

## Measuring the Distance Dependence of the Local Electromagnetic Field from Silver Nanoparticles

David D. Evanoff, Jr., Ryan L. White, and George Chumanov\*

Department of Chemistry, Clemson University, Clemson, South Carolina 29634

Received: September 29, 2003; In Final Form: December 12, 2003

The distance dependence of the local EM field associated with  $84 \pm 5$  nm silver particles is characterized by monitoring spectral shifts in the plasmon resonance due to changes in local dielectric environment, which was controlled by coating the particles with silica layers of various thicknesses. The local EM field that extends beyond the physical boundaries of the particles is defined as that providing “feedback” between the local environment and the electron oscillations in a particle.

Utilization of the unique optical properties resulting from the excitation of plasmon resonances in nanosize metallic particles can lead to significant advances in the areas of photocatalysis, information processing and sensor development. Plasmon resonances which are collective oscillations of the conduction electrons, generate an electromagnetic (EM) field which has absorbing, scattering, and near-field components.<sup>1</sup> For silver particles larger than several tens of nanometers, the absorption component at the plasmon resonance is small and optical properties in the far-field are dominated by elastic scattering,<sup>2</sup> while the near-field component is strongest at the particle surface ( $R = 0$ ) and rapidly decays as  $E \sim 1/R^2$ .<sup>3</sup> This component determines the intensity of the local EM field that is enhanced as compared to the incident radiation leading to the enhancement of several optical phenomena such as Raman scattering,<sup>4</sup> fluorescence,<sup>5,6</sup> absorption,<sup>7</sup> photoinduced electron transfer,<sup>8</sup> second and third harmonic generation, four wave mixing,<sup>9</sup> etc. for molecules in close proximity to the particle surface. Direct measurement of the distance dependence of the local EM field is important not only from the fundamental point of view but is also crucial for controlling the enhancement as well as the light-induced near-field interparticle interactions that have a potential of yielding novel photonic and plasmonic devices.<sup>10</sup> For example, surface-enhanced fluorescence results from two competing phenomena, the increased excitation rate due to interaction with the local EM field and the quenching rate due to deactivation of the molecular excited state by energy transfer to the metal surface. Because quenching decays from the surface faster than the local EM field, there should be an optimum distance where fluorescence enhancement is largest. Optimization of the fluorescence enhancing system requires knowledge of the distance dependence of the local EM field.

In this vein, we present a simple approach for measuring the extension of the local EM field from the surface of a silver nanoparticle by gradually changing the local dielectric environment. The spectral position of the plasmon resonances depends not only on the size and shape of the nanoparticles but also on the dielectric function of the surrounding medium, which was controlled in these experiments by coating the nanoparticles with a silica layer. The thickness of the silica layer was continuously increased and the spectral position of the plasmon resonance was monitored by UV–visible extinction measurements. We

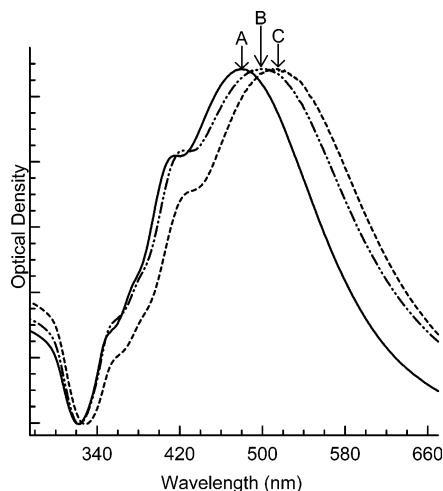
found that after reaching a certain limiting thickness the addition of more silica does not induce any further spectral shift of the plasmon resonance. Assuming that the dielectric medium affects the plasmon resonance only within the boundaries of the local EM field, this limiting thickness of the silica layer is considered as the distance to which the local EM field extends from the surface of silver nanoparticles.

Silica layers of varying thickness were synthesized around silver nanoparticles by the well-known sol–gel technique.<sup>5,11,12</sup> A silicon alkoxide was hydrolyzed in a basic environment and condensed around silver nanoparticles forming a silica layer of uniform density and porosity. Changing the initial concentration of the alkoxide resulted in silica layers of various thicknesses. The red spectral shift of the plasmon resonance was monitored by UV–visible spectrophotometry (Shimadzu UV-2501PC) as the local dielectric function increased due to the increase in the silica layer thickness.

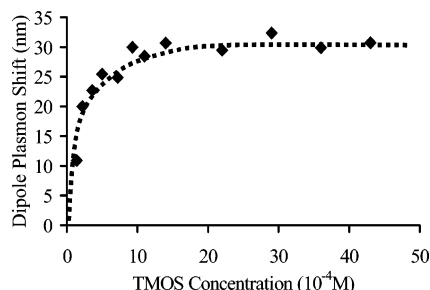
An aqueous colloidal suspension of silver nanoparticles of optical density ca. 130 at the maximum of the plasmon resonance was synthesized in our laboratory using chemical reduction of silver salts. These particles exhibit two characteristic spectral features corresponding to the dipole component of the plasmon resonance centered at 480 nm and the quadrupole component at ca. 420 nm (Figure 1A). Analysis of SEM (Hitachi S-4700) micrographs of the silver nanoparticles adsorbed on poly(vinylpyridine) modified ITO glass reveals totally non-aggregated, mainly spherical particles with a diameter of  $84 \pm 5$  nm (Figure 4A). The silica coating protocol was similar to that previously reported.<sup>5</sup> 50 mL of 2-propanol (Optima grade, Fisher Scientific) was mixed under constant stirring with 6 mL of 18 MΩ cm water (Millipore) and 2 mL of the aforementioned colloidal suspension. 600 μL of 30% ammonium hydroxide (Fisher Scientific) and immediately after, an appropriate amount of tetramethoxysilane (TMOS) (Gelest, Inc.) were added to the reaction mixture. To obtain different silica layer thicknesses, amounts between 2 and 60 μL of TMOS were added to the suspension. The reaction was stirred at room temperature for 10 minutes and then allowed to age without agitation for 24 h at 4 °C. Each suspension of silica-coated silver nanoparticles was centrifuged (Beckman J2-HS) three times at approximately 150 g for 8 h followed by resuspension in water.

UV–visible spectra of bare and coated silver nanoparticles were compared to determine the plasmon resonance spectral

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



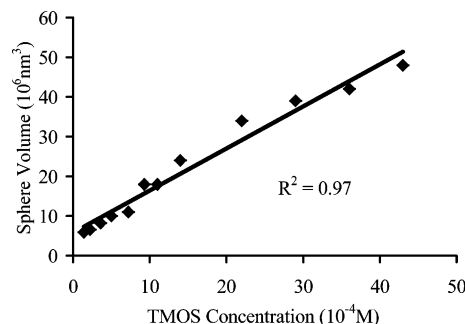
**Figure 1.** UV-visible extinction spectra of (A) bare silver nanoparticles ( $\lambda_{\text{max}} = 480$  nm) and (B, C) silica-coated particles resulting from reactions with two concentrations of silicon alkoxide: (B)  $2.2 \times 10^{-4}$  M ( $\lambda_{\text{max}} = 500$  nm) and (C)  $2.9 \times 10^{-3}$  M ( $\lambda_{\text{max}} = 512$  nm).



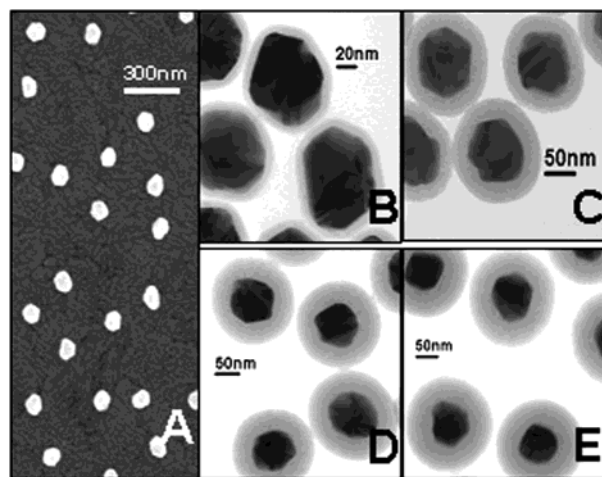
**Figure 2.** Dependence of the spectral shift in the position of the plasmon resonance on the concentration of TMOS in the reaction mixture.

shift for the different amounts of TMOS used. The spectra corresponding to TMOS concentrations of  $2.2 \times 10^{-4}$  M and  $2.9 \times 10^{-3}$  M are shown in Figure 1, parts B and C, respectively. As can be seen in Figure 2, the dipole component of the plasmon resonance initially shifts rapidly with increasing TMOS concentration and then levels off around a concentration of  $1.5 \times 10^{-3}$  M indicating that the local dielectric function reaches its saturation value and that further addition of silica does not affect the spectral position of the plasmon resonance. The data can be fitted by a smooth line with little deviation. Self-nucleation of TMOS, i.e., free silica formation, causing a thinner than expected silica layer as well as limited aggregation at the beginning of the hydrolysis reaction leading to red spectral shifts can account for this deviation. The linear relationship between TMOS concentration and the total volume of the resultant core-shell structure, however, indicates that almost all of the hydrolyzed silica is condensed around the silver particles and that the formation of free silica is minimal (Figure 3).

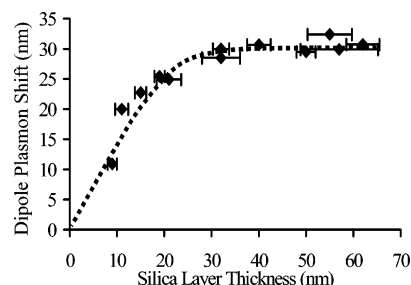
The thickness of the silica layers was determined from STEM (Hitachi HD2000) images to be from 9 to 55 nm (Figure 4B–E). Analysis of the micrographs revealed that the overall thickness of the silica layer is uniform over the entire surface of the nanoparticle and that the thickness continues to increase with the addition of more TMOS, however, the position of the plasmon resonance remains constant. Such behavior indicates that changes to the local dielectric environment beyond a certain distance from the surface no longer affect the electron oscillations in silver nanoparticles. The data in Figure 5 illustrate the relationship between silica coating thickness and shift in the plasmon resonance position, from which the value of the limiting



**Figure 3.** Dependence of the volume of the resulting core-shell structure on the concentration of TMOS in the reaction mixture.



**Figure 4.** Electron micrographs of (A) bare silver nanoparticles ( $d = 84 \pm 5$  nm) and silica-coated silver nanoparticles with layer thicknesses of (B)  $9 \pm 1$ , (C)  $21 \pm 3$ , (D)  $40 \pm 3$ , and (E)  $55 \pm 5$  nm.



**Figure 5.** Dependence of the observed shift in the position of the plasmon resonance on the thickness of the silica layer surrounding the silver nanoparticles.

thickness can be determined. The shift in the plasmon resonance increases steadily for thicknesses below 20 nm, after which the rate decreases and the shift reaches the saturation value at a limiting thickness of ca. 40 nm. This limiting thickness of the silica layer corresponds to the distance to which the local EM field extends from the surface of silver nanoparticles.

Uncertainty in the thickness of the silica layers is mainly associated with STEM measurements; in particular changing the brightness and contrast during scanning can change the apparent thickness of the layer. Depending on the brightness and contrast, the outer edges of the silica layer may disappear or the boundary between silver and silica may be difficult to discern. Another conceivable problem with STEM measurements is that the silica layer may shrink when the coated particles are dried in the vacuum of the microscope causing the layers to appear thinner than that in suspension.

It is well-known that changing the dielectric medium in which nanoparticles are immersed affects the spectral position of the

plasmon resonance in that increasing the dielectric function of the surrounding medium causes the plasmon resonance position to shift to longer wavelengths.<sup>13,14</sup> Because the oscillating electrons and the local EM field are inseparable parts of the same system, any changes to the field will affect the frequency of electron oscillation. The local EM field extends beyond the physical boundaries of the particles into the dielectric environment and the induced polarization in this medium reduces the local EM field thereby lowering the frequency of the electron oscillation. We define the local EM field associated with plasmon resonances in metallic nanoparticles as that providing "feedback" between the surrounding medium and the oscillating electrons in the nanoparticles. This feedback makes the plasmon and the associated local EM field a self-adjusting system in that any direct modification of the plasmon resonance changes the local fields and conversely, perturbations to the local field affect the frequency of the plasmon resonance. The region around the nanoparticles where there is appreciable feedback corresponds to the maximum extension of the local EM field. Once the dielectric function within this region is established, the position of the plasmon resonance stops shifting regardless of what happens further away from the surface. Within this region the EM field consists of two components, the local field and the scattering field. The former is enhanced as compared to the latter and is responsible for the aforementioned enhanced phenomena.<sup>1,3</sup> Conceivably the distance of maximum extension of the local EM field depends on the size of the particles and the dielectric function of the surrounding medium. In our experiments with 84 nm silver particles coated with sol-gel derived silica layers this distance is equal to ca. 40 nm. At larger distances the EM field consists mainly of the scattering

component, which determines the optical properties of the nanoparticles in the far field.

**Acknowledgment.** This research was supported by the National Science Foundation through the NSE NER program. The authors also thank J. Katrina Daniels for assistance in sol-gel techniques and Ames Laboratory (U.S. Department of Energy) for the equipment used for this work.

## References and Notes

- (1) Messinger, B. J.; von Raben, K. U.; Chang, R. K.; Barber, P. W. *Phys. Rev. B* **1981**, *24*, 649.
- (2) Kreibig, U.; Vollmer, M. *Optical Properties of Metal Clusters*; Springer-Verlag: Berlin and Heidelberg, Germany, 1995.
- (3) Quinten, M. *Appl. Phys. B: Laser Opt.* **2001**, *73*, 245.
- (4) Kneipp, K.; Kneipp, H.; Itzkan, I.; Dasari, D. R.; Feld, M. S. *Chem. Rev.* **1999**, *99*, 2957.
- (5) Sokolov, K.; Chumanov, G.; Cotton, T. M. *Anal. Chem.* **1998**, *70*, 3898.
- (6) Geddes, C. D.; Cao, H.; Gryczynski, I.; Gryczynski, Z.; Fang, J.; Lakowicz, J. R. *J. Phys. Chem. A* **2003**, *107*, 3443.
- (7) Nishikawa, Y.; Nagasawa, T.; Fujiwara, K.; Osawa, M. *Vib. Spec.* **1993**, *6*, 43.
- (8) Zheng, J. W.; Lu, H.; Cotton, T. M.; Chumanov, G. *J. Electroanal. Chem.* **2002**, *518*, 6.
- (9) Poliakov, E.; Shalaev, V. M.; Shubin, V.; Markel, V. A. *Phys. Rev. B* **1999**, *60*, 10739.
- (10) Malynych, S.; Chumanov, G. *J. Am. Chem. Soc.* **2003**, *125*, 2896.
- (11) Liz-Marzán, L. M.; Giersig, M.; Mulvaney, P. *Langmuir* **1996**, *12*, 4329.
- (12) Hardikar, V. V.; Matijevic, E. *J. Colloid Interface Sci.* **2000**, *221*, 133.
- (13) Chumanov, G.; Sokolov, K.; Gregory, B. W.; Cotton, T. M. *J. Phys. Chem.* **1995**, *99*, 9946.
- (14) Jensen, J. R.; Duval, M. L.; Kelly, K. L.; Lazarides, A. A.; Shatz, G. C.; Van Duyne, R. P. *J. Phys. Chem. B* **1999**, *103*, 9846.