

Tuning the Optical Properties of Large Gold Nanoparticle Arrays

Beomseok Kim, Steven L. Tripp, and [Alexander Wei](mailto:alexwei@purdue.edu) (alexwei@purdue.edu)
Department of Chemistry, Purdue University, West Lafayette, IN 47907-1393

ABSTRACT

Gold nanoparticles in the mid-nanometer size regime can undergo self-organization into densely packed monoparticulate films at the air-water interface under appropriate passivation conditions. Films could be transferred onto hydrophilic Formvar-coated Cu grids by horizontal (Langmuir-Schaefer) deposition or by vertical retraction of immersed substrates. The latter method produced monoparticulate films with variable extinction and reflectance properties. Transmission electron microscopy revealed hexagonally close-packed arrays on the micron length scale. The extinction bands of these arrays shifted by hundreds of nanometers to near-infrared wavelengths and broadened enormously with increasing periodicity. Large particle arrays also demonstrated extremely high surface-enhanced Raman scattering (SERS), with enhancement factors greater than 10^7 . Signal enhancements could be correlated with increasing periodicity and are in accord with earlier theoretical and experimental investigations involving nanoparticle aggregate structures.

INTRODUCTION

The synthesis of nanostructured materials with useful and tunable properties is central to developments in nanoscale science and technology. Nonlithographic bottom-up approaches based on self-assembly and self-organization are especially appealing because of their intrinsically low overhead for large-scale production. This approach has been useful in the self-organization of monolayer-protected metal nanoparticles into periodic two-dimensional (2D) arrays, with many of these assemblies demonstrating novel optical or electronic properties as a function of particle size or interparticle spacing.¹ Interestingly, numerous examples of 2D arrays comprised of small (<10 nm) gold nanoparticles have been reported, but well-ordered 2D arrays of larger gold nanoparticles have not.² Particles beyond a certain size (about 15 nanometers) tend to agglomerate into multilayers or three-dimensional aggregates rather than form two-dimensional monoparticulate films.³ This can be attributed to the large Hamaker constant for gold⁴ and the rapid increase in van der Waals attraction between particles as a function of size,⁵ as well as the loss of surfactant chain mobility of the on the planar facets of the nanoparticles.

We have recently developed strategies that enable large (>15 nm) gold nanoparticles to self-organize into well-ordered 2D arrays at the air-water interface. The choice of surfactant is critical in the formation and physical properties of these nanoparticle ensembles: the surfactant layer is required to be hydrophobic and highly repulsive at close range but thin enough to maintain short interparticle separations, a crucial factor in the electronic and optical properties of metal nanoparticle assemblies.^{1,6} Simple extension of established surfactant methodologies does not provide adequate control during particle aggregation; for example, passivating 20-nm colloidal gold particles with a surfactant monolayer of dodecanethiol results in the formation of multilayered aggregates at the air-water interface (see Figure 1a). We therefore sought to design a surfactant monolayer with greater spacing between chains, with the premise that their relatively high conformational entropies (greater exclusion volumes) would increase the barrier against steric compression.⁷

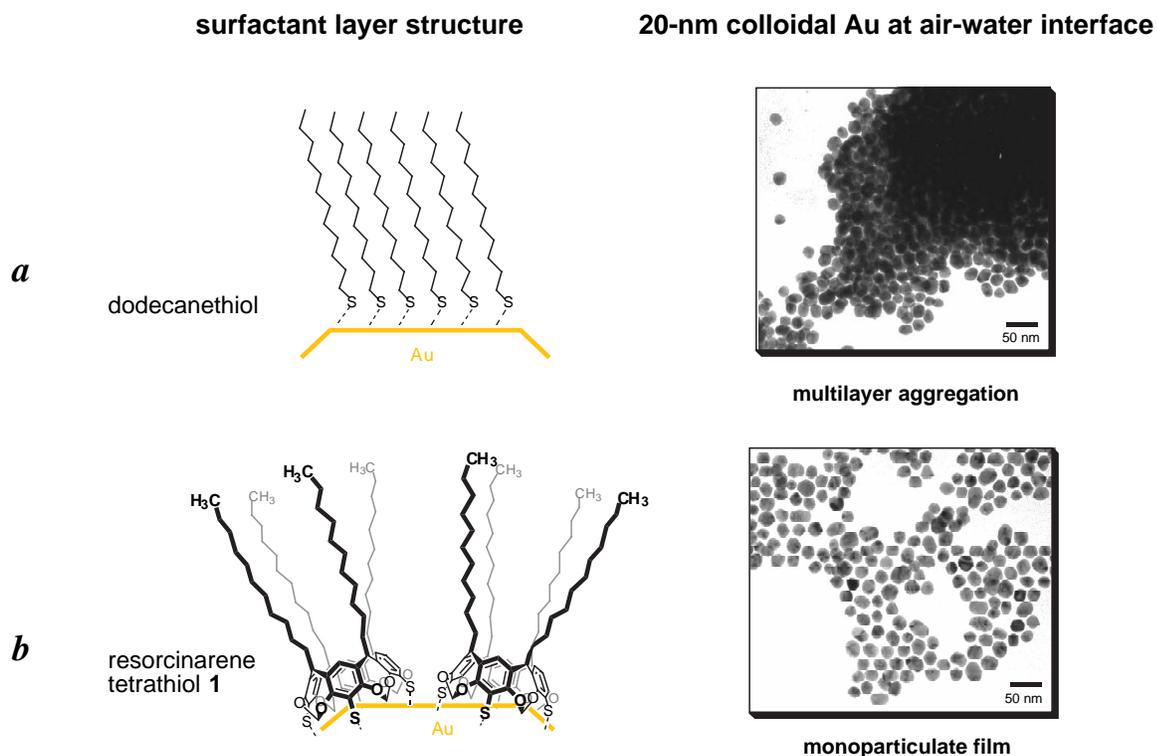


Figure 1. *a*, 20-nm gold nanoparticles coated with dodecanethiol form multilayered aggregates at the air-water interface. *b*, the same size nanoparticles coated with **1** form monoparticulate films.

EXPERIMENTAL RESULTS AND DISCUSSION

Having previously demonstrated calix[4]resorcinarenes to be excellent dispersants of nanoparticles in organic solvents,⁸ we synthesized resorcinarene tetrathiol **1** as a surfactant for large colloidal gold nanoparticles.⁹ The adsorption of the tetrathiol resorcinarenes to the nanoparticles was expected to be robust, given the multivalent nature of the surfactants¹⁰ and the very low rates of desorption of aryl monothiols from gold surfaces.¹¹ Aqueous solutions of citrate-stabilized 20-nm gold nanoparticles were treated with millimolar solutions of **1** in THF and extracted several times against toluene. Evaporation of the solvent resulted in a blue film at the solvent interface, which was directly transferred by horizontal (Langmuir-Schaefer) deposition onto a carbon-coated copper grid. Analysis of the film by transmission electron microscopy (TEM) revealed several important features (see Figure 1b). First, the resorcinarene surfactant layer was indeed effective at enhancing the steric barrier around the nanoparticles, as demonstrated by the larger interparticle spacings. Second, the nanoparticles were transferred as a monoparticulate film, inferring a similarly dispersed state at the air-water interface.¹² Third, the nanoparticles appeared to spontaneously self-organize into densely packed ensembles, suggesting the potential for planar array formation with long-range order.

The generality and scope of these initial observations were systematically investigated by changing the unit size of the gold nanoparticles. Citrate-stabilized colloidal gold particles of low size dispersity (<15%) ranging from 16 to 170 nm were treated with **1** and washed as before, then extracted and densified in a silanized pipette. These were carefully spread at the air-water interfaces in silanized tubes, then transferred by Langmuir-Schaefer deposition onto Formvar-

coated TEM grids for evaluation of the local structure and order (see Figure 2). In every case, submicron-sized domains of hexagonally close-packed nanoparticle arrays were observed. The average interparticle distance appears to decrease with increasing particle size, possibly due to the stronger attractive van der Waals forces between the larger particles. Although the present quality of particle monodispersity and periodicity in the arrays prevents a rigorous measurement of the interparticle spacings, direct analysis of the TEM images enables the interparticle spacings to be described in relative terms, and clearly indicate a trend toward decreasing average interparticle separations with increasing periodicity.¹³

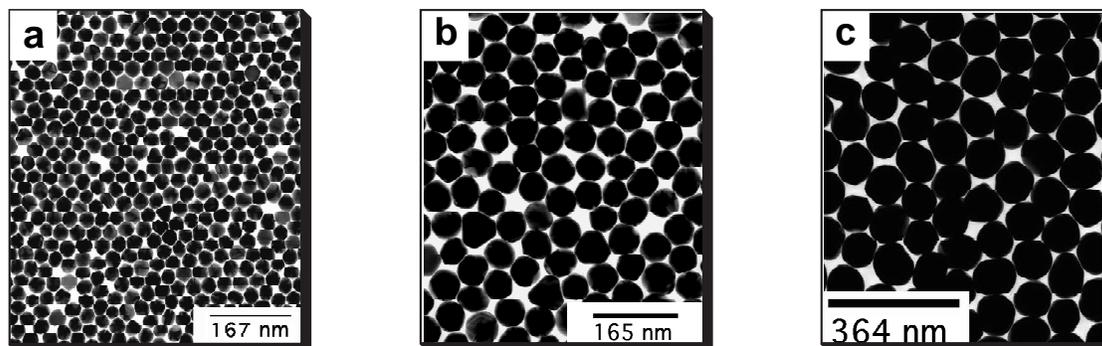


Figure 2. TEM images (Philips EM400, 80 keV) of 2D arrays of mid-nanometer sized gold nanoparticles formed by self-organization at the air-water interface. The arrays were transferred onto Formvar-coated Cu TEM grids by Langmuir-Schaefer deposition. *a*, 34 ± 2 nm particle array; *b*, 70 ± 5 nm particle array; *c*, 111 ± 8 nm particle array.

Monoparticulate films at the air-water interface could also be transferred onto freshly ionized Formvar-coated TEM grids by slow vertical retraction of partially immersed substrates in the absence of externally applied pressure,¹⁴ producing essentially hexagonally close-packed domains with micrometer dimensions (see Figure 3a). This method was used to transfer films onto hydrophilic annealed quartz substrates for investigating their optical properties as a function of periodic structure.



Figure 3. *a*, 87 ± 7 nm particle array transferred from the air-water interface onto hydrophilic TEM grid by slow vertical retraction of the substrate without lateral surface compression. *b*, Specular reflectances of 16-, 34-, 42-, 70-, 87-, and 111-nm particle arrays transferred onto annealed quartz substrates (white light, $\theta_i = 60^\circ$). Substrates are approximately 1 cm wide.

Vertical deposition of the gold nanoparticle arrays resulted in films which exhibited periodicity-dependent optical properties, presumably as a function of both particle size and interparticle spacing (see Figure 3b). Reflectance of white light from the nanostructured films was highly variable, with maximum specular reflectance observed for the 42- and 70-nm particle arrays. The

changes in reflectivities of the nanoparticle arrays as a function of size are probably due to several effects. One is the angular dependency of attenuated reflection as a function of surface roughness, a well-established phenomenon in metallic thin films.¹⁵ Reflectivity studies of gold and silver films evaporated onto optically transparent surfaces with nanometer-scale features have shown that the attenuated reflection minima broaden and shift toward wider angles of incidence as the roughness amplitude increases.¹⁶ A second effect is related to the size-dependent optical absorption properties of the nanostructured films; the nanoparticle arrays with periodicities <40 nm demonstrated significant absorptivities at visible wavelengths (see below). Thirdly, electromagnetic Mie scattering is responsible for the lower specular reflectances of the larger (>70 nm) particle arrays, which again is a well-characterized property of rough metal surfaces¹⁵ as well as for isolated gold nanoparticles in this size range.¹⁷

The monoparticulate gold films varied in hue from blue to a faint grey and were strongly to moderately absorptive in the visible and near infrared (NIR) wavelength regions (see Figure 4a). Absorption spectroscopy indicated that the plasmon resonance bands of the planar arrays shifted by hundreds of nanometers toward longer wavelengths as periodicity increased, accompanied by considerable peak broadening. Size effects on the Mie extinction properties of individual metal nanoparticles are well known, but the changes observed for the collective electromagnetic properties of the nanoparticle arrays are much more pronounced. Interparticle spacing has an especially important influence on the electromagnetic coupling between metal nanoparticles and has been experimentally demonstrated in several studies, most notably by the groups of Heath¹⁸ and Mulvaney.¹⁹ The latter were able to apply the Maxwell-Garnett model to quantitatively explain the optical extinction properties of silica-coated gold nanoparticle films with effective packing densities as high as 0.6. Current theoretical descriptions of the electromagnetic properties of densely packed nanoparticle arrays are more limited in their accuracy, but may still be useful for suggesting relative trends with respect to packing density.²⁰

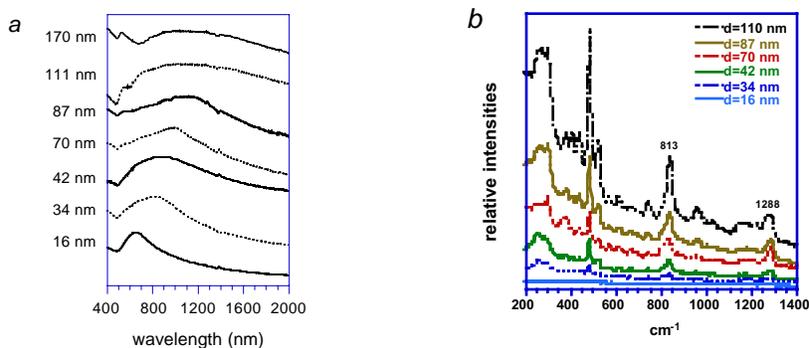


Figure 4. *a*, Absorption spectra of large gold nanoparticle arrays transferred onto annealed quartz substrates.¹³ Spectra were obtained with an HP 8453 UV-visible spectrophotometer (400-1100 nm) and a modified OLIS Cary-14 spectrophotometer equipped with a NIR photodiode (850-2000 nm). Spectral intensities have been modulated for clarity of presentation with minimal effect on the extinction maxima. Spectra reproduced with permission from the American Chemical Society. *b*, Surface-enhanced Raman spectra of **1** from gold nanoparticle arrays which had been transferred onto glass slides. Spectra were acquired with a micro-Raman spectrometer²¹ operating at 785 nm and 40X magnification (N.A.=0.75) with an input power of 10 mW at the sample (spot size= 700 μm^2 , integration time= 30 sec.). Spectra have been shifted for clarity of presentation.

The large gold nanoparticle arrays were also characterized by surface-enhanced Raman scattering (SERS), which integrates high chemical sensitivity with spectroscopic identification and has enormous potential for applications involving ultrasensitive chemical detection.²¹ Spectra were obtained using a home-built dispersive micro-Raman imaging system operating at NIR (785 nm) excitation²² with adsorbed tetrathiol **1** as the analyte. Irradiation of approximately one femtomole²³ of **1** with 30-second exposure times yielded Raman spectra with signal intensities that varied by over two orders of magnitude (see Figure 4b). The strength of the Raman signals improved as the periodicity increased, with the largest particle arrays providing the greatest enhancements. However, it must be mentioned that this trend is strongly dependent on excitation wavelength, such that the signal intensities generated at visible wavelengths are produced by particle arrays with intermediate periodicities and less pronounced shifts in plasmon resonance.

Comparison of the signal intensities at 831 and 1288 cm^{-1} in the SERS spectra with unenhanced Raman signals from noncrystalline resorcinarene films (thickness = 17-30.5 nm) suggest signal enhancement factors in excess of 10^7 , a remarkably large value given the potential for reproducibility of the nanostructured gold films.²⁴ The enormous SERS enhancements in the larger nanoparticle arrays are likely to be a function of both the greater scattering cross-sections of the individual gold nanoparticles (increases roughly with particle diameter to the sixth power) as well as the strong electromagnetic coupling between particles, with the latter being highly sensitive to the interparticle spacing (see above). This is in accord with previous theoretical²⁵ and experimental²⁶ studies which suggest that controlled aggregation of metal nanoparticles can increase signal strength by several orders of magnitude relative to that of isolated particles because of localized electromagnetic field effects between surfaces, such that the majority of the observed enhancements are due to highly active hot spots in the pores and crevices created by the dense packing of the nanoparticles.

The tunable periodicities of the large gold nanoparticle arrays are especially appealing in light of theoretical approaches for approximating electromagnetic SERS enhancements as a function of size and interparticle distance.²⁷ However, other variables such as particle shape anisotropy,²⁸ surface potential of the transferred nanoparticle arrays,²⁹ and optical configurations for efficient scatter collection need to be addressed in order to provide a valid comparison between theory and measurement. Such systematic investigations are expected to improve our understanding of the basis of the SERS enhancements observed in the large gold nanoparticle arrays.

ACKNOWLEDGMENTS

The authors gratefully acknowledge financial support from the National Science Foundation (0086804-BES) and the Research Corporation Innovation Award program (RI-0333). This work is also supported by the Integrated Detection of Hazardous Materials (IDHM) Program, a Department of Defense project managed jointly by Center for Sensing Science and Technology (CSST), Purdue University, and Naval Surface Warfare Center (NSWC), Crane, Indiana.

REFERENCES

- ¹ (a) Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Science* **1995**, *270*, 1335-38. (b) Brust, M.; Bethell, D.; Schiffrin, D. J.; Kiely, C. J. *Adv. Mater.* **1995**, *7*, 795-97. (c) Andres, R. P.; Bielefeld, J. D.; Henderson, J. I.; Janes, D. B.; Kolagunta, V. R.; Kubiak, C. P.; Mahoney, W. J.; Osifchin, R. G. *Science* **1996**, *273*, 1690-93. (d) Whetten, R. L.; Khoury, J. T.; Alvarez, M. M.; Murthy, S.; Vezmar, I.; Wang, Z. L.; Stephens, P. W.; Cleveland, C. L.; Luedtke, W. D.; Landman, U. *Adv. Mater.* **1996**, *8*, 428-33. (e) Shalaev, V. M.; Moskovits, M. *Nanostructured Materials: Clusters, Composites, and Thin Films*; ACS Symposium Series, Vol. 679; American Chemical Society: Washington, DC, **1997**.
- ² To the best of our knowledge, the largest unit size reported for a 2D gold nanoparticle array (assembled by electrophoretic deposition) is 18 nm: (a) Giersig, M.; Mulvaney, P. *J. Phys. Chem.* **1993**, *97*, 6334-36. (b) Giersig, M.; Mulvaney, P. *Langmuir* **1993**, *9*, 3408-13.
- ³ Osifchin, R. G. Ph.D. thesis, Purdue University, **1994**. The flocculation of alkanethiol-coated Au nanoclusters with diameters larger than 10 nm has also been studied in some detail as a function of surfactant: Weisbecker, C. S., Merritt, M. V., Whitesides, G. M. *Langmuir* **1996**, *12*, 3763-72.
- ⁴ (a) Biggs, S.; Mulvaney, P. *J. Chem. Phys.* **1994**, *100*, 8501-05. (b) Kane, V.; Mulvaney, P. *Langmuir* **1998**, *14*, 3303-11.
- ⁵ Israelachvili, J. *Intermolecular and Surface Forces*; 2nd ed.; Academic Press: New York, **1992**. Chapter 10.
- ⁶ (a) Kreibig, U.; Vollmer, M. *Optical Properties of Metal Clusters*; Springer: New York, **1995**; Vol. 25. (b) Henrichs, S.; Collier, C. P.; Saykally, R. J.; Shen, Y. R.; Heath, J. R. *J. Am. Chem. Soc.* **2000**, *122*, 4077-83. (c) Remacle, F.; Levine, R. D. *J. Am. Chem. Soc.* **2000**, *122*, 4084-91.
- ⁷ The effect of chain density on conformational free energies has been theoretically modeled for surfactant monolayers. See: Szleifer, I.; Ben-Shaul, A.; Gelbart, W. M. *J. Phys. Chem.* **1990**, *94*, 5081-89. and references cited within.
- ⁸ (a) Stavens, K. B.; Puszta, S. V.; Zou, S.; Andres, R. P.; Wei, A. *Langmuir* **1999**, *15*, 8337-39. (b) Wei, A.; Stavens, K. B.; Puszta, S. V.; Andres, R. P. *MRS Symp. Proc. Ser.* **1999**, *581*, 59-63.
- ⁹ The synthesis of resorcinarenes similar to **1** is described in the literature: (a) Moran, J. R.; Karbach, S.; Cram, D. *J. Am. Chem. Soc.* **1982**, *104*, 5826-28. (b) Gibb, B. C.; Mezo, A. R.; Causton, A. S.; Fraser, J. R.; Tsai, F. C. S.; Sherman, J. C. *Tetrahedron* **1995**, *51*, 8719-32.
- ¹⁰ Surfactants with several well-spaced thiol groups have been suggested for enhanced adsorption to gold surfaces because of cooperative binding as well as low probability of desorption via disulfide formation: Schlenoff, J. B.; Li, M.; Ly, H. *J. Am. Chem. Soc.* **1995**, *117*, 12528-36.
- ¹¹ Mohri, N.; Matsushita, S.; Inoue, M. *Langmuir* **1998**, *14*, 2343-47.
- ¹² Fendler, J. H. *Curr. Op. Colloid Interface Sci.* **1996**, *1*, 202-07.
- ¹³ Kim, B.; Tripp, S. L.; Wei, A. *J. Am. Chem. Soc.* **2001**, *123*, 7955-56.
- ¹⁴ Blodgett, K. A.; Langmuir, I. *Phys. Rev.* **1937**, *51*, 964.
- ¹⁵ Raether, H. *Surface Plasmons on Smooth and Rough Surfaces and on Gratings*; Springer: Berlin, **1988**; Vol. 111.
- ¹⁶ (a) Hornauer, D.; Kapitza, H.; Raether, H. *J. Phys. D* **1974**, *1*, L100. (b) Kapitza, H. *Opt. Comm.* **1976**, *16*, 73.
- ¹⁷ (a) Yguerabide, J.; Yguerabide, E. E. *Anal. Biochem.* **1998**, *262*, 137-56. (b) Yguerabide, J.; Yguerabide, E. E. *Anal. Biochem.* **1998**, *262*, 137-56.
- ¹⁸ (a) Collier, C. P.; Saykally, R. J.; Shiang, J. J.; Henrichs, S. E.; Heath, J. R. *Science* **1997**, *277*, 1978-81. (b) Shiang, J. J.; Heath, J. R.; Collier, C. P.; Saykally, R. J. *J. Phys. Chem. B* **1998**, *102*, 3425-30.
- ¹⁹ Ung, T.; Liz-Marzán, L. M.; Mulvaney, P. *J. Chem. Phys.* **2001**, *105*, 3441-52.
- ²⁰ Wasileski, S. A.; Zou, S.; Weaver, M. J. *Appl. Spectrosc.* **2000**, *54*, 761-72.
- ²¹ (a) Vo-Dinh, T. *Trends Anal. Chem.* **1998**, *17*, 557-82. (b) Kneipp, K.; Kneipp, H.; Itzkan, I.; Dasari, R. R.; Feld, M. S. *Chem. Rev.* **1999**, *99*, 2957-75.
- ²² Gift, A. D.; Ma, J. Y.; Haber, K. S.; McClain, B. L.; Ben-Amotz, D. *J. Raman Spectrosc.* **1999**, *30*, 757-765.
- ²³ The number of adsorbates in a 30- m diameter spot was approximated by using the surface area of an ideally planar array of hexagonally close-packed particles, which has a surface roughness of 1.8 independent of unit particle size. If surfactant adsorption is assumed to be at 75% maximum coverage (ca. 2 nm²/molecule), the number of adsorbates contributing toward the Raman signal is estimated to be 6.3 × 10⁸ molecules. For experimentally measured cross-sectional areas of **1** in a densely packed geometry, see: (a) Moreira, W. C.; Dutton, P. J.; Aroca, R. *Langmuir* **1994**, *10*, 4148-52. (b) Kurita, E.; Fukushima, N.; Fujimaki, M.; Matsuzawa, Y.; Kudo, K.; Ichimura, K. *J. Mater. Res.* **1998**, *8*, 397-403.
- ²⁴ For further studies, see: Wei, A.; Kim, B.; Sadler, B.; Tripp, S. L. *ChemPhysChem* **2001**, *2*, in press.

-
- ²⁵ (a) Liver, N.; Nitzan, A.; Gersten, J. I. *Chem. Phys. Lett.* **1984**, *111*, 449-54. (b) Tsai et al (1984) (c) Garcia-Vidal, F. J.; Pendry, J. B. *Phys. Rev. Lett.* **1996**, *77*, 1163-66.
- ²⁶ (a) Blatchford, C. G.; Campbell, J. R.; Creighton, J. A. *Surface Sci.* **1982**, *120*, 435-55. (b) Albano, E. V.; Daiser, S.; Ertl, G.; Miranda, R.; Wandelt, K. *Phys. Rev. Lett.* **1983**, *51*, 2314-17. (c) 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*, 1629-32. (d) Xiao, T.; Ye, Q.; Sun, L. *J. Phys. Chem. B* **1997**, *101*, 632-38. (e) Kneipp, K.; Kneipp, H.; Manoharan, R.; Hanlon, E. B.; Itzkan, I.; Dasari, R. R.; Feld, M. S. *Appl. Spectrosc.* **1998**, *52*, 1493-97.
- ²⁷ Jensen, T.; Kelly, L.; Lazarides, A.; Schatz, G. C. *J. Cluster Sci.* **1999**, *10*, 295-317.
- ²⁸ Recently, Natan and coworkers have reported a methodology for preparing large colloidal gold nanoparticles with low size dispersity and ellipticity: Brown, K. R.; Walter, D. G.; Natan, M. J. *Chem. Mater.* **2000**, *12*, 306-13.
- ²⁹ Blatchford, C. G.; Siiman, O.; Kerker, M. *J. Phys. Chem.* **1983**, *87*, 2503-08.