Characterization of nanoplasmonic structures by locally excited photoluminescence

Alexandre Bouhelier,[a] Michael R. Beversluis, and Lukas Novotny
The Institute of Optics, University of Rochester, Rochester, New York 14627

(Received 18 August 2003; accepted 23 October 2003)

A method is presented for the characterization of locally enhanced fields at laser-irradiated metal nanostructures. Excitation with 120 fs laser pulses gives rise to photoluminescence mediated by two-photon absorption. A metal tip used to locally scatter the photoluminescence renders a map of regions with high field strengths. Near-field photoluminescence images of particle clusters reveal the dipole nature of the electromagnetic field surrounding the particles. Spectra acquired with and without the presence of the tip show no significant shift of the surface plasmon resonance of the particle clusters, confirming that the tip acts as a passive probe. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1634383]

The optical properties of metal nanoparticles are strongly influenced by their size, their shape, and by their environment such as the proximity to other particles. When the dimensions of nanoparticles becomes smaller than the wavelength of the exciting light, energy can be confined in small spatial regions through the local excitation of surface plasmon resonances. The enhanced fields in these regions are used in a wide range of applications including surface enhanced Raman scattering (SERS),[1] near-field microscopy,[2–5] and nanoscale optical devices.[6,7] It was predicted that the electromagnetic field enhancement may be very large when two resonant particles are brought close to each other and that most of the energy is located between the particles.[8] More recently, several authors have investigated the spectroscopic behavior of resonant coupled systems as a function of particle separation and polarization direction[9–11] and predicted molecular trapping by the forces associated with the strong field gradient.[12] Direct experimental measurements of electromagnetic fields localized between closely spaced nanostructures are needed to validate theoretical predictions and to develop systems with improved properties. In this letter, we experimentally study the three-dimensional spatial variation of the electromagnetic field as a function of the separation between a gold nanoparticle and a sharp gold tip. In the context of scanning probe microscopy, studies have shown that a metallic tip can influence the spectroscopic response of a gold substrate or resonant particles. The spectral shifts of the resonances are ascribed to resonant gap modes,[13–15] or to material transport from the tip to substrate.[16]

To measure the field distribution in nanoparticles, we take advantage of their intrinsic photoluminescence properties. Two-photon excited luminescence was found to be sensitive to the local field enhancement on rough metal films.[17,18] In our experiments, we localize regions of strong field enhancement by measuring the spatial distribution of the photoluminescence yield. A colloidal solution of 40 nm gold particles was spin cast on a clean glass cover slip resulting in a broad distribution of particle arrangements ranging from single particles to micron-sized aggregates. The nanoparticles were excited by the field of a tightly focused femtosecond laser. The high peak intensity (1–10 GW/cm^2) associated with ultrashort pulses (~120 fs) excites electrons in the metal particles from the *d* band to the *sp* conduction band by two-photon absorption.[17,18] Subsequent photoluminescence is collected with the same objective as used for excitation and is directed toward either a sensitive avalanche photodetector for imaging purposes or to a CCD spectrometer to acquire luminescence spectra. We discriminated small clusters (typically dimers) from large aggregates by the shape of their luminescence spectra. Only combinations of two to three particles in contact with each other had a distinct luminescence peak in the visible region. Interestingly, single particles did not render any detectable photoluminescence. Figure 1(a) shows the photoluminescence originating from a gold dimer scanned through the focal region. An electron micrograph of the dimer is shown in Fig. 1(b). The excitation wavelength was set to 780 nm. The photoluminescence was collected with a spectral passband filter (500–700 nm). Figure 1(a) shows that the photoluminescence originating from the dimer responds to the total field in the focal region, and not to any particular polarization component.[19] The signal at its maximum intensity is approximately 230 KCnts/s for an average excitation power of 780 μW. The quadratic dependence of the luminescence on excitation power confirms the two-photon absorption process (data not shown).

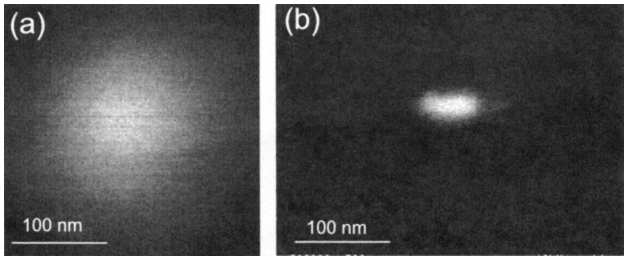

FIG. 1. (a) Two-photon photoluminescence image of a gold dimer scanned through the focal region of a 120 fs pulsed Gaussian beam. (b) Scanning electron micrograph of the dimer consisting of two 40 nm gold particles. The orientation of the dimer differs in the two images.

[a]Electronic mail: bouhelie@optics.rochester.edu

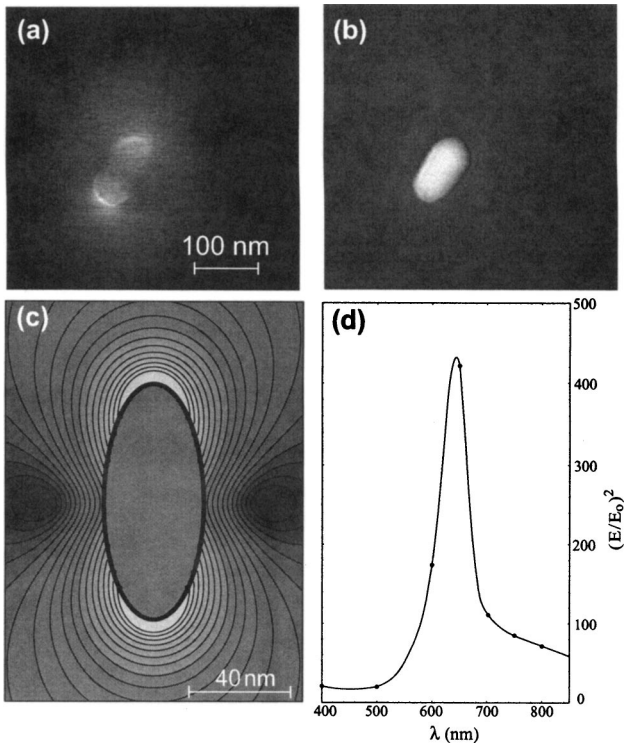

FIG. 2. (a) and (b) two-photon excited photoluminescence images of an elliptical cluster of gold particles imaged with a stationary gold tip and the respective topography. The elliptical dimer is the same particle as the one shown in Fig. 1(b). (c) Calculated intensity distribution of ellipsoid with the same dimensions excited near resonance (650 nm). (d) Normalized intensity enhancement as a function of the excitation wavelength (circle). The enhancement is maximized at 644 nm. The solid curve is a guide for the eyes.

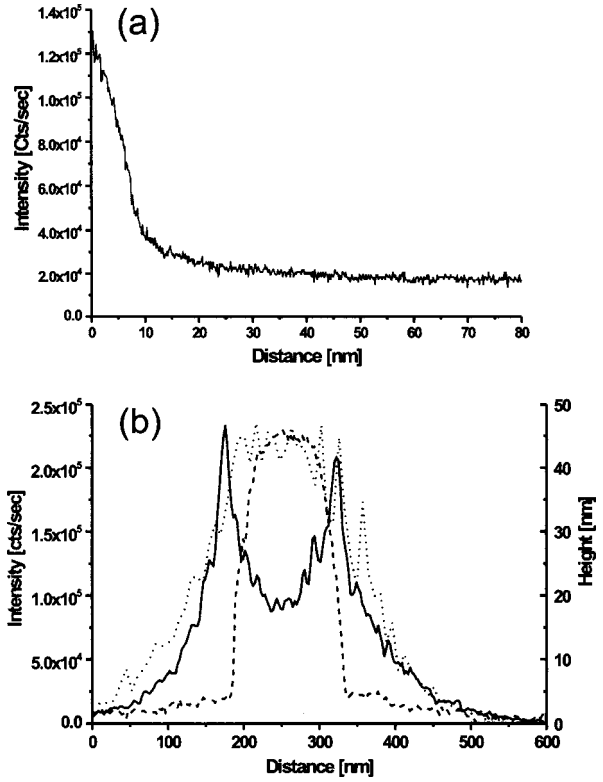

FIG. 3. (a) Photoluminescence decay on top of one the field maxima shown in Fig. 2(a). (b) Cross section of the photoluminescence (solid curve), topography (dashed curve), and farfield photoluminescence (dotted curve). The luminescence enhancement is experienced within a nanometric volume of $10\times10\times10$ nm^3.

Next, a gold tip (tip radius 10 nm) was brought in the focal region and positioned over the particle dimer by using a piezoactuator. The vertical distance between the tip and the dimer was kept constant at approximately 1 nm by shear-force regulation.[20] The tip was then held at a fixed position while the particle was laterally raster scanned underneath it. Unlike metal tip-enhanced Raman or fluorescence microscopy, the tip was not placed into a region with fields polarized along the tip axis,[19] and no significant photoluminescence originating from the tip was recorded. Under these experimental conditions, the tip's response is similar to a particle that can be positioned with nanometer control. Figure 2(a) shows how the tip influences the photoluminescence yield of the cluster as a function of its position. Figure 2(b) depicts the simultaneously acquired topography. Note that this is the same dimer as imaged in Fig. 1(b). The original farfield pattern seen in Fig. 1(a) is still visible as a faint background. Superimposed to this background is a higher resolution image with details originating from the tip–particle interaction. At the extremities of the dimer, the photoluminescence response is strongly enhanced relative to the farfield background. On the other hand, the signal intensity is reduced at the two diametrically opposed points along the short axis of the dimer. These two effects are not influenced by the polarization direction of the excitation and were observed on all investigated dimers (data not shown). The image of Fig. 2(a) strongly resembles the calculated surface intensity distribution of an ellipsoid excited at resonance, as shown in Fig. 2(c). The image demonstrates the dipolar character of the excited particle: charge accumulation at both ends along the long axis and charge depletion along the short axis. The calculation was based on the multiple multipole method[21] for an excitation wavelength of 650 nm and $\varepsilon_{Au} = -12.9 + 1.09i$. Figure 2(d) shows the maximum normalized intensity of the ellipsoid as a function of excitation wavelength. The enhancement is maximal for $\lambda = 644$ nm. Figure 3(a) demonstrates the near-field nature of the field confinement and associated photoluminescence. The particle was positioned at a position of maximum field intensity. The photoluminescence signal was recorded as the tip was gradually withdrawn from the particle. A fast decrease of the signal for the first 10 nm is observed. When the tip is a few tens of nanometers above the particle, the strength of the photoluminescence signal corresponds to the farfield value. Cross sections taken along the long axis of the dimer are plotted in Fig. 3(b). The solid curve represents the photoluminescence signal whereas the dashed curve is the topographic profile at the same location. The width of the photoluminescence peaks at the dimer extremities are approximately 17 nm (FWHM), indicating a high degree of confinement. The near-field contrast becomes evident for tip–particle separations less than 10 nm, consistent with the fast decay of the approach curve. Integrating the total near-field luminescence in Fig. 2(a) leads to a similar value of the integrated farfield luminescence [the dotted curve in Fig. 3(b)]. Thus, the presence of the tip does not increase the overall photoluminescence yield, indicating that there is no resonant coupling between tip and particle cluster. To support this observation, the spectrum of the luminescence emitted from the elliptical

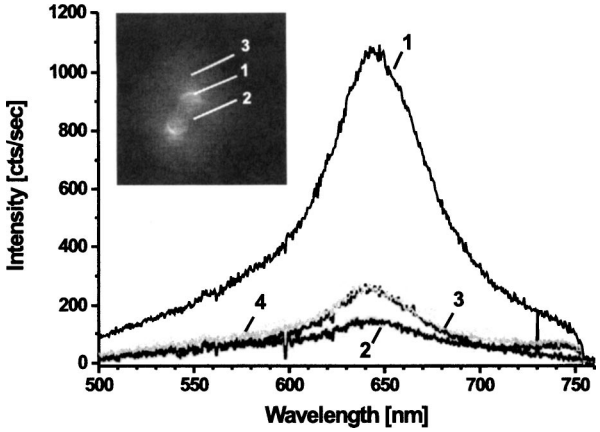

FIG. 4. Spectra of the dimer photoluminescence taken at different relative tip–dimer positions as indicated in the onset. The gray curve (4) represents the spectral response without the tip.

dimer was recorded. The gray curve in Fig. 4 represents the emission of the dimer without the tip. The spectrum is peaked at 644 nm, in agreement with the calculated resonance [Fig. 2(d)], and its shape originates from the convolution of the density of states available at these energies with the intrinsic surface plasmon resonances of the particle cluster.[18] Next, the spectrum was investigated as a function of particle position. As shown in Fig. 4, spectra were acquired where the photoluminescence signal was at a maximum (curve 1), at a minimum (curve 2), and unperturbed by the tip (curve 3). No shift of the resonance peak is observed. Only the signal amplitude is affected by the tip and the overall shape of the spectrum is conserved. We therefore conclude that the tip has a negligible influence on the intrinsic response of the particle. We thus have the analogous situation to two coupled oscillators, one of which is much weaker than the other. Because the tip can be regarded as a passive probe, we obtain a direct measurement of the field enhancement and thus of the local charge distribution on the surface of the dimer.

In conclusion, we showed that local field enhancement at nanoscale metal structures leads to local photoluminescence excited by two-photon absorption. A direct map of the distribution of local fields (hot spots) can be recorded by locally scattering the photoluminescence intensity using a metal tip. The presented method is a promising approach for the characterization of field enhancing structures used in future plasmonic devices. It will also be useful in the study of ''hot spots'' responsible for the giant enhancement of Raman cross sections in SERS.

This work was funded by the U.S. Department of Energy (DOE) through Grant No. DE-FG02-01ER15204, NSF grant No. DMR-0078939, and partially by the Swiss National Science Foundation (A.B.).

[1] S. Nie and S. R. Emory, Science **275**, 1102 (1997).
[2] B. Knoll and F. Keilmann, Nature (London) **399**, 134 (1999).
[3] T. J. Yang, G. A. Lessard, and S. R. Quake, Appl. Phys. Lett. **76**, 378 (2000).
[4] N. Hayazawa, Y. Inouye, Z. Sekkat, and S. Kawata, Chem. Phys. Lett. **335**, 369 (2001).
[5] A. Hartschuh, E. J. Sanchez, X. S. Xie, and L. Novotny, Phys. Rev. Lett. **90**, 095503 (2003).
[6] M. Quinten, A. Leitner, J. R. Krenn, and F. R. Aussenegg, Opt. Lett. **23**, 1331 (1998).
[7] S. A. Maier, P. G. Kik, and H. A. Attwater, Phys. Rev. B **67**, 205402 (2003).
[8] P. K. Arawind, A. Nitzan, and H. Metiu, Surf. Sci. **110**, 189 (1981).
[9] J. P. Kottmann and O. J. F. Martin, Opt. Express **18**, 655 (2001).
[10] H. Tamaru, H. Kuwata, H. T. Miyazaki, and K. Miyano, Appl. Phys. Lett. **80**, 1826 (2002).
[11] W. Rechberger, A. Hohenau, A. Leitner, J. R. Krenn, B. Lamprecht, and F. R. Aussenegg, Opt. Commun. **200**, 137 (2003).
[12] H. Xu and M. Käll, Phys. Rev. Lett. **89**, 246802 (2002).
[13] P. André, F. Charra, and M. P. Freund, J. Appl. Phys. **91**, 3028 (2002).
[14] J. A. Porto, P. Johansson, S. P. Apell, and T. López-Ríos, Phys. Rev. B **67**, 085409 (2003).
[15] A. Pack, W. Grill, and R. Wannemcher, Ultramicroscopy **94**, 109 (2003).
[16] N. Nilius, E. Ersnt, and H.-J. Freund, Phys. Rev. B **65**, 115421 (2002).
[17] G. T. Boyd, Z. H. Yu, and Y. R. Shen, Phys. Rev. B **33**, 7923 (1986).
[18] M. R. Beversluis, A. Bouhelier, and L. Novotny, Phys. Rev. B **68**, 115433 (2003).
[19] A. Bouhelier, M. Beversluis, A. Hartschuh, and L. Novotny, Phys. Rev. Lett. **90**, 013903 (2003).
[20] K. Karrai and R. D. Grober, Appl. Phys. Lett. **66**, 1842 (1995).
[21] Ch. Hafner, *The Generalized Multiple Multipole Technique for Computational Electromagnetics* (Artech, Boston, 1990).