A Phase-Transfer Identification of Core−Shell Structures in Ag−Pt Nanoparticles

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Ag−Pt nanoparticles with a confirmed core−shell structure could only be formed by the successive reduction method using Ag nanoparticles as the seeds. The core−shell structure could be conveniently inferred from the transferability of the particles from water to toluene. Independent measurements by UV−vis spectroscopy, transmission electron microscopy, energy-dispersive X-ray analysis, and X-ray photoelectron spectroscopy were used to validate the experimental results. The reverse order of synthesis using Pt nanoparticles as the seeds did not result in any core−shell product. Instead a physical mixture of Ag nanoparticles and the original Pt seeds was obtained under the same experimental conditions.

Introduction

Bimetallic nanoparticles can be obtained as alloy or core−shell particles to provide the latitude required for property tuning according to the needs of the intended application.[1−6] Alloy nanoparticles are often produced by the simultaneous reduction of two or more metal ions,[3] while the growth of the core−shell structure can be accomplished by the successive reduction of one metal ion over the core of the other metal.[4,7] Turkevich and Kim had used the successive reduction method in the 1970s to prepare gold-layered Pd nanoparticles.[2,8,9] Many reports on the preparation of core−shell nanoparticles of Au−Ag,[10−18] Ag−Au,[19,20] Au−Pd,[21] Pd−Au,[22] Ag−Pt,[23] Au−Pt,[24−26] and Pt−Au[25,26] were also based on this particular growth technique. However, with the help of a phase-transfer technique which is able to differentiate different surface properties,[27] we found that a majority of the allegedly core−shell nanoparticles in these works are actually physical mixtures of monometallic nanoparticles. Herein we report our experimental results on the formation of bimetallic Ag−Pt nanoparticles with a *confirmed* core−shell structure, based on the successive reduction method using Ag nanoparticle seeds. The reverse order of using Pt nanoparticles as the seeds was found to yield only a physical mixture of isolated nanoparticles of Pt and Ag under the same experimental conditions.

Experimental Section

AgNO$_3$, K$_2$PtCl$_4$, and 1-dodecanethiol (98%) from Aldrich, sodium citrate (98%) and ethanol (99%) from Merck, and toluene from Bake were used as received. Deionized water was distilled by a Milli-Q water purification system. All glassware and Teflon-coated magnetic stir bars were cleaned with aqua regia, followed by copious rinsing with distilled water before drying in an oven.

Successive reduction, also known as the seed-mediated growth method, was used to obtain bimetallic Ag−Pt nanoparticles with the core−shell structure. Citrate-stabilized Ag seeds were first prepared from the NaBH$_4$ reduction of AgNO$_3$. Briefly, 20 mL of 1 mM aqueous AgNO$_3$ solution was mixed with 1.6 mL of 38.8 mM aqueous sodium citrate solution used as a stabilizer. A 0.4 mL sample of 112 mM aqueous NaBH$_4$ solution was then added dropwise under vigorous stirring, giving rise to a yellow-green Ag hydrosol. The Ag hydrosol was aged for 24 h to decompose the residual NaBH$_4$ before it was used in subsequent steps. Citrate-stabilized Pt seeds were prepared by a slight modification of the procedure initially developed for gold nanoparticles.[28,29] An aqueous solution of K$_2$PtCl$_4$ (1 mM, 20 mL) was refluxed with stirring for 1 h at 110 °C in a silicon oil bath. A 2 mL sample of a 38.8 mM aqueous trisodium citrate solution was added quickly. The mixture was refluxed for another 60 min to form the Pt nanoparticles, and was allowed to cool to room temperature naturally. A deep-brown-colored Pt hydrosol was obtained in the end.

For the preparation of bimetallic Ag−Pt nanoparticles with the core−shell structure, 10 mL of 1 mM aqueous K$_2$PtCl$_4$ solution was first refluxed for 1 h, and then a calculated quantity of Ag hydrosol for a 1:1 Ag/Pt ratio in the final core−shell particles and 0.8 mL of sodium citrate solution were added. The mixture thus obtained was further refluxed for 1 h to reduce Pt(II) to Pt(0), and the final product was a red-brown Ag−Pt colloidal solution.

For the phase transfer of monometallic seeds and bimetallic nanoparticles with the core−shell structure, 5 mL of ethanol containing 100 μL of 1-dodecanethiol was mixed with 5 mL of the monometallic or bimetallic hydrosol. After 1 min of stirring, 5 mL of toluene was introduced and stirring continued for 3 min more. Phase transfer of the 1-dodecanethiol-stabilized monometallic or bimetallic nanoparticles from water to toluene occurred quickly, as evinced by the complete bleaching of the color in the aqueous phase.

A JEOL JEM2010 field emission microscope was used to obtain transmission electron microscopy (TEM) images of the nanoparticles. For TEM measurements a drop of the nanoparticle solution was placed onto a 3 mm copper grid covered with a

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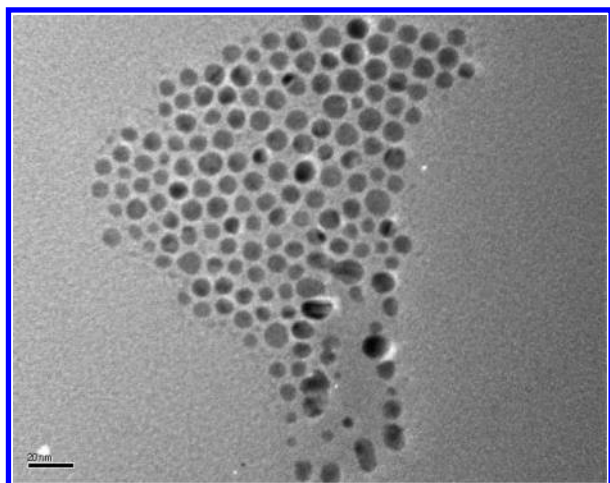　§ Department of Biochemistry, National University of Singapore.

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Figure 1. TEM image of citrate-stabilized Ag nanoparticles prepared by NaBH$_4$ reduction of AgNO$_3$ in the presence of sodium citrate.
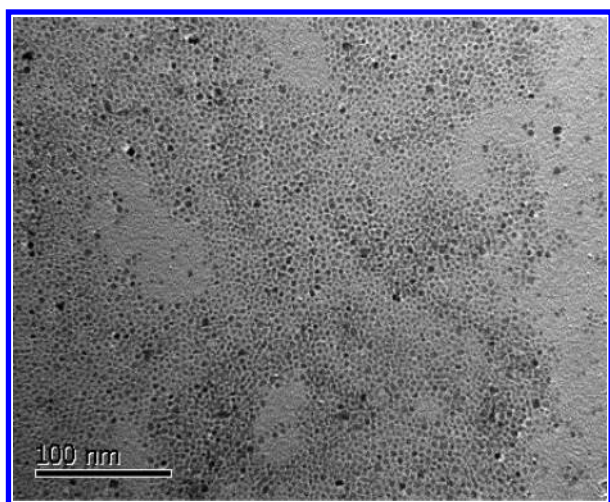

Figure 2. TEM image of citrate-stabilized Pt nanoparticles prepared by refluxing K$_2$PtCl$_4$ in the presence of sodium citrate.

continuous carbon film. Excess solution was removed by an adsorbent paper, and the sample was dried under vacuum at room temperature. UV−vis spectroscopy of the monometallic or bimetallic nanoparticle solution was performed on a Shimadzu UV-2450 spectrophotometer.

Energy dispersive X-ray (EDX) and X-ray photoelectron spectroscopy (XPS) analyses were carried out by a JEOL MP5600 scanning electron microscope and a VG ESCALAB MKII spectrometer, respectively. Sample preparation for EDX and XPS analyses began with concentrating the toluene solution of the bimetallic nanoparticles to 0.5 mL using flowing Ar. A 10 mL sample of ethanol was then added, and the mixture was stored at −20 °C for 24 h to precipitate the bimetallic nanoparticles. The product nanoparticles were recovered by centrifugation and washed with ethanol several times to remove nonspecifically bound alkanethiol. The nanoparticles were then dried at room temperature in a vacuum.

Results and Discussion

Figures 1 and 2 are TEM images of citrate-stabilized nanoparticles of Ag and Pt, which were used as seeds in the successive reduction reactions. These colloidal solutions were stable up to a few days of storage. The Pt nanoparticles could be easily extracted into toluene by the phase-transfer technique described in the Experimental Section. The transfer as indicated

Figure 3. Digital camera images showing the transferability of the bimetallic nanoparticles. (A) Bimetallic Ag−Pt nanoparticles obtained from the Ag seeds were completely transferable from water to toluene (top). (B) Bimetallic Ag−Pt nanoparticles obtained from the Pt seeds could only be partially transferred. The transferred particles were Pt only. Most of the Ag nanoparticles congregated at the wall or the water−toluene interface.
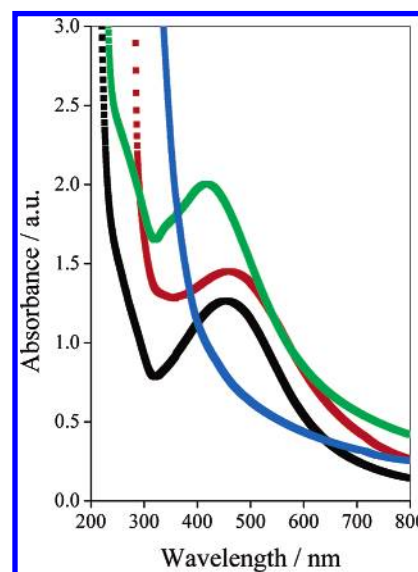

Figure 4. UV−vis spectra of an aqueous solution of Ag-seeded Ag−Pt bimetallic nanoparticles before phase transfer (black dots), a toluene solution of Ag-seeded Ag−Pt bimetallic nanoparticles after phase transfer (red dots), an aqueous solution of Pt-seeded Ag−Pt bimetallic nanoparticles before phase transfer (green dots), and a toluene solution of Pt-seeded Ag−Pt bimetallic nanoparticles after phase transfer (blue dots).

TABLE 1: Average Particle Size and Phase-Transfer Characteristics of Ag and Pt Nanoparticle Seeds

nanoparticle	av size (nm)	phase transfer to toluene?
citrate-protected Ag	9.6	N
citrate-protected Pt	3.6	Y

by a vivid transfer of color from the aqueous phase to toluene occurred quickly and completely to leave a colorless aqueous solution behind. The mechanism for the phase transfer of the Pt nanoparticles has been described previously.[27] Briefly, ethanol, a water-miscible and good solvent for 1-dodecanethiol, is used as an intermediate solvent to enhance the interfacial contact between citrate-stabilized metal nanoparticles and al-
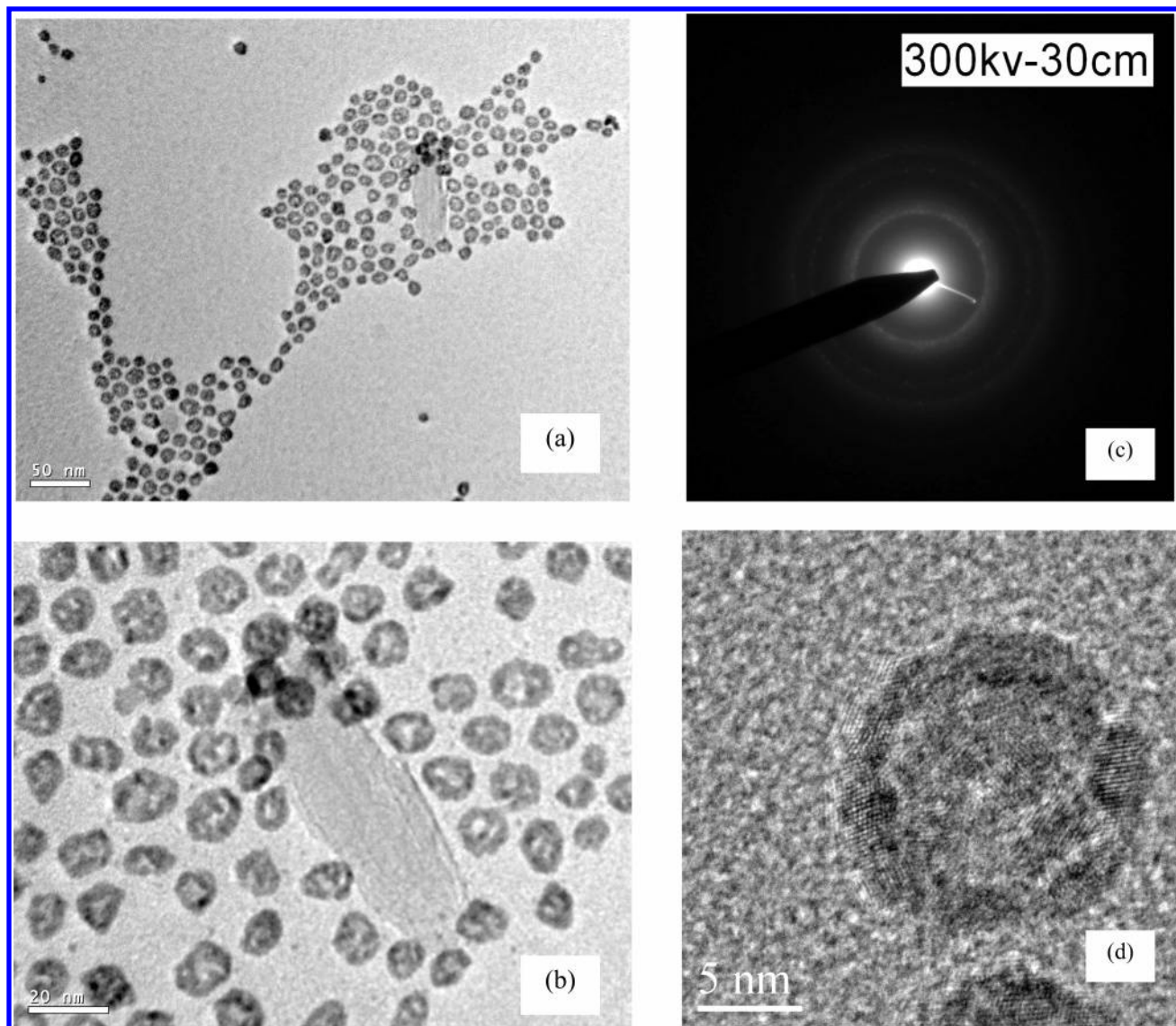
Figure 5. (a) Large-area TEM image of the core−shell Ag−Pt nanoparticles. (b) High-resolution TEM image of core−shell Ag−Pt nanoparticles. (c) Typical SAED pattern of core−shell Ag−Pt nanoparticles. (d) HRTEM image of one of the core−shell Ag−Pt nanoparticles.

kanethiol for the progressive displacement of the citrate ions. However, citrate-stabilized Ag nanoparticles could not be transferred by the same procedure. Instead the Ag particles were found to accumulate at the oil−water interface or adhere to the container walls. The failure in transferring the Ag nanoparticles is not fully understood. The current work is not at odds with the earlier findings of Rao and co-workers, who reported the preparation of thiol-derivatized Ag nanoparticles by phase transfer.[30] In that work, the Ag nanoparticles were unprotected before the transfer and concentrated HCl was used to facilitate the phase transfer. We have experimentally verified that Rao's protocol would not work with citrate-stabilized Ag nanoparticles. The average particle size and the transferability of the seed particles are summarized in Table 1. The different phase-transfer characteristics of Pt and Ag nanoparticles could be used to differentiate between core−shell nanoparticles and a mixture of monometallic nanoparticles in a successive reduction experiment (based on the understanding that only a particle surface enriched in Pt or Pt nanoparticles are transferable). This technique is in a way similar to the use of CO chemisorption to identify the surface composition of bimetallic nanoparticles,[31,32] except that it can be implemented more conveniently in the liquid phase. Both methods rely on the use of an affinity

agent that can differentiate between different types of surface atoms. The phase-transfer method has the added advantage of being quick and simple, and makes use of visual inspection instead of an instrument-based method of detection.

The digital camera images in Figure 3A show that the Ag−Pt system constructed upon citrate-stabilized Ag seeds was completely transferable from water to toluene. EDX analysis produced a Ag-to-Pt ratio of 47:53, which is in good agreement with the metal ratio in the starting precursor salts. The successful transfer of the Ag-seeded bimetallic Ag−Pt nanoparticles proves convincingly that the reduction of Pt salts had occurred heterogeneously on the preformed Ag nanoparticles rather than homogeneously in the solution to form isolated Pt nanoparticles. If the latter were to occur, phase transfer would be partial because the nontransferable monometallic Ag nanoparticles had to remain in the aqueous phase (Table 1). Hence, the reduction of $PtCl_4^{2-}$ in the presence of Ag nanoparticles had resulted only in the formation of $Ag_{core}Pt_{shell}$ nanoparticles. In addition, XPS analysis of the surface of the bimetallic Ag−Pt nanoparticles showed a much higher Pt-to-Ag ratio of 3.8:1, confirming that the surface of the bimetallics was enriched with Pt. The difference in elemental compositions between XPS (a surface analysis technique) and EDX (a bulk analysis technique)

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measurements is strong evidence for the formation of a Pt shell on the Ag nanoparticle cores which seeded the growth process.

However, EDX analysis of "bimetallic" Ag−Pt nanoparticles prepared in the reverse order (i.e., successive reduction using citrate-stabilized Pt seeds) and recovered from toluene after the phase transfer showed only the exclusive presence of Pt nanoparticles, without any trace of Ag. Figure 3B also shows some agglomeration of nanoparticles on the container walls and at the water/toluene interface which is characteristic of the nontransferable Ag nanoparticles (subsequently confirmed by EDX analysis). These experimental findings when examined collectively clearly demonstrate the nonexistence of $Pt_{core}Ag_{shell}$ nanoparticles (the Ag overlayer forbids any attempt of nanoparticle transfer) and the product obtained with the Pt seeds was a physical mixture of isolated Pt and Ag nanoparticles.

An interesting property of the bimetallic core−shell Ag−Pt nanoparticles is that they still possess the optical properties of Ag nanoparticles even with the abundant presence of Pt atoms in the shell. This is evinced particularly by the UV−vis spectra of bimetallic Ag−Pt nanoparticles after the phase transfer (red dots in Figure 4, bearing in mind that only core−shell Ag−Pt nanoparticles are transferable). The broad absorption centered at 454 nm was contributed exclusively by the surface plasmon resonance of Ag particles. The large red shift (ca. 54 nm) of the Ag surface plasmon band in the core−shell Ag−Pt nanoparticles relative to the pristine Ag nanoparticle seeds (ca. 400 nm, data not shown) is an indication of the influence of the Pt shell. The ability to retain a useful property of the core component (in this case the optical property of nanosilver) while modulating the surface with a chemically more active metal (Pt) is a powerful technique in the engineering of new functional materials. The effect of phase transfer on the UV−vis spectra for the Pt-seeded growth of bimetallic nanoparticles is shown in Figure 4 (green and blue dots). The Ag surface plasmon band (green dots in Figure 4) is fairly apparent in the hydrosol before the phase transfer. After the phase transfer, the UV−vis spectrum of the toluene solution was featureless and devoid of the Ag surface plasmon band, confirming the lack of transfer of Ag particles from the aqueous phase to toluene. The difference in the UV−vis spectra before and after phase transfer is strong evidence for the presence of only a physical mixture of isolated Ag and Pt nanopartiucles when citrate-stabilized Pt nanoparticles were used as the seeds.

Figure 5a is a typical large-area TEM image of the core−shell Ag−Pt nanoparticles, where the core and shell components can be easily differentiated by brightness differences. Additional structural details are revealed by the high-resolution TEM (HRTEM) image in Figure 5b. The discontinuous Pt shell is composed of individual Pt spheres decorating the Ag cores. The continuous ring in the SAED pattern of Figure 5c indicates that the core−shell nanoparticles are polycrystalline. The location of the ring is consistent with the fcc structure, and hence, the core−shell nanoparticles are made of fcc grains. The HRTEM examination of one of the core−shell Ag−Pt nanoparticles is shown in Figure 5d. The lack of a preferred orientation for the lattice fringes is another proof for the polycrystalline structure of the nanoparticles. In the core, in particular, the superposition of interference patterns arising from two highly similar fcc metals (*d*(111) for Ag and Pt are 0.2356 and 0.2255 nm, respectively) also makes it difficult to differentiate Ag from Pt, and vice versa, in the HRTEM image.

The core−shell structure in Figure 5a is in strong contrast with the TEM image of bimetallic Ag−Pt particles based on the Pt seeds where different size particles instead of uniformly sized core−shell particles were found randomly distributed on the TEM grid (data not shown).

Conclusions

A simple phase-transfer protocol that can unambiguously identify core−shell Ag−Pt nanoparticles prepared by the seed-mediated growth method is presented here. The phase-transfer protocol was verified by independent measurements using UV−vis spectroscopy, TEM, EDX analysis, and XPS. It was found that core−shell Ag−Pt nanoparticles could be obtained by the seed-mediated growth method using Ag nanoparticles as the seeds. However, a physical mixture of isolated Ag and Pt nanoparticles was obtained if the synthesis order was reversed, using Pt nanoparticles as the seeds. The UV−vis spectra of core−shell Ag−Pt nanoparticles still exhibited the optical characteristics of the Ag nanoparticles, a property that is highly valuable to the engineering of new nanoscale composite materials. The presence of a Pt shell on the Ag nanoparticles had nevertheless resulted in a large red shift in the SPR band of the Ag nanoparticles.

References and Notes

(1) Schmid, G. *Clusters and Colloids*; VCH: Weinheim, Germany, 1994.

(2) Toshima, N.; Yonezawa, T. *New J. Chem.* **1998**, *11*, 1179.

(3) Link, S.; Wang, S. Z. L.; El-Sayed, M. A. *J. Phys. Chem. B* **1999**, *103*, 3529.

(4) Mallin, M. P.; Murphy, C. J. *Nano Lett.* **2002**, *2*, 1235.

(5) Ah, C. S.; Hong, S. D.; Jang, D.-J. *J. Phys. Chem. B* **2001**, *105*, 7871.

(6) Cao, Y.-W.; Jin, R.; Mirkin, C. A. *J. Am. Chem. Soc.* **2001**, *123*, 7961.

(7) Smova-Sloufova, I.; Lednicky, F.; Gemperle, A.; Gemperlova, J. *Langmuir* **2000**, *16*, 9928.

(8) Caruso, F. *Adv. Mater.* **2001**, *13*, 11.

(9) Toshima, N. In *Fine Particles Science and Technology-From Micro to New Particles*; Pelizzetti, E., Ed.; Kluwer: Dordrecht, The Netherlands, 1996; pp 371−383.

(10) Jana, N. R. *Analyst* **2003**, *128*, 954.

(11) Flynn, N. T.; Gewirth, A. A. *J. Raman Spectrosc.* **2002**, *33*, 243.

(12) Lu, L.; Wang, H.; Zhou, Y.; Xi, S.; Zhang, H.; Hu, J.; Zhao, B. *Chem. Commun.* **2002**, 144.

(13) Shibata, T.; Tostmann, H.; Bunker, B.; Henglein, A.; Meisel, D.; Cheong, S.; Boyanov, M. *J. Synchrotron Radiat.* **2001**, *8*, 545.

(14) Mandal, S.; Selvakannan, P.; Pasricha, R.; Sastry, M. *J. Am. Chem. Soc.* **2003**, *125*, 8440.

(15) Zhu, J.; Wang, Y.; Huang, L.; Lu, Y. *Phys. Lett. A* **2004**, *323*, 455.

(16) Mandal, M.; Jana, N. R.; Kundu, S.; Ghosh, K.; Panigrahi, M.; Pal, T. *J. Nanopart. Res.* **2004**, *6*, 53.

(17) Mandal, M.; Kundu, S.; Ghosh, K.; Jana, N. R.; Panigrahi, M.; Pal, T. *Curr. Sci.* **2004**, *86*, 556.

(18) Shankar, S. S.; Rai, A.; Ahmad, A.; Sastry, M. *J. Colloid Interface Sci.* **2004**, *275*, 496.

(19) Chen, D. H.; Chen, C. J. *J. Mater. Chem.* **2002**, *12*, 1557.

(20) Srnova-Sloufova, I.; Vlckova, B.; Bastl, Z.; Hasslett, T. L. *Langmuir* **2004**, *20*, 3407.

(21) Kan, C.; Cai, W.; Li, C.; Zhang, L.; Hofmeister, H. *J. Phys. D: Appl. Phys.* **2003**, *36*, 1609.

(22) Shiraishi, Y.; Ikenaga, D.; Toshima, N. *Aust. J. Chem.* **2003**, *56*, 1025.

(23) Doudna, C. M.; Bertino, M. F.; Blum, F. D.; Tokuhiro, A. T.; Lahiri-Dey, D.; Chattopadhyay, S.; Terry, J. *J. Phys. Chem. B* **2003**, *107*, 2966.

(24) Damle, C.; Kumar, A.; Sastry, M. *J. Phys. Chem. B* **2002**, *106*, 297.

(25) Rivas, L.; Sanchez-Cortes, S.; García-Ramos, J. V.; Morcillo, G. *Langmuir* **2000**, *16*, 9722.

(26) Henglein, A. *J. Phys. Chem. B* **2000**, *104*, 2201.

(27) Yang, J.; Lee, J. Y.; Deivaraj, T. C.; Too, H. P. *J. Colloid Interface Sci.* **2004**, *277*, 95.

(28) Grabar, K. C.; Freeman, R. G.; Hommer, M. B.; Natan, M. *J. Anal. Chem.* **1995**, *67*, 735.

(29) Gearheart, L. A.; Ploehn, H. J.; Murphy, C. J. *J. Phys. Chem. B* **2001**, *105*, 12609.

(30) Sarathy, K. V.; Raina, G.; Yadav, R. T.; Kulkarni, G. U.; Rao, C. N. R. *J. Phys. Chem. B* **1997**, *101*, 9876.

(31) Siepen, K.; Bonnemann, H.; Brijoux, W.; Rothe, J.; Hormes, J. *Appl. Organomet. Chem.* **2000**, *14*, 549.

(32) D'Souza, L.; Sampath, S. *Langmuir* **2000**, *16*, 8510.