CHEMISTRY OF MATERIALS
Article

Chem. Mater. **2009,** *21,* 2835–2839 2835
DOI:10.1021/cm900436n

Encapsulation of Silver Nanoparticles into Polystyrene Microspheres

Amar S. Kumbhar[†,‡] and George Chumanov*[,†]

[†]*Department of Chemistry, Clemson University, Clemson, South Carolina 29634-0919.*
[‡]*Current Address: CHANL Instrumentation Facility, Institute for Advanced Materials, NanoScience and Technology, Chapel Hill, North Carolina 27599-3216.*

Received February 15, 2009. Revised Manuscript Received April 21, 2009

Hydrogen reduction of a saturated silver(I) oxide solution at elevated temperatures in the presence of ~200 nm polystyrene (PS) microspheres followed by acetone treatment lead to the encapsulation of the resulting silver nanoparticles (Ag NPs) into the PS microspheres. Extinction spectra reveal an expected red-shift of the characteristic plasmon resonance frequency of Ag–PS core–shell particles due to the increase in the surrounding dielectric constant. The Ag–PS core–shell particles maintain their stability when redispersed back into water.

Introduction

Inorganic–polymer hybrid nanocomposites have been an important topic of current research. Inorganic–polystyrene nanocomposites are particularly interesting because polystyrene (PS) polymers can be synthesized to form highly monodisperse spheres in the nanometer to micrometer size range. There have been two approaches used to synthesize inorganic–PS hybrid nanoparticles. One approach involves coating PS spheres with an inorganic layer prepared using various surface modification techniques.[1–9] Due to the difference in the dielectric properties between the PS core and the inorganic shell, tunable plasmonic properties were observed for Au- and Ag-coated PS spheres.[2,7] The PS core–inorganic shell spheres can also form highly ordered three-dimensional structures and were investigated as photonic band gap materials, for example, ZnS-coated polystyrene core–shell particles.[1] The second approach involves encapsulating inorganic nanoparticles with a thin dielectric layer of PS to form an inorganic core–PS shell nanostructure. Emulsion polymerization in the presence of inorganic nanoparticles is extensively used for preparing such inorganic–PS hybrid core–shell nanostructures.[10–14] The PS layer surrounding the particles imparts chemical resistance, preserving properties of the encapsulated inorganic particles in aggressive environments. Recently, a new method has been reported which involves swelling of the PS beads in the presence of toluene followed by heat treatment, leading to the encapsulation of iron oxides inside the polymer beads.[15] Here, we report the synthesis of Ag NPs in the presence of PS spheres. Silver nanoparticles exhibit surface plasmons in the visible spectral region owing to the favorable frequency dependence of the real and imaginary parts of the metal dielectric function. Complete encapsulation of the Ag NPs within the PS microspheres was achieved using acetone as a swelling agent. The formation of the Ag–PS core–shell structure was monitored using UV-extinction spectra because the frequency and the strength of the plasmon resonance depend on the shape, size, and surrounding dielectric media.[16–18] Red-shifts of the plasmon resonance and electron microscopy images confirmed the formation of Ag–PS core–shell structures.

Experimental Section

Materials. Silver(I) oxide (Alfa Aesar, 99.998%), ultra-high-purity hydrogen gas (Air Gas), polybead polystyrene microspheres (~200 nm; Polysciences Inc.), and acetone (Fisher Scientific) were used without further purification. Millipore pure water (18 MΩ) was used throughout the synthesis procedures.

---

*Corresponding author. E-mail: gchumak@clemson.edu.

(1) Breen, M. L.; Dinsmore, A. D.; Pink, R. H.; Qadri, S. B.; Ratna, B. R. *Langmuir* **2001**, *17*(3), 903–907.
(2) Peceros, K. E.; Xu, X.; Bulcock, S. R.; Cortie, M. B. *J. Phys. Chem. B* **2005**, *109*, 21516–21520.
(3) Li, Y.; Liu, E. C. Y; Pickett, N.; Skabara, P. J.; Cummins, S. S.; Ryley, S; Sutherland, A J.; O'Brien, P. *J. Mater. Chem.* **2005**, *15*, 1238–1243.
(4) Dong, A. G.; Wang, Y. J.; Tang, Y.; Ren, N.; Yang, W. L.; Gao, Z. *Chem. Commun.* **2002**, 350–351.
(5) Song, C.; Wang, D.; Lin, Y.; Gu, G.; Fu, X.; Hu, Z. *Nanotechnology* **2004**, *15*, 962–965.
(6) Zhang, J.; Liu, Z.; Han, B.; Li, J.; Li, Z.; Yang, G. *J. Nanosci. Nanotech.* **2005**, *5*, 945–950.
(7) Yong, K.; Sahoo, Y.; Swihart, M. T.; Prasad, P. N. *Colloids Surf., A* **2006**, *290*, 89–105.
(8) Zhang, J.; Liu, Z.; Han, B.; Liu, D.; Chen, J.; He, J.; Jiang, T. *Chem. Eur. J.* **2004**, *10*, 3531–3536.
(9) Liu, J-Bi.; Li, N.; Wang, S.-Z.; Zhang, J.-H.; Wang, Z.-L. *Chin. Phys. Lett.* **2005**, *22*, 975–977.
(10) Quaroni, L.; Chumanov, G. *J. Am. Chem. Soc.* **1999**, *121*, 10642–10643.
(11) Obare, S. O.; Jana, R. J.; Murphy, M. J. *Nano Letters*. **2001**, *11*, 601–603.
(12) Ge, Z.; Kang, Y.; Taton, A.; Braun, P. V.; Cahill, D. G. *Nano Letters*. **2005**, *5*, 531–535.
(13) Landfester, K.; Ramírez, L. P. *J. Phys: Condens. Matter*. **2003**, *15*, S1345–S1361.
(14) Bao, H.; Chumanov, G.; Czerw, R.; Carroll, D. L.; Foulger, S. H. *Colloid Polym. Sci.* **2005**, *283*, 653–661.
(15) Im, S. H.; Jeong, U.; Xia, Y. *Nat. Mater.* **2005**, *4*, 671–675.
(16) Kreibig, U.; Vollmer, M. Optical Properties of Metal Clusters. In Springer Series in Material Science; Springer-Verlag: Heidelberg, Germany, 1995; Vol 25.
(17) Bohren, C. F.; Huffman, D. R. Absorption and Scattering of Light by Small Particles; John Wiley & Sons: New York, 1998.
(18) Mulvaney, P. *Langmuir*. **1996**, *12*, 788–800.

© 2009 American Chemical Society Published on Web 05/13/2009

Synthesis of Silver−Polystyrene Core−Shell Nanoparticles. A controlled and chemically clean synthesis of single-crystal Ag nanoparticles in the size range 10−250 nm has been previously reported.[19,20] The synthetic procedure involves the reduction of an aqueous saturated silver(I) oxide solution by an ultrapure hydrogen gas atmosphere of 10 psi at a temperature of 70 °C. The hydrogen gas reduces silver(I) oxide to form small Ag seeds followed by their slow uniform growth along all crystallographic axes, resulting in a narrow size distribution. This time-dependent reaction can be terminated at any stage, yielding nanoparticles of controlled size and desired plasmon resonance. A total of 3 h of hydrogen reduction results in the formation of Ag particles in the size range of 70−80 nm, as determined from transmission electron microscope (TEM) images. The same synthetic procedure was used to prepare Ag NPs in the presence of 0.5 mL of PS microspheres (∼200 nm). The reaction is terminated within the first 3 h of reduction to ensure that the resulting Ag particle size would be smaller than the size of the PS microspheres. The reaction solution was centrifuged in glass tubes to remove unreacted silver(I) oxide from the suspension. A certain amount of acetone was added to the precipitate of the Ag NPs and the PS microspheres; for example, ca. 100 μL of acetone was added to a 2 mL centrifuged reaction mixture. Further sonication of the precipitate with acetone resulted in the formation and dispersion of the Ag−PS composite particles. An instantaneous, distinct color change associated with the formation of a core−shell hybrid nanostructure was observed.[21]

Characterization. UV−vis absorption spectra were recorded using a Shimadzu UV-2501PC spectrophotometer. The morphology of the hybrid nanoparticles was observed with a HITACHI H7600 TEM using an acceleration voltage of 100 kV and a HITACHI HD2000 scanning transmission electron microscope (STEM) using 200 kV. TEM samples were prepared by evaporating a drop of a concentrated suspension on a carbon-stabilized copper grid (Ted Pella Inc.).

Results and Discussion

Comparison of the growth of Ag NPs in the absence and presence of PS microspheres was monitored by UV−visible extinction spectroscopy, as presented in Figure 1. In the early stages of the formation of Ag NPs in the absence of polystyrene microspheres, the extinction spectrum (Figure 1a) revealed the presence of a dipole plasmon resonance at 430 nm attributed to the formation of small Ag "seeds". With the increase of the particle size, the dipole resonance progressively red-shifted, rendering a green muddy color to the colloidal suspension due to strong resonance scattering of light. The frequency of the plasmon resonance depends on the size of the particles and the surrounding dielectric medium. For ca. 100 nm Ag NPs in water, the dipole resonance was at 516 nm, and a new distinct resonance band corresponding to the quadrupole mode appeared in the spectrum at 425 nm. A similar trend was observed when Ag NPs were synthesized in the presence of PS microspheres. The dipole and quadrupole modes of the plasmon resonance appeared somewhat broadened and red-shifted (Figure 1b) to 532 and 440 nm, respectively, as compared to the nanoparticles grown for the same duration without the PS microspheres. The broadening and the shift were attributed to the increase of the dielectric function of the medium surrounding the Ag NPs due to the adsorption of the NPs to the surface of the microspheres. Indeed, electron microscopy (TEM) confirmed that Ag NPs were attached to the PS microspheres (Figure 2).

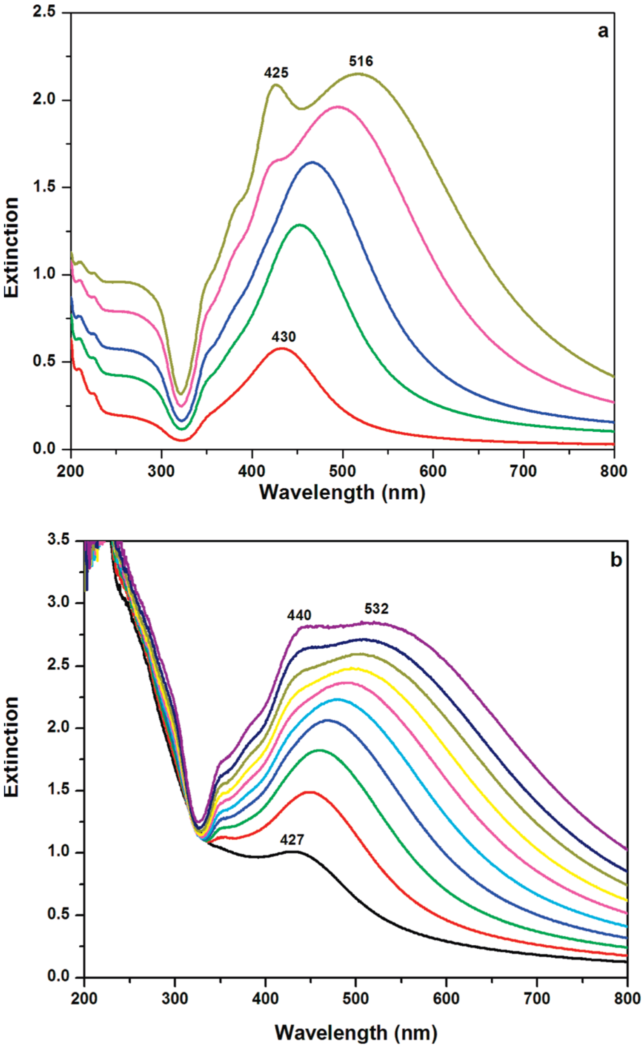

Figure 1. Extinction spectra of Ag NPs as they grew in the absence (a) and presence (b) of ∼ 200 nm PS microspheres.

It is known that the surface of the PS microspheres has anionic charge due to the presence of the sulfate ester groups. These anionic groups capture Ag$^+$ ions produced in the saturated silver(I) oxide solution at elevated temperatures that are further reduced by the hydrogen gas to Ag^0. These atoms are not strongly attached to the surface of the PS sphere because of the low affinity of the ester groups to the Ag metal. The weakly attached atoms undergo surface diffusion until they coalesce with each other to form a small seed on the surface of a PS sphere that further grows to form a NP as the reduction proceeds. This process is similar to the formation of islands during the vacuum deposition of metals onto poorly wettable substrates where metal atoms arriving at the substrate come together to form an island that grows as more metal is evaporated.[22] As the

---

(19) Evanoff, D. D.Jr; Chumanov, G. *J. Phys. Chem. B* **2004**, *108*, 13948–13956.

(20) Kumbhar, A.; Kinnan, M.; Chumanov, G. *J. Am. Chem. Soc.* **2005**, *127*, 12444–12445.

(21) Kumbhar, A.; Chumanov, G. *J. Nanosci. Nanotechnol.* **2004**, *4*, 299–303.

(22) Malynych, S.; Chumanov, G. *J. Vac. Sci. Technol. A* **2003**, *21*, 723–727.

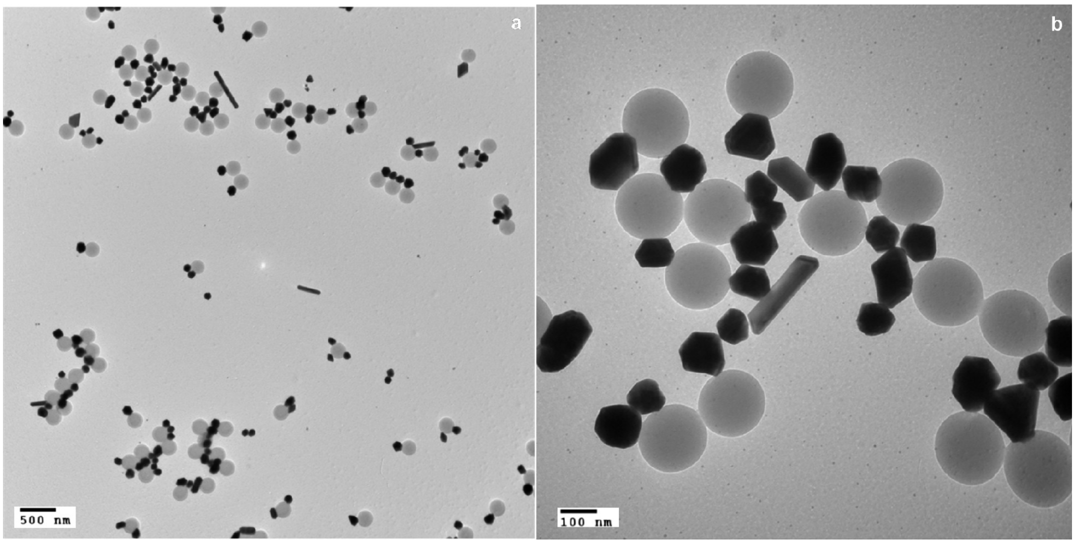

Figure 2. TEM images of Ag NPs adsorbed onto PS microspheres at low (a) and high magnifications (b).

Ag seeds grow in the course of the reduction, they remain weakly attached to the surface of the polystyrene microspheres. This process leads to the synthesis of only one or a few Ag NPs per PS microsphere. Electron microscopy images in Figure 2 appear somewhat misleading about a true arrangement of the Ag NPs and the PS spheres in solution because they reflect not only the adsorption of Ag NPs onto PS spheres but also the aggregation of particles that occurred during drying of the sample for TEM measurements. Conceivably, using smaller PS spheres will result in fewer Ag NPs per sphere. The images also revealed that the hydrogen reduction conditions do not compromise the integrity of the PS microspheres.

Centrifugation and redispersion of the PS microspheres with attached Ag NPs in acetone resulted in a distinct color change (Figure 3). The UV−vis extinction spectrum was shifted further to the red spectral range compared to the that of the suspension immediately after the reduction reaction. The dipole and the quadrupole plasmon modes in this case appeared at 654 and 488 nm, respectively. It is well-known that the frequency and the strength of the resonance depend upon the dielectric function of the surrounding media; it shifts to the red spectral region and increases in intensity with the increase of the dielectric function according to the following expression for the small particle limit:

$$\sigma_{\mathrm{ext}}(\omega) = 9\frac{\omega}{c}\varepsilon_{\mathrm{m}}^{3/2}V_0\frac{\varepsilon_2(\omega)}{[\varepsilon_1(\omega)+2\varepsilon_{\mathrm{m}}]^2+\varepsilon_2(\omega)^2}$$

where $\sigma_{\mathrm{ext}}(\omega)$ is the extinction coefficient, ε_{m} is the dielectric function of the surrounding medium, and $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are real and imaginary parts of the dielectric function of the metal, respectively.[16] The observed red-shifts and change of color were attributed to the change of the dielectric function surrounding the silver nanoparticles[21] due to both the presence of acetone that has the refractive index $n = 1.36$ and PS ($n \approx 1.57$). However, it was concluded that the main contribution came from the PS because the observed large red-shifts were not commensurate with a relatively small increase of the refractive index from water to acetone. Electron microscopy images revealed that the exposure of Ag NPs adsorbed on PS microspheres to acetone led to complete encapsulation of the NPs into a PS shell (Figure 4).

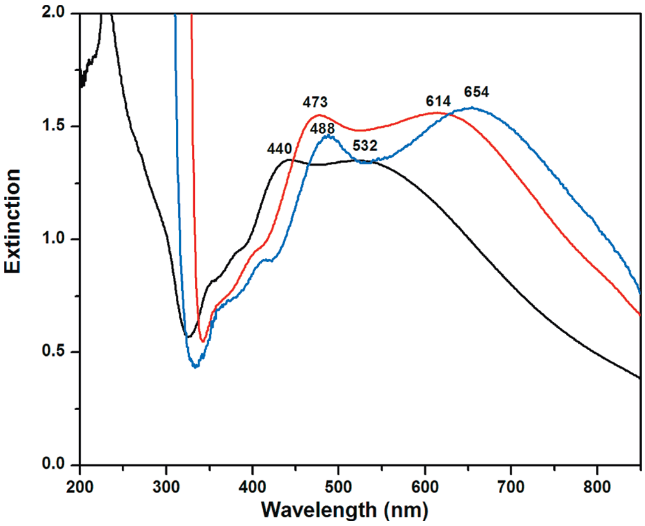

Figure 3. Extinction spectra of as-prepared Ag−PS microspheres (black), Ag−PS microspheres dispersed in acetone (blue), and redispersed back in water (red).

The exact mechanism for this encapsulation is not fully understood at this time. It is know that PS microspheres can be swollen when dispersed from water into “good” solvents such as toluene or acetone and can form hollow spheres with controllable surface holes when the solvents are evaporated.[15] This fact indicates that swelling of the PS microspheres in acetone is an important step leading to the encapsulation of Ag NPs reported in the current work.

The main question relates to the driving force that makes the polymer wrap the Ag NPs or, in other words, makes the NPs sink into the PS microspheres. In order for the NPs to sink into the polymer spheres, the interaction between the polymer chains and the metal surface must overcome several factors. It should be stronger than the interaction between the polymer chains themselves and stronger than

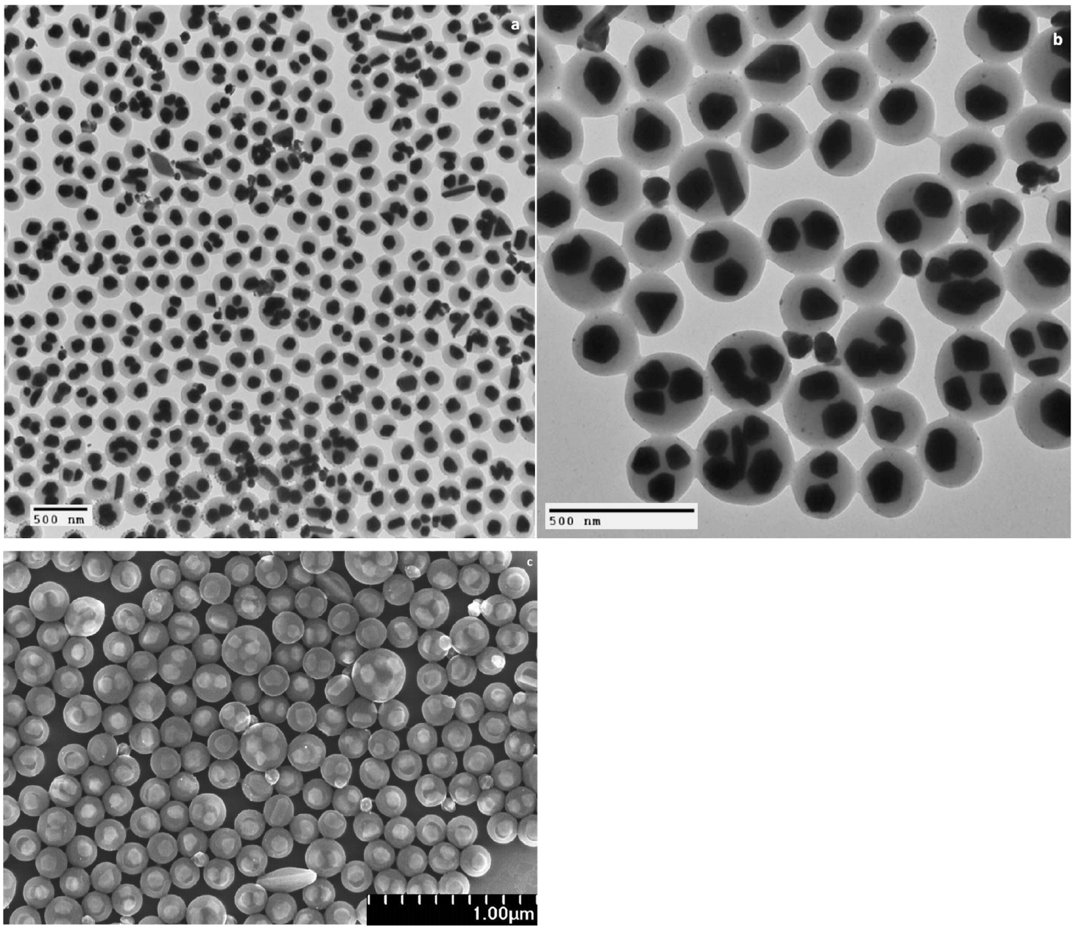

Figure 4. Low- (a) and high-magnification (b) TEM and STEM (c) micrographs of Ag−PS core−shell particles.

solvation forces for the Ag NPs in acetone. The interaction should surmount the increase of the surface free energy due to the creation of the additional interface between the metal and the polymer as well as due to an overall increase of the external polymer surface area of the composite microsphere. Also, the polymer chains in the immediate contact with the metal NPs are compressed above the bulk density of the polymer, and this compression produces an entropically unfavorable state, resulting in an entropic rejection force.[23] In a relevant publication, vacuum deposition of several nonmetals and metals, including silver, on PS films at elevated temperatures (120 °C) led to the formation of subsurface structures in which NPs were submersed into the polymer film several depths below its surface.[24] It was proposed that the difference between the adhesion work and cohesion work is the main reason that NPs sink into the polymer films.[25]

Even though PS is not known to strongly interact with silver under normal conditions, we speculate that, in the case of Ag NPs and PS microspheres in acetone, relatively strong interaction can be induced between PS and the metal surface. Acetone acts as a plasticizer, and swelling of the microspheres increases the flexibility of the polymer chains. This swelling allows benzene rings to adapt a configuration most favorable to the interaction with the metal surface. This interaction most likely is an induced dipole-induced dipole attraction (London dispersion force) that is expected to be substantial due to the delocalized nature of π electrons in the benzene ring and free electrons in the metal. Both electron systems are easily polarizable. The presence of acetone inside the (swollen) PS microspheres and in the surrounding environment also reduces the surface free energy of the polymer at both interfaces, thereby further promoting the sinking of Ag NPs into the microspheres.

A blue-shift of the extinction spectra was observed when the core−shell Ag−PS microspheres were resuspended in water. The dipole and the quadrupole modes shifted from 654 to 614 nm and from 488 to 473 nm, respectively. This shift was attributed to the decrease of the effective dielectric function of the medium surrounding the Ag NPs when the microspheres were transferred from acetone (n = 1.36) to water (n = 1.33).

Conclusions

Swelling of PS microspheres in acetone in the presence of attached Ag NPs resulted in the formation of the Ag−PS core−shell nanostructures. A large red-shift of the plasmon resonance was observed in the extinction spectra, owing to the complete encapsulation of the Ag NPs within the PS microspheres. These core−shell structures maintain

---

(23) Fowkes, F. M. *Adv. Chem.* **1964**, *43*, 99.
(24) Kovacs, G. J.; Vincett, P. S.; Tremblay, C.; Pundsack, A. L. *Thin Solid Films* **1983**, *101*, 21–40.
(25) Kovacs, G. J.; Vincett, P. S. *J. Colloid Interface Sci.* **1982**, *90*, 335–351.

their integrity when resuspended in water. The core−shell structures represent a new class of metal−polymer composite materials that can be used for photonic and biomedical applications exploiting optical properties of Ag NPs and chemical properties of the polymer. In addition to protecting Ag NPs in aggressive environments, the PS shell can be used as a scaffold for introducing chemical functionalities. The described method is not limited to Ag NPs and PS and can be extended to other NPs and polymers.

Acknowledgment. This work was supported by the United States Department of Energy, Grant No. DE-FG02-06ER46342. We also extend our acknowledgements to Dr. Igor Luzinov for his fruitful discussions.