Lai, W.-C.; Wang, C. R. C. *Langmuir* **1999**, *15*, 701.
(34) Pérez-Juste, J.; Correa-Duarte, M. A.; Liz-Marzán, L. M. *Appl. Surf. Sci.* **2004**, *226*, 137.
(35) Pastoriza-Santos, I.; Gomez, D.; Pérez-Juste, J.; Liz-Marzán, L. M.; Mulvaney, P. *Phys. Chem. Chem. Phys.* **2004**, *6*, 5056.

10.1021/cm060293g CCC: $33.50
Published on Web 04/25/2006

nucleation,[38] we observed nucleation of silica particles, which stick onto the gold nanorod surface, but no homogeneous coating (see the Supporting Information, Figure S1).

We report here a novel silica-coating procedure that has been devised for CTAB-stabilized gold nanorods but that can be readily extended to other CTAB-stabilized nanoparticles. The method comprises a combination of the polyelectrolyte layer-by-layer (LBL) technique[39−41] and the hydrolysis and condensation of tetraethoxy silane (TEOS) in a- 2-propanol−water mixture and leads to homogeneous coatings with tight control on shell thickness. As previously reported,[42] the silica shell thickness affects the position of the surface plasmon band; it can be used to control the dipolar interactions between particles but also improves the versatility of the particles, because it enhances the stability in polar solvents and can be easily functionalized to allow transfer to organic solvents.

The gold nanorods were prepared by the seeding growth method in aqueous CTAB solution (see the Supporting Information for experimental details).[14] Several parameters can be manipulated in this method to tune the geometry of the particles, through which the optical response can be easily manipulated. Although this procedure can be applied to colloids with various dimensions, we selected for demonstration a colloid with an average length of 52.1 ± 8.2 nm and width of 12.9 ± 1.9 nm, which combines small size and a notable deviation from sphericity (aspect ratio ≈ 4). In agreement with many previous publications, the aqueous dispersion showed a plasmon absorption band centered around 870 nm. Because the CTAB-stabilized gold nanorods possess a high positive surface charge (+20 mV), LBL wrapping of negative polyelectrolyte chains around the metal nanoparticles is strongly favored. After removing excess surfactant by centrifugation, the particles were redispersed in water and added dropwise under vigorous stirring to an aqueous solution of polystyrene sulfonate (PSS). PSS adsorption was allowed to proceed for 3 h; the process was then repeated with a positively charged polyelectrolyte (poly(allylamine hydrochloride), PAH) after a washing step to remove excess PSS. Two polyelectrolyte layers have been found to completely screen the effect of CTAB on the gold nanoparticle surface. It was necessary to use polyelectrolytes with low molecular weight and polymer solutions with low ionic strength (see experimental details at the Supporting Information) because high-molecular-weight polymers induced bridging flocculation and high ionic strength led to aggregation through double-layer compression, as previously reported for polyelectrolyte deposition on Au nanospheres.[39] The key point at this stage for successful silica coating is the transfer of the nanoparticles into a 2-propanol−water mixture, which is hindered by the high positive surface potential (+36 mV) of PAH-coated nanoparticles, promoting rapid aggregation. PVP (slightly negatively charged under these experimental conditions) was used to partially screen the surface charge ($\zeta = +16$ mV), allowing redispersion in 2-propanol and subsequent silica coating through the well-known Stöber method.[43] The transmission electron micrographs in Figure 1 show the effectiveness of this method for deposition of silica shells with accurate thickness control. For thin shells (Figure 1a), the silica surface is rough, probably because of the presence of polyelectrolyte chains on the nanoparticles,[44] whereas upon subsequent additions of TEOS, the thickness of the silica shells increases and the surface quickly becomes smoother. It is interesting to point out that isotropic hydrolysis and condensation of TEOS occurs on anisotropic nanoparticles, in such a way that the ellipticity of silica-coated gold nanorods decreases as the shells become thicker.

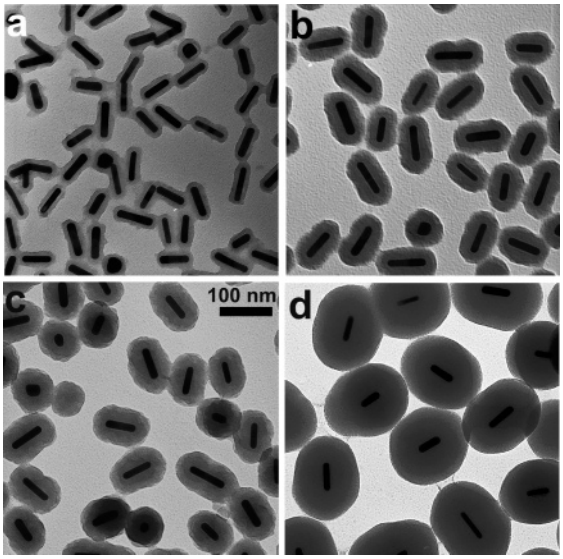

Figure 1. Transmission electron micrographs (TEM) of silica-coated gold nanorods, with silica shell thickness increasing from a to d. The scale is the same for all images.

The effect of the coating on the optical response of these silica-coated gold ($Au@SiO_2$) nanorods is shown in Figure 2a. Whereas the transverse plasmon band remains almost unaltered, the longitudinal surface plasmon (SPL) band redshifts upon the first silica deposition because of an increase in the local refractive index around the rods produced by the silica shell; for shells thicker than 30 nm, no further shift is observed.[21] Additionally, the absorbance at wavelengths bellow 650 nm clearly increases because of the stronger light scattering derived from the larger particle size as the silica shell is further grown. Simple calculations based on Mie-Gans theory for coated ellipsoids[4] (Figure 2b) show a very similar trend, though the longitudinal plasmon bands peak at lower wavelengths, as previously reported, probably due to geometrical differences between the experimental rods and the ellipsoids considered in the model.[45−47]

(36) Kim, W.-J.; Yang, S.-M. *Chem. Mater.* **2000**, *12*, 3227.
(37) Nooney, R. I.; Thirunavukkarasu, D.; Chen, Y.; Josephs, R.; Ostafin, A. E. *Chem. Mater.* **2002**, *14*, 4721.
(38) Im, S. H.; Herricks, T.; Xia, Y. *Chem. Phys. Lett.* **2005**, *401*, 19.
(39) Gittins, D. I.; Caruso, F. *J. Phys. Chem. B* **2001**, *105*, 6846.
(40) Schneider, G.; Decher, G. *Nano Lett.* **2004**, *4*, 1833.
(41) Gole, A.; Murphy, C. J. *Chem. Mater.* **2005**, *17*, 1325.
(42) Liz-Marzán, L. M.; Mulvaney, P. *J. Phys. Chem. B* **2003**, *107*, 7312.
(43) Stöber, W.; Fink, A.; Bohn, E. *J. Colloid Interface Sci.* **1968**, *26*, 62.
(44) Wang, Y.; Tang, Z.; Liang, X.; Liz-Marzán, L. M.; Kotov, N. A. *Nano Lett.* **2004**, *4*, 225.
(45) Brioude, A.; Jiang, X. C.; Pileni, M. P. *J. Phys. Chem. B* **2005**, *109*, 13138.
(46) Lee, K.-S.; El-Sayed, M. A. *J. Phys. Chem. B* **2005**, *109*, 20331.
(47) Pecharromán, C.; Pérez-Juste, J.; Mulvaney, P.; Liz-Marzán, L. M. Manuscript in preparation.

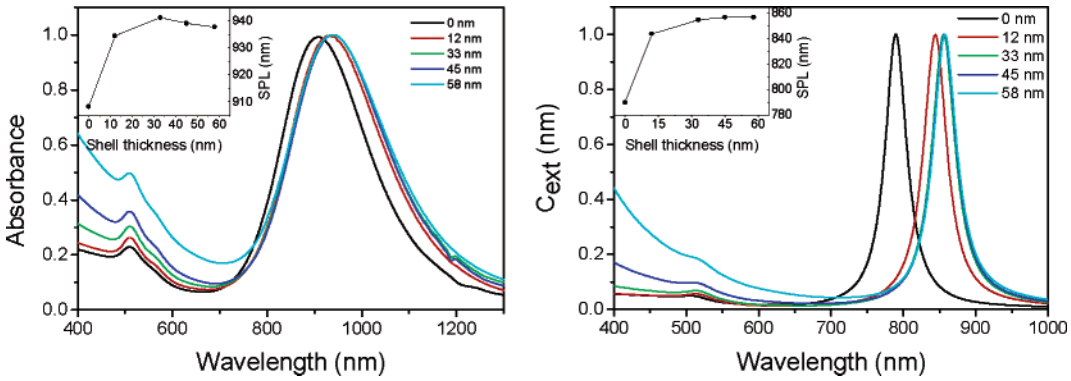

Figure 2. Normalized experimental (left) and calculated (right) UV−visible−NIR spectra of Au@SiO_2 gold nanorods in 2-propanol, with increasing silica shell thickness. The insets summarize the shift of the longitudinal surface plasmon (SPL) with increasing shell thickness.

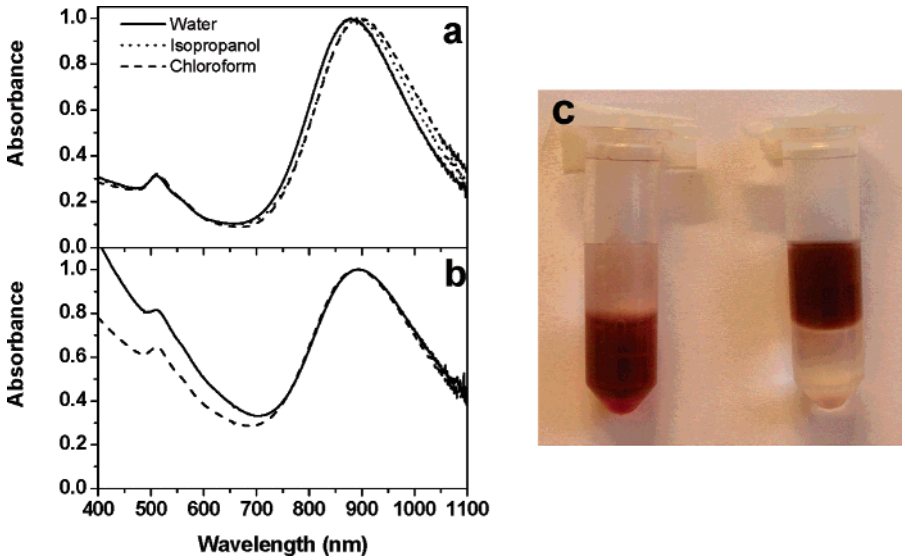

Figure 3. (a,b) UV−visible−NIR spectra of Au@SiO_2 gold nanorods with (a) thin and (b) thick silica shells in various solvents. (c) Photographs of silica-coated nanorod dispersions in water and chloroform mixtures before (right) and after (left) hydrophobation of the silica shell with OTMS.

Because the surface chemistry of the silica-coated gold rods is identical to that of pure silica colloids, functionalization can be achieved through chemical bonding with a large variety of available silane coupling agents. As a useful example, we demonstrate here functionalization with octadecyltrimethoxysilane (OTMS),[48,49] which contains a long hydrophobic hydrocarbon chain, thus allowing the particles to be transferred into nonpolar organic solvents such as chloroform. TEM images of OTMS-modified Au@SiO_2 nanorods (see the Supporting Information, Figure S3) confirm that no aggregation occurred during the process, and an increased degree of order can be observed on the TEM grids. This technique can be used for controlling the ordering and orientation of the particles in one, two, or three dimensions through different well-established techniques such as sedimentation or Langmuir−Blodgett deposition (experiments in this direction are underway). The stability of the resulting organosols is also reflected in the absorbance spectra, as illustrated in Figure 3 for rods with thin (15 nm) and thick (40 nm) shells. Whereas for thickly coated rods (Figure 3b), the peak positions remain unaltered and only scattering is reduced (because of a lower refractive index contrast between shells and solvent), rods with thin shells can still "feel" the refractive index of the solvent and therefore there is a further red-shift upon transfer into solvents with increasing refractive index.

In summary, we have successfully developed a method for the silica coating of CTAB-stabilized nanoparticles with excellent shell-thickness control. Coating of Au nanorods has been demonstrated, but the protocol can be readily extended to other CTAB-capped nanoparticles and opens a new avenue for further processing through silica coating, such as solvent transfer, biofunctionalization, and creation of nanostructured materials with controlled dimensions and interactions. Additionally, because the aspect ratio is observed to decrease upon growth of the silica shell, we foresee the possibility of creating spherical silica particles with controlled (anisotropic) optical response in the visible and NIR, which can be used for fabrication of sophisticated photonic structures.

Acknowledgment. Support from the Spanish Ministerio de Educación y Ciencia/FEDER (Project MAT2004-02991) is gratefully acknowledged. The authors thank Ana Sánchez-Iglesias for technical assistance.

Supporting Information Available: Experimental and instrumental details, TEM images of noncoated Au@PVP nanorods, CTAB-stabilized gold nanoparticles coated with silica, and OTMS-modified Au@SiO_2 nanorods. This material is available free of charge via the Internet at http://pubs.acs.org.

CM060293G

(48) Wang, W.; Gu, B.; Liang, L. Y.; Hamilton, W. *J. Phys. Chem. B* **2003**, *107*, 3400.
(49) Pastoriza-Santos, I.; Pérez-Juste, J.; Kickelbick, G.; Liz-Marzán, L. M. *J. Nanosci. Nanotechnol.* **2006**, *6*, 4.