

Polarized Surface Enhanced Raman Scattering from Aligned Silver Nanowire Rafts

Dae Hong Jeong,[†] You Xiang Zhang, and Martin Moskovits*

Department of Chemistry and Biochemistry and the California Nanosystems Institute, University of California, Santa Barbara, California 93106

Received: December 22, 2003; In Final Form: June 10, 2004

Flat arrays (rafts) of aligned silver nanowires were fabricated by electrodepositing silver in the nanopores of highly ordered anodic alumina templates and then releasing the silver nanowires and depositing them on an oxidized, single-crystal silicon surface. SERS spectra were recorded from Rhodamine 6G molecules adsorbed onto the rafts. The SERS spectra showed striking polarization dependence according to the relative disposition of the E-vector with respect to the nanowires' axes. The observations can be adequately described by the classical electromagnetic (EM) response of the strongly interacting metal nanowires to the optical fields when surface plasmon resonances are induced. The discussion relates these observations to the origin of the giant surface enhanced Raman effect with single-molecule detectivity as well as to possible strategies that one might use to construct systems that predictably and repeatedly produce such giant EM fields.

Introduction

Surface enhanced Raman spectroscopy (SERS) was discovered^{1–3} and successfully explained in terms of the excitation of localized surface plasmons (the so-called EM theory of SERS)⁴ some twenty-five years ago. SERS-active systems typically produced Raman enhancements of the order of $10^{5–6}$. More recently, S. Nie⁵ and K. Kneipp⁶ independently reported much larger enhancements with effective Raman cross-sectional increases of $\sim 10^{14}$, large enough to make SERS detection from single molecules routinely possible. The fact that SERS at certain “hot spots” could be as high as $\sim 10^{11}$ or so was known for decades. Metiu et al., for example, showed that the local EM fields in the interstice between two small silver particles⁷ or between a silver nanoparticle and a smooth silver surface (i.e., between a nanoparticle and its charge-conjugate image) could reach very large values.^{8,9} The field enhancement is strongly dependent on polarization; only fields polarized along the interparticle axis are strongly enhanced. Computation of the fields at such interstitial locations was performed recently using modern computational techniques. For example, Garcia-Vidal and Pendry¹⁰ reported the fields in the crevices among arrays of small hemispheres, and Xu and Käll¹¹ have published calculations of the field strength in the neighborhood of coupled nanosphere dimers. High-quality calculations on assemblies of 2-D metal circles by Martin¹² have also appeared. Also, the experimental results of Hildebrandt and Stockberger¹³ and Pettinger et al.¹⁴ in the 1980s had already convincingly alluded to the possibility of unusually intense SERS enhancements far in excess of the $\sim 10^6$ normally quoted as the typical average enhancement in “good” SERS-active systems.

Despite these insights, the origin of the remarkable enhancements reported by Nie and Kneipp (and corroborated by others) were initially thought to be mysterious and reports continue to appear claiming that single-molecule SERS and, indeed, that the basic physics of the SERS effect remain, somehow,

controversial. This results from the long-standing skepticism expressed by some regarding the EM theory⁵ in contraindication to almost all of the existing experimental and theoretical evidence. This situation is sustained by the fact that, experimentally, SERS is a very simple phenomenon easily accessible to most chemistry labs and hence is now practiced in many laboratories worldwide, while at the same time its origin, although straightforward, requires a detailed knowledge of the sometimes subtle physics describing the optical, near-field response of nanostructures.

Stated simply, some 10–11 orders of magnitude of SERS enhancement are routinely achievable at special hot spots in properly crafted, strongly interacting metal nanostructures as a result of the very high concentration of the EM field at those hot locations. Two or three further orders of magnitude of enhancement are possible through the judicious choice of molecule so as to profit from the inherent, resonant electronic transitions of the molecule or from charge-transfer resonances that appear as a result of the formation of the molecule–metal surface bond. Hot structures and hot locations fall roughly into two categories. In small nanoparticle dimers or aggregates (of certain metals), the hot spots are interstitial locations. In large fractal nanoparticle aggregates, these hot spots appear naturally as a result of the symmetry breaking that occurs when an object possessing scaling symmetry is excited by a field that does not possess this symmetry.⁶ The location of these hot spots are strongly wavelength and polarization dependent.

Armed with this knowledge, one can now begin to apply the methods of nanoscience and technology to fabricate systems with well-characterized structures engineered to produce enhancements, routinely and predictively, large enough for single-molecule (or near single-molecule) SERS detection.

For this study, we fabricated oriented arrays of silver nanowires and used them to illustrate the special and strongly polarization-dependent enhancement possible in the interwire region, illustrating the above points. Bosnick et al.¹⁷ have recently reported the polarization dependence of SERS originating from a single R6G molecule and found it fully consistent with what is expected for a molecule confined to the interstitial

* Address correspondence to this author.

[†] Current address: Department of Chemistry Education, Seoul National University, Seoul 151-742, Korea.

space between two nanospheres. Käll et al.¹⁸ reported a similar study using hemoglobin.

Experimental Section

Silver nanowires were grown in highly ordered porous anodic alumina (PAO) templates, electrochemically fabricated on 0.25-mm superpurity aluminum sheet in 0.3 M oxalic acid using the two-step anodization process reported by Masuda.¹⁹ The templates were grown at 40 VDC at 6 °C. The anodizing voltage was stepped down to 10 VDC for 20 min at the end of the anodization process to decrease the barrier layer thickness facilitating the subsequent metal deposition. Silver metal deposition was carried out at room temperature by AC electrolysis in a 0.05 M AgNO₃ electrolyte by applying 15 V (RMS) at 200 Hz to the preanodized templates. Graphite counter electrodes were used in both processes. On average, the silver nanowires so fabricated were 35 nm in diameter and 10 μ m in length. The silver nanowires were released from the oxide templates by etching a small coupon of the sample in 0.05 M NaOH aqueous solution. The resulting nanowire deposit was ultrasonically dispersed in methanol. A few drops of dispersed silver wire solution were placed on the surface of a precleaned oxide-covered silicon wafer and dried for use in the Raman measurements.

Rhodamine 6G dye (R6G) adsorbate was applied to the SERS substrate out of a very dilute methanol solution. Backscattered SERS spectra were collected with a LabRam microRaman system (Jobin-Yvon/ISA) and detected on a thermoelectrically cooled CCD detector. Spectra were excited using the 514.5-nm line of a cw Ar ion laser (SpectraPhysics 2016). The polarization of the incident light was changed by rotating a half-wave plate placed in the optical path before the notch filter that served as both a reflector for the incident light and a Rayleigh light rejection filter for the collected signal. The incident laser beam was focused, and the Raman signal was collected using a $\times 100$ lens with an NA of 0.80. Approximately 50 μ W of laser radiation was used to excite samples at a signal collection time of 0.5 s.

Structural characterization of the silver nanowires was carried out using optical microscopy for macroscopic imaging and a high-resolution SEM (JEOL 6340F) and a high-resolution TEM (JEOL 2010HR) for more detailed structural analyses.

Results and Discussion

When dried, a drop of dispersed silver wire solution leaves a variety of different structures composed of silver nanowires on the surface of a silicon-oxide-covered silicon wafer. Some nanowires are well separated, and others comprise small, overlapping nanowire bundles. If diluted appropriately, several large nanowire bundles can be found of which some are rather flat bundles with many of the nanowires retaining their parallel alignment, presumably as a result of van der Waals interactions both among themselves and with the substrate. The silver nanowires in Figure 1, for example, comprise a nanowire raft consisting of three regions in each of which the nanowires are largely parallel. A close examination of the roots (the part of the nanowire that grew at the bottom of the PAO pores, Figure 1c) of the largest unit of this nanowire raft indicates that this portion of the raft has fused, creating a compact region of nanoparticles. This process was presumably aided by the branching induced at the bottoms of nanopores by stepping down of the anodizing voltage at the end of the pore-growth period. The central portions of nanowires, however, are rather smooth and well aligned (Figure 1b).

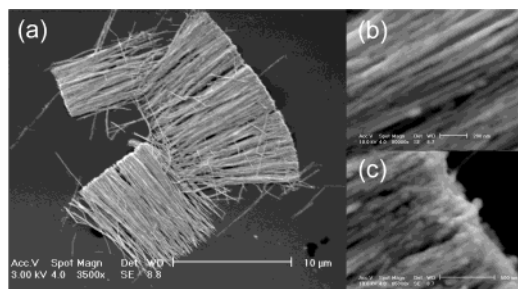


Figure 1. (a) SEM image of a "raft" of silver nanowires with three sections each showing significant nanowire alignment. Detailed views of a midwire section (b) and the region of the roots (c) of nanowires.

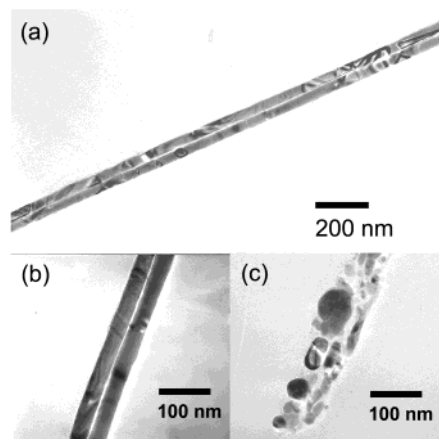


Figure 2. (a) TEM image of two closely interacting, aligned silver nanowires. Detailed views of a midwire section (b) and the roots (c) of nanowires.

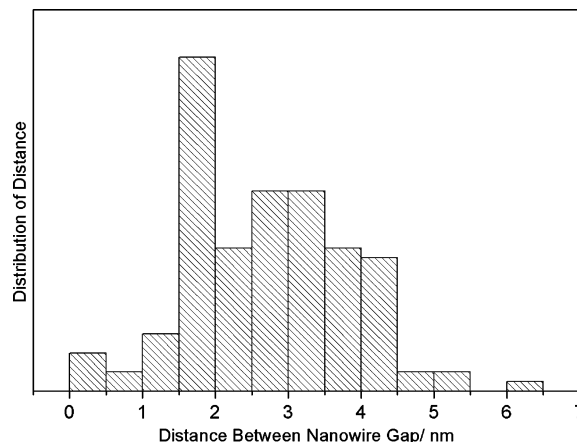


Figure 3. A histogram of the gap distance between the two silver nanowires shown in Figure 2.

A significant portion of the distribution of the distances between nanowires is in the 0 ~ 2 nm range which calculations show^{7,8,11,20} are required for the very intense optical fields responsible for giant SERS to exist (Figures 2, 3). Figure 2 shows the image of a (rarely occurring) single pair of parallel nanowires, for which the measured interwire distance distribution is shown in Figure 3. The SERS from molecules residing in this gap would be dominated by the interwire gaps at the low end of this distribution. (Recalling the prediction of the EM theory of SERS that under most circumstances the enhancement varies as the fourth power of the local field, a simple-minded calculation for light polarized appropriately (i.e., along the line which simultaneously cuts across the diameters of the two nanowires) has the enhancement increase approximately as d^{-8} where d is the gap size between the two nanowires.)

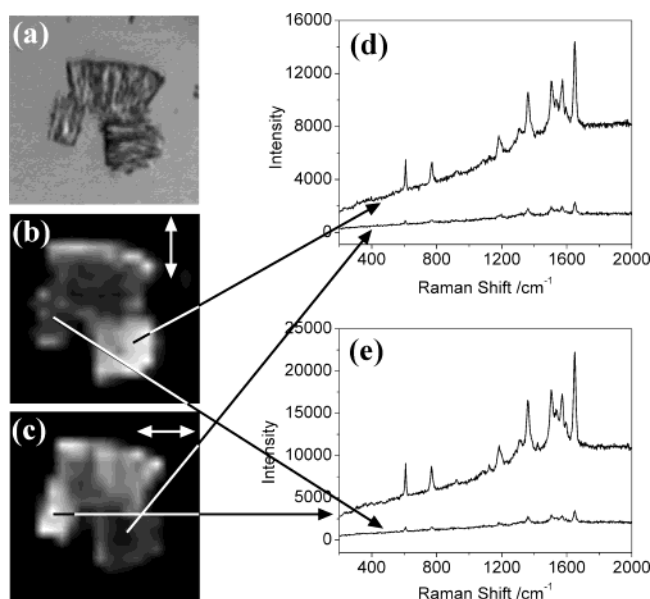


Figure 4. SERS intensity maps (a and b) recorded with the incident light polarized as indicated. “Vertical” and “horizontal” refer to the orientation of the electric vector of the light with respect to the nanowire raft whose optical image is shown in the upper right-hand corner. Typical SERS spectra recorded at the locations indicated are shown at the right of each of the SERS intensity maps. The maps were produced using the baseline-corrected intensities of the 1649 cm^{-1} Raman band of R6G. Raman spectra were excited with 514.5-nm Ar ion laser light. Note the strong polarization dependence of the SERS spectra with the strongest signal obtained when the laser light is polarized across the nanowires.

Laser excitation of R6G-dosed silver nanowire rafts produced intense SERS spectra of the dye molecules. The spectra agree well with those reported by others.⁵ SERS intensity maps of a nanowire raft were produced by selecting a rectangular ($38 \times 32\text{ }\mu\text{m}^2$) area (Figure 4) and then recording the SERS spectrum at $0.5\text{-}\mu\text{m}$ intervals. Figure 4 shows the SERS intensity map obtained at two orthogonal polarizations by plotting the (baseline-corrected) intensity of the 1649 cm^{-1} line of R6G excited with 514.5-nm argon laser light. (The polarization was rotated using a half-wave plate placed before the sample. No crossed-polarizer was used after signal collection.)

The polarization dependence is striking and in keeping with expectation. In principle, one is capable of choosing three canonical and orthogonal polarizations for a system of aligned nanowires. The first corresponds to the electric vector lying across the long axes of the nanowires and in the plane of the nanowires. The second has the electric vector in the plane of the nanowires but aligned along their long axes. In the third, the electric vector is normal to the plane containing the nanowires. (If both the directions of the wavevector and the electric vector are considered together, six distinct excitation configurations are possible.) With our experimental configuration, only the first two polarizations were possible. (The wavevector of the light is normal to the silicon substrate, although the small NA of the focusing lens does introduce components of the E-vector normal to the substrate’s surface.) The first (which we will call “across the nanowires”) corresponds to the most favorable condition for observing strong SERS. This, indeed, is what is observed. Referring to Figure 4, one notes the effect especially striking in the rectangular portion of the nanowire raft at its lower right corner in which the nanowires are particularly well aligned in a direction parallel to the lower edge of the figure. Light polarized across the nanowires produces a SERS signal that, on average, is ap-

proximately 10-fold more intense than what is observed with light polarized along the nanowires. With a raft of more randomly aligned nanowires (Figure 5), the polarization dependence is less dramatic. (Even here, the well-aligned portion at the lower right-hand corner of the raft illustrates the effect of orientation well.) Likewise, in the rather disordered portion near the tips of the nanowires (Figure 4) the polarization dependence essentially disappears.

The polarization effect illustrates the strong and localized enhancement of the EM field possible at favorable locations in systems of interacting nanostructures. In brief, when two nanoparticles interact by approaching each other closely, the optical field in the interstice between them can become enhanced some 6 orders of magnitude above that expected for the individual particle (i.e., some 11 orders of magnitude altogether) assuming the exciting illumination is appropriately polarized. This insight is not new. Metiu et al.^{7–9} showed this for two silver spheres and for a silver sphere sitting above a silver surface. For systems with dimensions small compared to the wavelength of light, the electromagnetic behavior of two wires excited with light polarized across the nanowires is isomorphic with the two-dimensional problem of two interacting “metal” circles which is also the limiting case for two metal spheres illuminated with light polarized along the interparticle line. This problem was solved in high-quality calculations by several groups including Metiu et al.,⁷ Käll et al.,¹¹ and Martin et al.¹² The more general two-wire problem which includes all six canonical configurations of illumination direction and polarizations has not yet been solved although aspects of this problem were treated by Shalaev et al.²¹ and Martin et al.²⁰

The origin of the special enhancement obtained when the polarization direction lies across the nanowires (or along the interparticle axis of a two-nanosphere system) can be understood qualitatively by referring to Figure 6(bottom). In that configuration, a molecule located in the interstice is flanked by two sets of (time-varying) conjugate charges arising from the polarization of the individual nanowires. As the nanowires are brought closer together, the proximity of these charges to the molecule can be made arbitrarily small and hence the field sensed by the molecule commensurately large. The mutual interaction of the two nanowires (or nanospheres) also leads to an increase in the magnitude of the dipole induced in each component of the two-component nanosystem. The dipole induced in each nano-object arises from the combined field of the incident light and the intense field of its partner, which, in this configuration, leads to an amplification of the polarization. Contrariwise, when the light is polarized in the other direction illustrated in Figure 6 (top), that is, normal to the plane containing the two nanowires, a molecule in the interstitial region does not benefit from proximity to the induced charges, however closely the nanowires are brought together. Also, there is not any other location where the field benefits distinctly from the fact that one has a system of two wires rather than one. Additionally, the mutual polarization of each of the two nanowires as a result of the field emitted by the other is not favorable.

The electromagnetic properties of several aligned, periodic nanowires was considered by Pendry and Garcia-Vidal.¹⁰ Their calculations indeed reveal that the local electromagnetic (EM) field is very intense in the interstitial region between the nanowires for polarization across the nanowires. The field continues to be intense even when the nanowires overlap, but for that situation the locus of the most intense fields resides (not unexpectedly) in the clefts formed by the overlapping

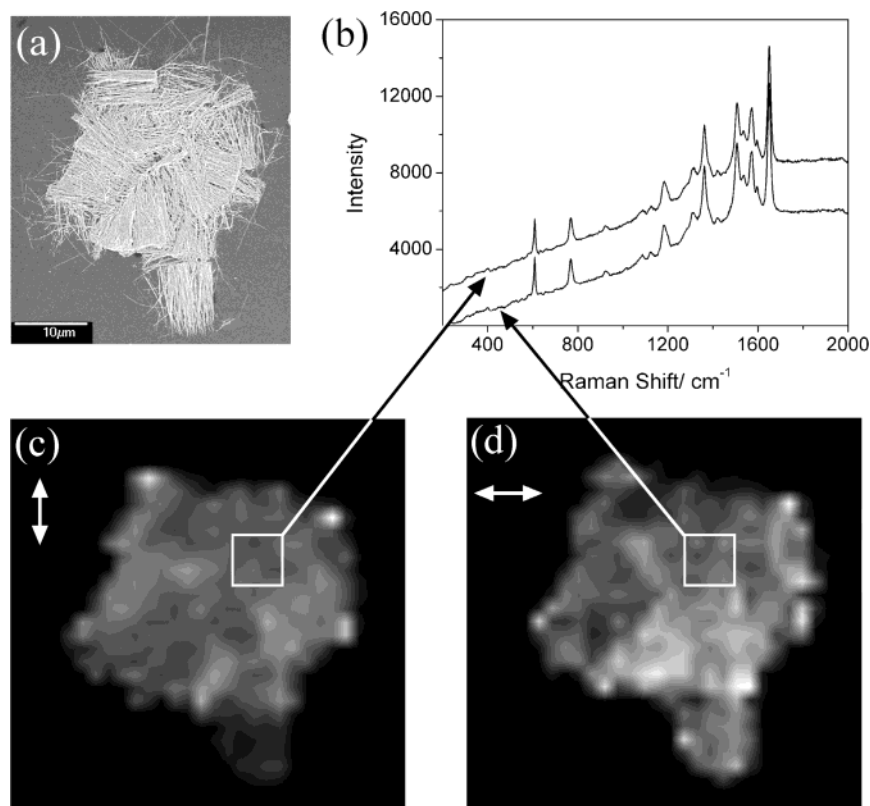


Figure 5. As for Figure 4 but for a raft of more randomly aligned Ag nanowires.

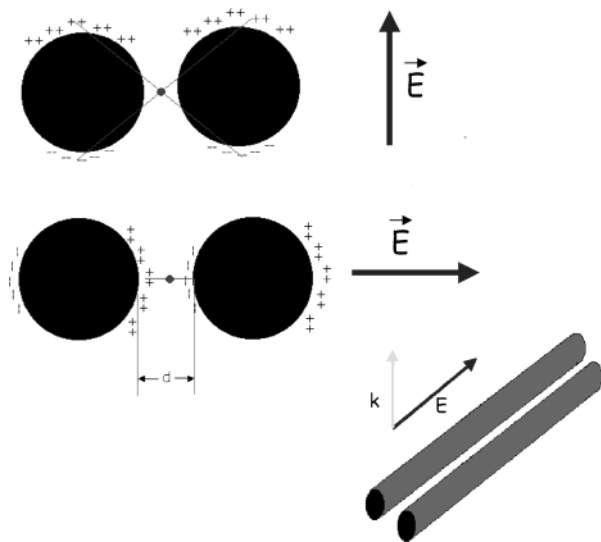


Figure 6. Simple graphical illustration of the reason that light polarized with the E-vector along the interwire axis can result in huge enhancements in the gap between the two nanowires while the orthogonal polarization cannot. For light polarized across the nanowires (bottom), the proximity of the charges (induced by the optical fields) to the molecule can be made arbitrarily small and hence the field sensed by the molecule commensurately large as the nanowires are brought closer together. That capability is not available for light polarized either normal to the plane of the nanowires (top, not available with our experimental configuration) or along their lengths (bottom right).

nanowires. Although the location of the greatest field enhancements is identical for a pair of nanowires (or nanospheres) as for a linear array of nanowires and nanospheres, the most intense fields occur for a single pair of interacting nano-objects. As one adds nanowires (or nanospheres) to the array, the induced charges become more equitably distributed among the many interstitial locations rather than concentrating in a unique

interstitial region, possible only with a single pair of nano-objects. This causes the field intensity at the “hot” interstices to decrease as nanowires (or nanospheres) are added to the array, although, because the coupling between nanowires falls off rapidly with distance, these reduced fields will rapidly approach an asymptotic value (at the most central interstices). Pendry and Garcia-Vidal¹⁰ show that the EM fields become most intense when the center-to-center distance between nanowires drops below ~ 3 times the radius of nanowires. (Also, because the curvature of the cleft starts getting smaller when the nanowire–nanowire overlap becomes too great, the enhancement peaks when the interwire distance reaches twice the nanowire radius).

The calculation on the system that most closely resembles the one we study here was carried out by Shalaev and et al.²¹ who used the discrete dipole approximation and modeled the nanowire as a linear array of overlapping nanospheres. Unfortunately, they did not consider the polarization directions we used in our study. Nevertheless, the calculation predicts several interesting wavelength-dependent and nanowire-length-dependent resonances when the wavevector of the light has a sizable component along the nanowires’ long axes.

In conclusion, the SERS signal of a dye molecule adsorbed on a raft of aligned silver nanowires shows striking polarization effects. The observations are adequately described using the classical electromagnetic response of the interacting metal nano-objects to the incident optical fields and to the intense scattered fields arising from the surface plasmons induced in the metallic nanostructures. The discussion is generalized so that on the basis of our observations one can better understand both the origin of the giant surface enhancements reported over the past few years leading to the observation of surface enhanced Raman from single molecules as well as the strategies that one might use to construct nanosystems that predictably and repeatedly produce such giant EM fields.

Acknowledgment. We are grateful to Dr. Andrei Kolmakov and Dr. Guosheng Cheng for valuable discussions and to Dr. Sung-Hyeon Baek for help with TEM measurements. This work made extensive use of the MRL Central Facilities at UCSB supported by the National Science Foundation under award No. DMR96-32716.

References and Notes

- (1) Fleischmann, M.; Hendra, P. J.; McQuillan, A. *Chem. Phys. Lett.* **1974**, 26, 163.
- (2) Jeanmaire, D. L.; Van Duyne, R. P. *J. Electroanal. Chem.* **1977**, 84, 1.
- (3) Albrecht, M. G.; Creighton, J. A. *J. Am. Chem. Soc.* **1977**, 99, 5215.
- (4) Moskovits, M. *J. Chem. Phys.* **1978**, 69, 4159.
- (5) Nie, S.; Emery, S. R. *Science* **1997**, 275, 1102.
- (6) Kneipp, K.; Wang, Y.; Kneipp, H.; Itzkan, I.; Dasari, R. R.; Feld, M. S. *Phys. Rev. Lett.* **1996**, 76, 2444.
- (7) Aravind, P. K.; Nitzan, A.; Metiu, H. *Surf. Sci.* **1981**, 110, 189.
- (8) Aravind, P. K.; Metiu, H. *J. Phys. Chem.* **1982**, 86, 5076.
- (9) Aravind, P. K.; Metiu, H. *Surf. Sci.* **1983**, 124, 506.
- (10) Garcia-Vidal, F. J.; Pendry, J. B. *Phys. Rev. Lett.* **1996**, 77, 1163.
- (11) Xu, H.; Aizpurua, J.; Käll, M.; Apell, P. *Phys. Rev. E* **2000**, 62, 4318.
- (12) Kottmann, J. P.; Martin, O. J. F.; Smith, D. R.; Schultz, S. *Phys. Rev. B* **2001**, 64, 235402.
- (13) Hildebrandt, P.; Stockburger, M. *J. Phys. Chem.* **1984**, 88, 5935.
- (14) Pettinger, B.; Krischer, K.; Ertl, G. *Chem. Phys. Lett.* **1988**, 151, 151.
- (15) Otto, A. *J. Raman Spectrosc.* **2002**, 33, 593.
- (16) Stockman, M. I. *Phys. Rev. E* **1997**, 56, 6494. Shalaev, V. M.; Botet, R.; Mercer, J.; Stechel, E. B. *Phys. Rev. B* **1996**, 54, 8235. Shalaev, V. M.; Sarychev, A. K. *Phys. Rev. B* **1998**, 57, 13265. Gresillon, S.; Aigouy, L.; Boccara, A. C.; Rivoal, J. C.; Quelin, X.; Desmarest, C.; Gadenne, P.; Shubin, V. A.; Sarychev, A. K.; Shalaev, V. M. *Phys. Rev. Lett.* **1999**, 82, 4520.
- (17) Bosnick, K. A.; Jiang, J.; Brus, L. E. *J. Phys. Chem. B* **2002**, 106, 8096.
- (18) Xu, H.; Käll, M. *Chem. Phys. Chem.* **2003**, 4, 1001.
- (19) Masuda, H.; Fukuda, K. *Science* **1995**, 268, 1466.
- (20) Kottmann, J. P.; Martin, O. J. F. *Opt. Express* **2001**, 8, 655.
- (21) Podolskiy, V. A.; Sarychev, A. K.; Shalaev, V. M. *Opt. Express* **2003**, 11, 735.