

Plasmon Resonance of Finite One-Dimensional Au Nanoparticle Chains

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ABSTRACT

We report experimental and theoretical studies on the plasmon resonances of finite one-dimensional chains of Au nanoparticles excited by evanescent light waves with polarization parallel to the chains. The experimental results show that the plasmon resonance peak wavelengths of these finite 1D chains are significantly red-shifted in comparison to that of single Au nanoparticle. Contrary to previous findings, the peak wavelengths are observed to be a nonmonotonic function of particle numbers in the chain. This phenomenon is reproduced in the theoretical results obtained by using the transfer-matrix method and is shown to occur only for larger particles where phase retardation effects are important in plasmon coupling.

Considerable recent interest has been paid to nanometal particles due to the numerous potential applications of their extraordinary optical properties.^{1–11} The strong interactions of nanometal particles with visible light originate from the excitation of collective oscillations of conduction electrons within these particles, an elementary excitation termed “surface plasmons”.¹³ The surface plasmons can be detected as resonance peaks in the light scattering spectra of these nanoparticles. The plasmon resonance energy of a particular nanometal particle depends on its size, shape, composition, and its surrounding medium.¹⁴ Coupling between surface plasmons of neighboring particles leads to energy shifts and energy confinements between particles, an effect playing an important role in surface enhanced Raman scattering experiments (SERS).^{10–12,15–19}

Near-field plasmon coupling in periodic arrays has been extensively studied. Of particular interest, recent theoretical and experimental work suggests that one-dimensional nanoparticle arrays can be utilized to transport energy.^{10–12,20–21} The minimum size of the guided modes in nanoparticle arrays is not limited by diffraction, which may enable nanoscale optical devices if the propagation loss can be minimized. Furthermore, near-field scanning optical microscopic studies of 1D chains of nanoparticles showed that enhanced local electromagnetic fields are primarily confined between particles, which may be utilized for producing efficient SERS-active substrates for molecular sensing applications.²² Since the energy transportation in a chain is sensitive to interparticle

plasmon coupling, thorough understanding of the resonance wavelength dependence on the chain length and particle spacing could provide useful guidance for designing nano-optical devices. Far-field spectroscopic studies and finite-difference time-domain (FDTD) simulations of chains of 50 nm diameter Au spheres show that the peak wavelength of plasmon resonances increases (decreases) with the chain lengths for the longitudinal (transverse) mode and saturates when the chain is longer than about seven particles.²⁰

In this letter, we report experimental and theoretical studies on the plasmon resonances of finite 1D chains of Au nanoparticles excited by optical waves with a polarization parallel to the chain (longitudinal mode). The experimental results show that the plasmon resonance peak wavelength of a finite 1D chain of Au nanoparticles is significantly red-shifted in comparison to that of single Au nanoparticles. In contrast to previous findings for smaller particles,^{20–21} the peak wavelength is found to be nonmonotonic and oscillating with the variation of the chain length. Theoretical calculations based on the transfer matrix method show satisfactory agreement with this experimental observation and demonstrate further that this resonance peak oscillation occurs only for large particles. This finding may help to provide a better understanding of the plasmon resonances in coupled nanoparticle chains.

The gold nanoparticles were prepared on quartz substrates by electron beam lithography (EBL) and a standard lift-off process. 10 nm-thick indium tin oxide (ITO) films were sputtered on the quartz substrates to reduce charging effects during the EBL process, and 100 nm-thick poly(methyl methacrylate) (PMMA) films were used as a positive

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photoresist for EBL. 3 nm-thick Ti films were used to promote adhesion between the ITO and Au films.

Evanescent light waves produced by a collimated light beam undergoing total internal reflection (TIR) were utilized to excite the particle plasmons. In our experiments, a collimated light beam delivered by a multimode optical fiber from a 150 W Xe white light source is incident on a right-angle prism at a 45° angle and totally reflected. The nanoparticle samples were sited on the top surface of the prism, and between their touching surfaces, index-matching oil was used to minimize stray scattering light due to surface defects and dust particles. This leads to a very high dark field contrast. The light scattered by the metal nanoparticles was collected by an optical microscope with a 50× long working distance objective and formed an image at the exit image plane. At this image plane, a small aperture was used to select individual particles or individual particle chains and also served to block the scattered light from the surrounding particles and substrate. The light emerging from this aperture was then imaged onto the entrance slit of a Triax Jobin Yvon spectrometer system equipped with a liquid nitrogen cooled charge coupled device (CCD) detector. The detailed experimental setup is similar to the one described in previous papers.^{17,23}

Figure 1a presents four typical SEM pictures of fabricated 1D chains of 1–4 Au nanoparticles. The elliptical particles are 74 nm in short axis diameter, 102 nm in long axis diameter, and 30 nm in thickness. The particle center–center spacing is 153 nm, and the long axis is oriented at 74° with respect to the chain. The chains of different particle numbers are separated by 20 μm from each other, a distance sufficiently large to ensure that only the scattering light from one single chain can be collected without the interference from other chains. These particles are pretty uniform in size, and the variation in resonance wavelength for different chains of the same length is within a few nanometers.

To obtain the scattering spectrum of these 1D periodic particle arrays, care must be taken to avoid the interference effect. As has been known from previous work,^{24–25} once the Bragg diffraction condition is fulfilled, the interference between the light scattered by individual particles in the array can lead to far field diffractions into the air or the substrate. The nonzero orders of far-field diffractions strongly affect the spectrum and lifetime of surface plasmons due to the consequential radiation damping. On the other hand, even without diffraction, the interference effect as a result of the periodicity of particle arrays can still make the light scattered into a specified direction, which may cause some difficulty in light collection for the spectrum measurements as shown below.

Figure 1b and c present optical microscope pictures of the 1D particle chains for two different chain orientations. Although illuminated with a white light source, these particles appear red in dark field, indicating the strong light scattering at red wavelengths or an excitation of surface plasmons. When the chains are parallel to the incident plane (Figure 1b), only the light scattered by particles at two opposite ends of the chains can be seen. When the chain is rotated to a 45° angle relative to the incidence plane, all the

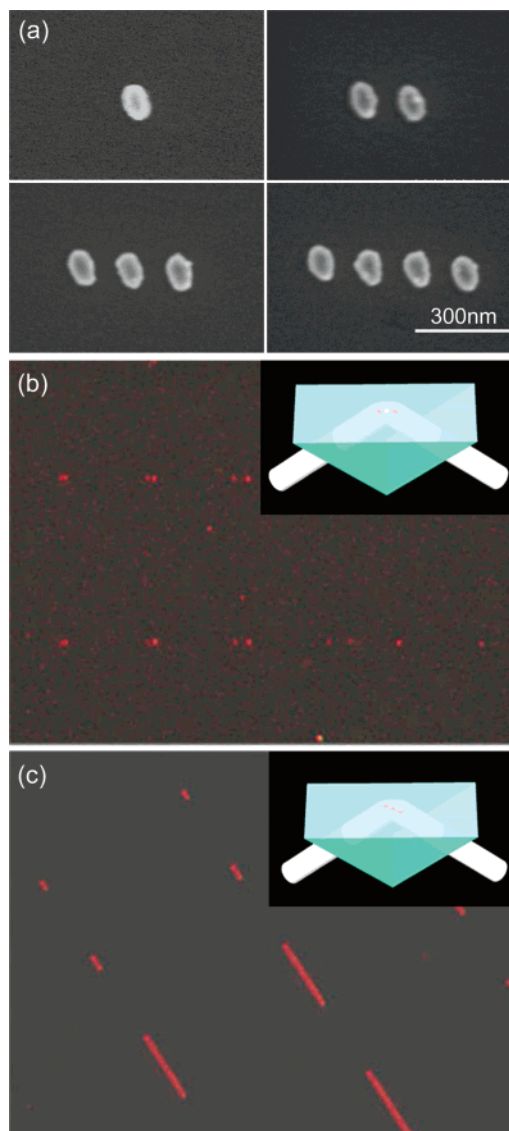


Figure 1. (a) Typical SEM pictures of 1, 2, 3, and 4 particles in a line fabricated by standard e-beam lithography and lift-off process on a quartz substrate. The particles are elliptical with a 74 nm diameter in the short axis, a 102 nm diameter in the long axis, 30 nm thickness, and 153 nm center–center spacing. (b, c) Optical microscopic pictures taken with a digital camera for chains parallel (b) and at a 45° angle (c) with respect to the incident plane. The inset shows the geometrical configurations.

particles in the chains can be observed together as a bright solid line. This phenomenon is an example of an interference effect due to the periodicity of particles in these chains and can be explained as follows.

Assuming a 1D chain of an infinite number of particles with a periodicity $d = 150$ nm (as in our experiments), it can be easily found out that the momentum conservation along the chain direction for the light diffracted into the air above the prism requires

$$k \cos \theta = nk \cos \theta_0 \pm mG \quad (1)$$

with θ_0 being the angle between the incident light and the chain, and θ the angle between the diffracted light and the

chain. Here $k = 2\pi/\lambda$ is the wave vector in air, $G = 2\pi/d$ is the reciprocal lattice vector, $n = 1.46$ is the refractive index of the prism, and m is an integer indicating the order of diffraction. With the plasmon resonance wavelength around 600 nm and the chain orientation of Figure 1b (i.e., $\theta_0 = 45^\circ$), it can be discovered that eq 1 cannot be held with any possible values of θ and m , which indicates that no propagating light exists in the air side. In the case of a finite chain, the deconstructive interference is incomplete especially for particles at the end of the chain where they have an asymmetric number of neighbors. Therefore, the end particles can still scatter some light into the air and can be observed under the optical microscope. For the particles in the middle of the chain, according to eq 1, there is still no direction (or θ) which could lead to a constructive interference for light scattered by them and their neighbors. This is the reason the middle particles of short chains cannot be seen in Figure 1b.

When the chain is unparallel to the incident plane such as a 45° angle with regard to the incident plane, the angle θ_0 between incident light and chain now becomes 60° . A solution $\theta = 43^\circ$ can be found out to satisfy eq 1 for $m = 0$. This zero order diffraction is within the collection angle of the 0.65 NA objective and makes the whole chain visible under the microscope. In the data presented below, the chains are oriented perpendicular to the incident plane, so that the scattered light can be maximally collected.

Figure 2a presents the measured scattering spectra for the chains as exemplified in Figure 1a. For single particles, two resonance peaks are observed. This is expected for elliptical particles. The incident electrical field along the chain projects two electrical field components along the particle's long and short axes, which excite two plasmon resonance modes. The right peak at 698 nm corresponds to the long axis mode, while the left peak at 594 nm corresponds to the short axis mode. The long axis mode is less pronounced than the short axis one because the projected incident electrical field component along the long axis is only about 29% ($\text{ctan}74^\circ$) of the component along the short axis. Our discussion below will be focused on the short axis plasmon mode.

For two particles, the resonant peak is red-shifted about 30 nm compared to that of the single-particle spectrum, signifying a strong near-field plasmon coupling. For three particles, the resonant peak, however, is only shifted 14 nm to red compared to that of single-particle plasmons, or blue-shifted with reference to that of two-particle plasmons. For four particles, the resonant peak wavelength is red-shifted again with regard to that of three particles. A plot of peak wavelength vs chain length in Figure 2b clearly shows that the peak wavelength is oscillating with particle numbers. This is in contrast to previous experimental and simulation observations that the plasmon resonance wavelength is a monotonic function of the chain length.²⁰

To explain this phenomenon and understand the physics behind it, we performed theoretical calculations by using the T-matrix method. The T-matrix, introduced by Watermann,²⁶ links the scattered field and the incident field based on the expansion of the scattering field in terms of spherical

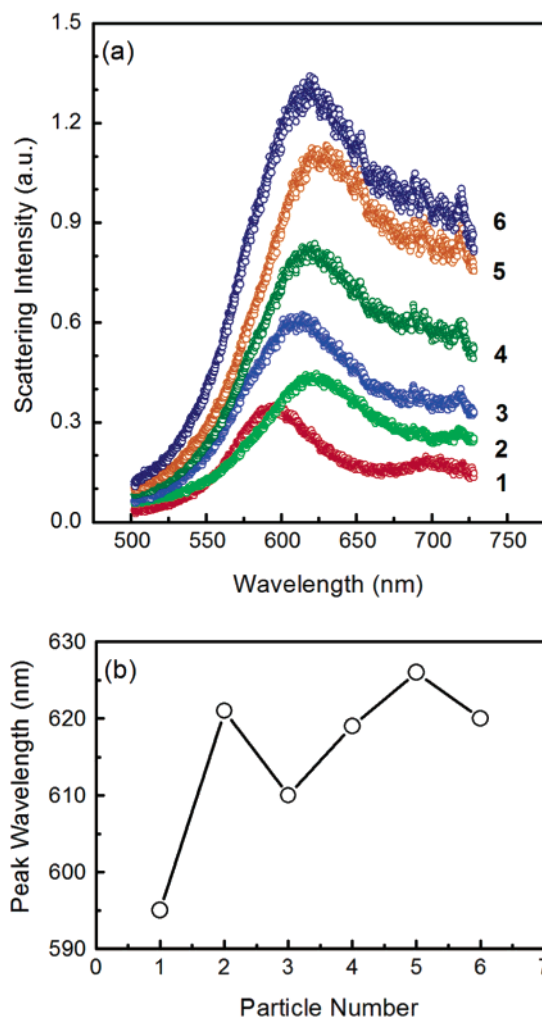


Figure 2. (a) Measured scattering spectra for finite 1D chains of Au nanoparticles as exemplified in Figure 1a. (b) Peak resonance wavelength vs particle numbers in the chains.

harmonics for arbitrarily shaped particles. Extinction ratio, absorption and scattering cross sections of the particles can be calculated accordingly once the T-matrix is determined.^{27,28} When the system is constituted of a collection of particles, the computation of the T-matrix can be simplified by using the T-matrix of each isolated particle. Especially for the case of spheres, the analytical solution of Mie theory can be utilized for calculating the T-matrix of each sphere, which makes the calculations straightforward.^{29,30}

We calculated the scattering spectra of finite 1D chains of a variable number of spheres. To compare the results with our experiments, the effect of the substrate is taken into account by embedding these spherical particles in an infinite medium with a refractive index $n = 1.5$, which is the average of the refractive indices of the air and the ITO films on substrates. Although the calculations shown here are based on spheres, the results, especially the general behavior of the resonant frequency shift, should be applicable to other particle shapes. Indeed, good agreements with experimental results have been obtained.

The results for two representative diameters are shown in Figure 3. For 40 nm diameter spheres (Figure 3a), the peak wavelengths of the plasmon resonance for 2–5 particle

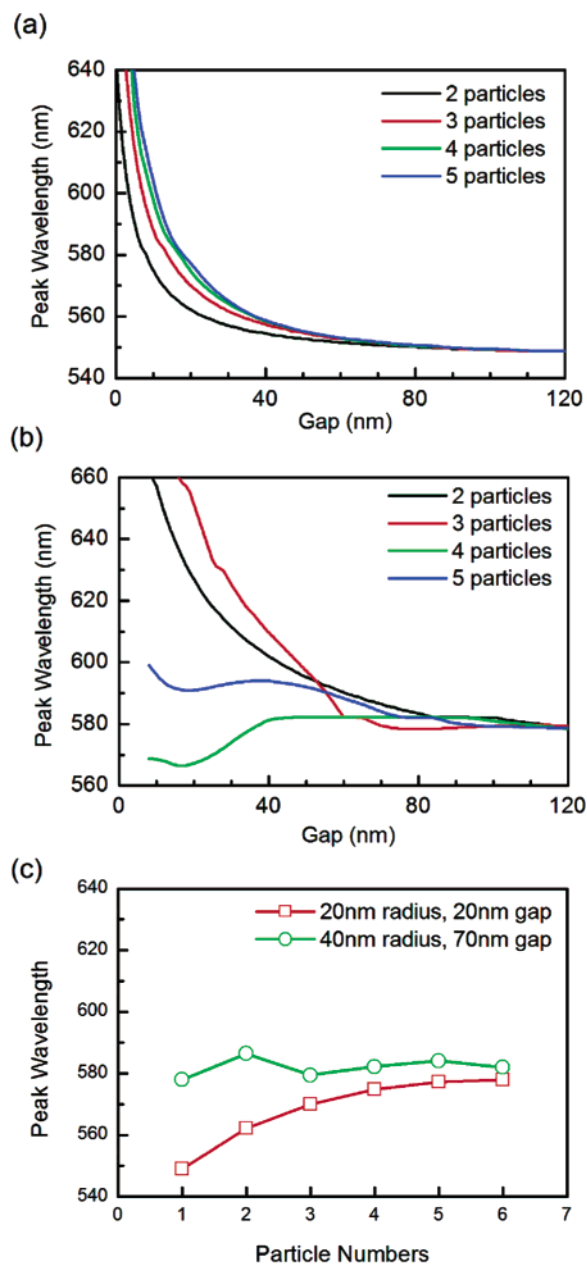


Figure 3. (a, b) Peak wavelengths of the scattering spectra calculated by using the T-matrix method for finite 1D chain of Au nanospheres with 40 nm diameter (a) and 80 nm diameter (b). (c) Peak wavelengths vs chain lengths for 40 nm particles with 20 nm gaps and for 80 nm particles with 70 nm gaps.

chains decay monotonically with the increase of the gap between neighboring particles. Meanwhile, the peak wavelength increases also monotonically with the increase of the particle number in the chain. This is in perfect agreement with previous simulation and experimental results for particles of similar sizes.^{20,21} However, for 80 nm diameter spheres (Figure 3b), although the peak wavelengths for two particles is still a monotonic decay function of gap between particles as shown before,^{16,17} the variation of peak wavelength for 3–5 particles shows dramatic nonmonotonic behavior not only versus the gap but also versus the particle numbers in the chain. Especially for the 70 nm gap, which is corresponding to the 150 nm center–center distance in

our experiment, the peak wavelength oscillation (Figure 3c) is in qualitative agreement with our experimental observations (Figure 2b). For instance, the resonance wavelength of three particles is lower than those for two- and four-particle chains, and the five-particle resonance wavelength is higher than those for four and six particles. Considering the different particle shapes and sizes used, this agreement is satisfactory.

This oscillation behavior of peak wavelength with the chain length varies with the gap size between particles. For instance, for a gap less than 50 nm, the sequence of wavelength shift for different particle numbers is $3 > 2 > 5 > 4$; while for a gap between 50 nm and 60 nm, the sequence is $2 > 5 > 3 > 4$ (Figure 3b).

This complex oscillating behavior can be considered as a collaborative effect of phase retardation and multiple plasmon coupling. As learned from previous work,¹⁷ the plasmon coupling range or the gap size between two identical particles is approximately 2.5 particle diameters. It can be confirmed that this coupling range applies also to the plasmon resonances of finite 1D chains. For instance, for 40 nm particles, when the gap becomes larger than 100 nm (or 2.5 particle diameter), the resonance wavelengths for different chain lengths reach a plateau which is corresponding to single-particle resonant wavelength (Figure 3a), while for 80 nm particles, this crossover occurs around 200 nm (not shown in the Figure 3b). The plasmon coupling between two particles is similar to the coupling of eigenmodes between two resonators such as optical microcavities or mechanical resonators. The resonance shift is approximately a linear function of the mode coupling coefficient which is proportional to the field on one particle generated by the other. In general, the coupling coefficient consists of an amplitude term decaying with the particle spacing and a phase term with the phase retardation growing with the spacing. The phase term determines the phase of the field on the second particle, and thus can reverse the field direction.³¹ In another word, the phase retardation can affect whether the resonance wavelength shifts to red or blue. A recent paper based on the recently developed plasmon hybridization method provided a vigorous physics picture for this plasmon mode coupling between two nanoparticles.¹⁹ For two small particles, this phase retardation effect is negligible since the total chain length within the coupling range is smaller than a quarter of the resonance wavelength. Additionally, the coupling between next nearest neighbors, as a second-order coupling, is also small.²¹ Therefore, even finite 1D chains of small particles such as with 40 nm diameter can be longer than a quarter of relevant wavelength, the phase retardation effect can be neglected because only nearest neighbor coupling is involved. This makes the resonance wavelength a monotonic function of the gap for 1D chains of small particles.

Since the chain length for two large particles is still less than half of the relevant wavelength where the coupling changes its sign, its resonance wavelength exhibits a monotonic decay function of the gap although the phase retardation effect cannot be neglected. For 1D chains of more

than two large particles, however, plasmon coupling between next nearest neighbors mediated by the middle particle become possible, because the scattering cross section of a particle increases dramatically with the sixth power of the particle diameter. Moreover, this next nearest neighbor coupling strengthens the retardation effect because the phase retardation is proportional to the spacing between next nearest neighbors in this case. Some of the nonmonotonic behaviors for 80 nm particle chains can be qualitatively explained based on this argument. For instance, the drop in the resonance wavelength for three-particle arrays (Figure 2b and Figure 3c) at 70 nm gap can be understood as a result of the fact that the coupling between two end particles has an opposite sign in reference to the end–middle particle coupling, because the center–center spacing between the first and third particles (~300 nm) is about half of the resonance wavelength, or the direction of the field generated by the first particle on the third particle is reverse to that on the middle particle.

It has been noticed that the resonant wavelength shift for two particles is usually a monotonic decay function of the spacing, even for large particles where phase retardation effects exist. Nevertheless, this monotonic behavior of two particles may be fortuitous for the particular particle shape here. An interesting paper recently shows that the resonance wavelength for two coupled particles can also be a non-monotonic function of the particle gap in the case of triangular “bow-tie” type of particles.¹⁸

It is worth noting the difference between the plasmon resonance of finite particle chains and that of nanorods or so-called nanoantennas.³² Both nanorods and nanochains consist of multipoles at their resonances, while for nanoantennas, the plasmon resonance wavelength of a specific mode is always a linear function of the antenna length.³²

In summary, we have studied the plasmon resonance of finite one-dimensional chains of Au nanoparticles both experimentally and theoretically. The results show that the plasmon resonance peak wavelength of coupled finite 1D chain of Au nanoparticles is significantly red-shifted when compared to that of single Au nanoparticles. Contrary to previous findings for small particle sizes, we found that for larger particle sizes, the peak wavelength is not a monotonic function of chain length. This phenomenon, originating from phase retardation and coupling effect, can be explained by theoretical calculation based on the T-matrix method.

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References

- (1) Kneipp, K.; Wang, Y.; Kneipp, H.; Perelman, L. T.; Itzkan, I.; Dasari, R.; Feld, M. S. *Phys. Rev. Lett.* **1997**, *19*, 1667.
- (2) Nie, S.; Emory, S. R. *Science* **1997**, *275*, 1102.
- (3) Schultz, S.; Smith, D. R.; Mock, J. J.; Schultz, D. A. *Proc. Natl. Acad. Sci. U.S.A.* **2000**, *97*, 996.
- (4) Cao, Y. W. C.; Jin, R. C.; Mirkin, C. A. *Science* **2002**, *297*, 1536.
- (5) Xu, H. X.; Käll, M. *Phys. Rev. Lett.* **2002**, *89*, 24802.
- (6) Cognet, L.; Tardin, C.; Boyer, D.; Choquet, D.; Tamarat, P.; Lounis, B. *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 11350.
- (7) McFarlan, A. D.; Van Duyne, R. P. *Nano Lett.* **2003**, *3*, 1057.
- (8) Haes, A. J.; Zou, S. L.; Schatz, G. C.; Van Duyne, R. P. *J. Phys. Chem. B* **2004**, *108*, 109.
- (9) Prikulis, J.; Svedberg, S.; Käll, M.; Enger, J.; Ramser, K.; Goksör, M.; Hanstorp, D. *Nano Lett.* **2004**, *4*, 115.
- (10) Quinten, M.; Leitner, A.; Krenn, J. R.; Aussenegg, F. R. *Optics Lett.* **1998**, *23*, 1331.
- (11) Brongersma, M. L.; Hartman, J. W.; Atwater, H. A. *Phys. Rev. B* **2000**, *62*, R16356.
- (12) Maier, S. A.; Kik, P. G.; Atwater, H. A.; Meltzer, S.; Harel, E.; Koel, B. E.; Requicha, A. A. G. *Nature Mater.* **2003**, *2*, 229.
- (13) Kreibig, U.; Vollmer, M. *Optical Properties of Metal Clusters*; Springer-Verlag: Berlin, 1995.
- (14) Kelly, K. L.; Coronado, E.; Zhao, L. L.; Schatz, G. C. *J. Phys. Chem. B* **2003**, *107*, 668.
- (15) Haynes, C. L.; McFarland, A. D.; Zhao, L. L.; Van Duyne, R. P.; Schatz, G. C.; Gunnarsson, L.; Prikulis, J.; Kasemo, B.; Käll, M. *J. Phys. Chem. B* **2003**, *107*, 7337.
- (16) Rechberger, W.; Hohenau, A.; Leitner, A.; Krenn, J. R.; Lamprecht, B.; Aussenegg, F. R. *Opt. Commun.* **2003**, *220*, 137.
- (17) Su, K.-H.; Wei, Q.-H.; Zhang, X.; Mock, J. J.; Smith, D. R.; Schultz, S. *Nano Lett.* **2003**, *3*, 1087.
- (18) Fromm, D. P.; Sundaramurthy, A.; Schuck, P. J.; Kino, G.; Moerner, W. E. *Nano Lett.* **2004**, in press.
- (19) Nordlander, P.; Oubre, C.; Prodan, E.; Li, K.; Stockman, M. I. *Nano Lett.* **2004**, in press.
- (20) Maier, S. A.; Kik, P. G.; Atwater, H. A. *Appl. Phys. Lett.* **2002**, *81*, 1714.
- (21) Maier, S. A.; Brongersma, M. L.; Kik, P. G.; Atwater, H. A. *Phys. Rev. B* **2002**, *65*, 193408.
- (22) Krenn, J. R.; Dereux, A.; Weeber, J. C.; Bourillot, E.; Lacroute, Y.; Goudonnet, J. P.; Schider, G.; Gotschy, W.; Leitner, A.; Aussenegg, F. R.; Girard, C. *Phys. Rev. Lett.* **1999**, *82*, 2590.
- (23) Barbic, M.; Mock, J. J.; Smith, D. R.; Schultz, S. *J. Appl. Phys.* **2002**, *91*, 9341.
- (24) Meier, M.; Wokaun, A.; Liao, P. F. *J. Opt. Soc. Am. B* **1985**, *2*, 931.
- (25) Lamprecht, B.; Schider, G.; Lechner, R. T.; Ditlbacher, H.; Krenn, J. R.; Leitner, A.; Aussenegg, F. R. *Phys. Rev. Lett.* **2000**, *84*, 4721.
- (26) Waterman, P. *Phys. Rev. D* **1971**, *3*, 825.
- (27) Mishchenko, M. I. *J. Opt. Soc. Am. A* **1991**, *8*, 871.
- (28) Mackowski, D. W. *J. Opt. Soc. Am. A* **1994**, *11*, 2851.
- (29) Bohren, C. F.; Huffman, D. R. *Absorption and Scattering of Light by Small Particles*; Wiley: New York, 1983.
- (30) Mackowski, D. W.; Fuller, K.; Mishchenko, M. I. *Calculation of the Scattering Properties for a Cluster of Spheres*; <http://www.giss-nasa.gov>, 1999.
- (31) Kottmann, J. P.; Martin, O. J. F. *Optics Lett.* **2001**, *26*, 1096.
- (32) Krenn, J. R.; Schider, G.; Rechberger, W.; Lamprecht, B.; Leitner, A.; Aussenegg, F. R.; Weeber, J. C. *Appl. Phys. Lett.* **2000**, *77*, 3379.

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