

Tunable Surface-Enhanced Raman Scattering from Large Gold Nanoparticle Arrays

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KEYWORDS:

calixarenes · gold · nanostructures · Raman spectroscopy · self-organization

Surface-enhanced Raman scattering (SERS) integrates high levels of sensitivity with spectroscopic precision and thus has tremendous potential for chemical and biomolecular sensing.^[1] Efforts to understand and develop SERS as an analytical tool are dependent on methods for fabricating materials with stable and reproducibly high activities. Typical SERS substrates, such as roughened gold and silver electrodes or colloidal aggregates, are disordered and often produce unpredictable signal enhancements; moreover, their structures are unstable and quickly lose their SERS activity.^[2] Controlled methods for preparing nanostructured metal substrates may provide more useful correlations between surface structure and signal enhancement. A wide variety of metallic nanostructures have been fabricated and investigated as SERS substrates, including silver-coated nanosphere arrays,^[3] metal-tipped and metal-coated nanosized posts,^[4] spherical gold nanoshells,^[5] submicron square-lattice gratings,^[6] pyramidal silver islands by nanosphere lithography,^[7] and colloidal metal films with controlled packing densities.^[8] The latter studies indicate that particle size and interparticle spacing are primary considerations for strong SERS activity.

In this Communication we describe the SERS properties of highly ordered, close-packed arrays of large (16–170 nm) gold nanoparticles. The SERS activities from these substrates are tunable as a function of both periodic nanostructure and incident wavelength, with empirical signal enhancement factors (*G*) ranging from 10⁴ to over 10⁷. We have recently shown that gold nanoparticles in the mid-nanometer size regime are capable of self-organizing into planar close-packed arrays when treated with resorcinarene tetrathiol **1** (Figure 1 a).^[9] The nanostructured films vary in their optical reflectivities and absorptivities, changing in hue from blue to a faint grey (see Figure 1 d). Extinction spectra reveal size-dependent shifts in dipolar plasmon resonance by hundreds of nanometers from the visible to the near infrared (NIR) region (see Figure 2).^[9] The dramatic changes in extinction as a function of periodicity suggest that the arrays are comparable to metallic thin films, whose plane

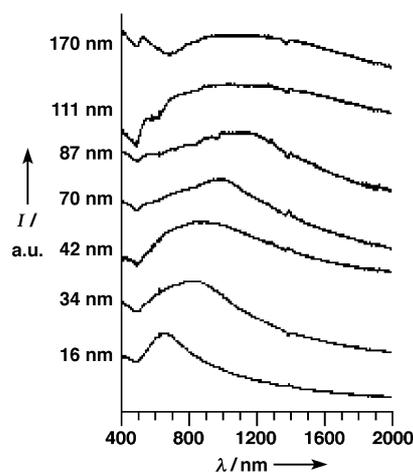


Figure 2. Extinction spectra of large gold nanoparticle arrays on smooth quartz substrates.^[9]

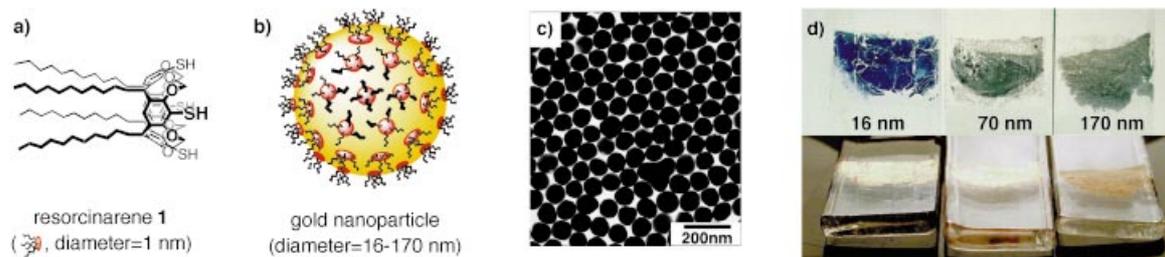


Figure 1. Large gold nanoparticle arrays with size-tunable optical properties. a, b) Aqueous suspensions of gold particles ranging from 16 to 170 nm were treated with resorcinarene tetrathiol **1** and dispersed at the air–water interface for self-organization into planar close-packed arrays.^[9] c) Transmission electron micrograph (Phillips EM-400, 80 keV) of 87 ± 7 nm gold particle array transferred by mechanically controlled vertical deposition onto a Formvar-coated copper grid (300 mesh) mounted on a glass slide. d) 16-, 70-, and 170-nm gold particle arrays on smooth quartz substrates photographed at 0° (top) and 60° (bottom) angles of incidence relative to the surface normal. Substrate width is approximately 1 cm.

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Supporting information for this article is available on the WWW under <http://www.chemphyschem.com> or from the author.

surface plasmons have been localized by periodic gratings and whose optical properties also vary as a function of periodic structure and incident wavelength.^[10, 11]

The SERS properties of the large gold nanoparticle arrays were evaluated by comparing relative changes in the Raman signal intensities of adsorbed tetrathiol **1**. Spectra were obtained from three instruments with different configurations and excitation

wavelengths (λ_{ex}) but approximately equal solid angles of collection as defined by their effective numerical apertures (N.A.): a) a dispersive spectrometer operating at 647.1 nm, b) a home-built Raman imaging microscope operating at 785 nm,^[12] and c) an FT spectrometer operating at 1064 nm (see Figures 3a and 3b). Empirical signal enhancement factors (G) were determined using peak integration ratios of the surface-enhanced Raman vibration of **1** at 813 cm^{-1} to the correspond-

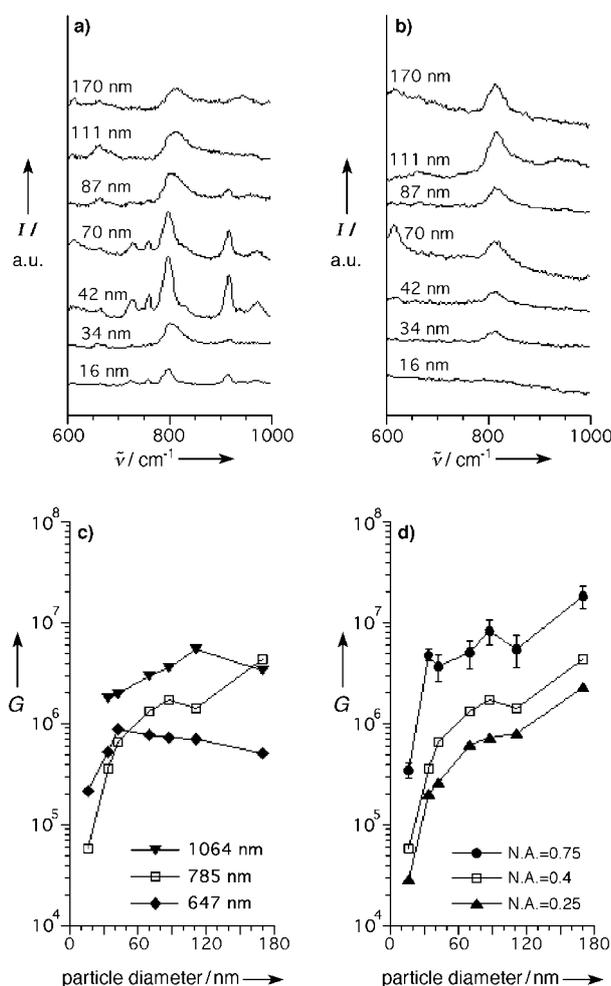


Figure 3. Surface-enhanced Raman scattering as a function of array structure. Raman spectra of adsorbate **1** were obtained at different excitation wavelengths from various nanoparticle arrays on smooth quartz substrates. a) Spectra obtained using a dispersive spectrometer (SpectraCode, N.A. = 0.4) at a Raman excitation wavelength of 647.1 nm by a krypton ion laser (Spectra-Physics, 50 mW at the sample). b) Spectra obtained using a FT spectrometer (Nicolet, N.A. = 0.5) at a Raman excitation wavelength of 1064 nm by a Nd:VO₄ laser (500 mW). Spectral intensities have been shifted for clarity of presentation. c) Signal enhancement factors (G) as a function of periodic structure and excitation wavelength, based on the characteristic Raman vibration of **1** at 813 cm^{-1} . G values were derived from the integrated signal intensities in (a) and (b) and from spectra obtained using a Raman microscope with a 20x objective lens (Olympus, N.A. = 0.4) at an excitation wavelength of 785 nm by a diode laser (SDL, 12 mW at the sample).^[12, 13] d) Signal enhancement factors as a function of periodic structure and numerical aperture at a fixed excitation wavelength (785 nm). G values were derived from spectra obtained using a Raman microscope with objective lenses of variable numerical aperture and input power at the sample (10x: Olympus, N.A. = 0.25, 20 mW; 20x: Olympus, N.A. = 0.40, 12 mW; 40x: Olympus, N.A. = 0.75, 10 mW).^[12] Error bars are equal to one standard deviation, based on replicate measurements at different positions on the sample.

ing unenhanced signal from noncrystalline films of defined thickness, with values ranging from 10^4 to over 10^7 (see Figures 3c and 3d).^[13] It must be noted that the measurements are macroscopic with respect to the periodicity of the arrays and do not necessarily correlate with *localized* signal enhancements, which may be several orders of magnitude greater than the spatially averaged factors (see below). However, the G values reported here are practical for defining minimum signal enhancements and can be used to evaluate periodic trends.

Overall, we find that unit particle size and excitation wavelength are strongly correlated with the SERS activity of the arrays (see Figure 3c). These observations are in accord with theoretical calculations describing signal enhancements in terms of electromagnetic field effects^[14, 15] and with other SERS studies on metal colloid suspensions comprised of variably sized particles and aggregates.^[16, 17] The extinction maxima of the arrays with the highest SERS activities do not correlate strongly with λ_{ex} as has been reported in earlier studies,^[16] which suggests significant contributions by other means. These include scattering efficiency, which is known to increase with particle diameter to the fourth power in isolated metal particles,^[10] and signal amplification by plasmon modes resonant at the Stokes-shifted Raman wavelength λ_{SR} , which can differ from λ_{ex} by as much as 100 nm for the vibrational band of interest.^[18]

Interestingly, the empirical enhancement factors demonstrate a strong dependence on the solid angle of collection. Micro-Raman spectra obtained at 785 nm excitation using objective lenses with N.A. values of 0.25, 0.40, and 0.75 yielded G values that varied by nearly an order of magnitude (see Figure 3d). The effective Raman scattering cross section β of unenhanced samples did not change with aperture by more than a factor of 50%, confirming the surface-enhanced nature of the phenomenon.^[13] Values for β are often dependent on the angle of observation and also the angle of incidence, which strongly influence the electric field intensity at metal surfaces. Raman scattering studies of adsorbates on smooth^[19] and electrochemically roughened^[20] silver surfaces have demonstrated marked changes in signal intensities as a function of observation angle, with a maximum between 55° and 60° relative to the surface normal. In comparison, the maximum half-angles from the objective lenses above are 15°, 24°, and 49° respectively, which correlate well with the considerable increases in G .

The resorcinarene-coated nanoparticle arrays are able to detect volatile organic compounds with spectroscopic precision and thus have promise as chemical sensors. Passage of approximately 30 mL of nitrobenzene-saturated air through a flow cell containing the 170-nm particle arrays resulted in the appearance of new peaks by SERS (see Figure 4b).^[13] Signal intensities in the Raman difference spectra increased with further vapor exposure and are clearly associated with the vibrational modes of nitrobenzene (see Figure 4c).^[21] The analyte presumably adsorbs to the resorcinarene surfactant layer in a non-specific manner, so that its signal is enhanced solely by the electromagnetic field of the underlying nanostructured substrate. Other surfactant-coated SERS substrates have also demonstrated detection of organic analytes in gaseous and

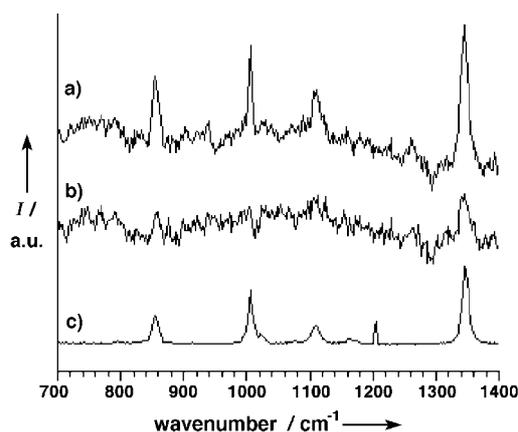


Figure 4. SERS difference spectra of nitrobenzene adsorbed to resorcinarene-encapsulated 170-nm particle array. Spectra were obtained using a Raman microscope with a 20x objective lens (Olympus, N.A. = 0.4) at an excitation wavelength of 785 nm and an irradiation time of 30 s.^[12, 13] Spectra a) and b) have been shifted and magnified for clarity of presentation. a) Difference spectrum after 5 min exposure to nitrobenzene vapor. b) Difference spectrum after 30 s exposure to nitrobenzene-saturated air. c) Raman spectrum of neat nitrobenzene. Peak assignment [cm^{-1}] are as follows: 854 (β , NO_2), 1005 (ν_{12} arom), 1110 (ν_{13} arom), 1345 (ν_s , NO_2).^[21]

aqueous environments, with heightened sensitivity and/or selectivity in some cases.^[22]

Theoretical studies on aggregate structures suggest that the electromagnetic field effects responsible for SERS are localized in the interstitial regions of the arrays, accompanied by field depletion outside of these areas.^[23] Recent SERS analyses of 50–60 nm metal colloid aggregates allege that NIR excitation produces giant local field effects corresponding to Raman enhancement factors on the order of 10^{11} or more.^[15, 24] This implies that the great majority of the SERS signal from the arrays is due to the excitation of a very small percentage of adsorbate at these interstitial sites, and that their true enhancements are greater than the surface-averaged G values by several orders of magnitude. Theoretical models of electromagnetic field intensities in periodic metal gratings offer additional insights: The field enhancements within the channels are predicted to increase commensurately with aspect ratio, and to resonate at wavelengths determined by the grating amplitude.^[25] Such models are congruent with the size-dependent SERS activities of the nanoparticle arrays: The interparticle spacings resemble grating channels with amplitudes and aspect ratios that vary as a function of periodic structure.

Finally, some practical aspects of the large gold nanoparticle arrays should be mentioned. The nanostructured films are stable in air and water at ambient temperatures and show no appreciable loss in SERS activity over a period of several months. The adsorption of volatile analytes is reversible, such that the substrates can be used multiple times. In addition, the SERS enhancements are reproducible for different sites on a given substrate as well as between replicate samples, with relative standard deviations of 14 to 35% (see Figure 3d). Such features complement the tunable SERS properties of the gold nanoparticle arrays and enhance their potential value for forensic applications.

This work was supported by the US National Science Foundation (BES-0086804) and the Research Corporation (RI-0333) and is in association with the Center for Sensing Science and Technology, Purdue University. We thank M. Weaver, B. McClain, and A. Gift for discussions and D. Thompson, J.-M. Kim, M. Weaver, M. Mrozek, P. Martoglio-Smith, J. Hupp, M. B. Williams, and R. Johnson for the use of their equipment.

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Received: June 21, 2001 [Z250]