PHYSICAL REVIEW B **80**, 161407(R) (2009)

Intermittency in second-harmonic radiation from plasmonic hot spots on rough silver films

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(Received 16 September 2009; published 16 October 2009)

Surface enhancement of electromagnetic fields in plasmonic hot spots formed on rough silver films enables the observation of second-harmonic generation (SHG) from single metal nanoparticles. Nonlinear light scattering from these particles exhibits blinking in analogy to luminescence from single quantum dots, molecules and atoms; and fluctuations in single molecule surface-enhanced Raman scattering. Hot spots also display multiphoton white light emission besides SHG. In contrast to SHG, white light emission is stable with time, demonstrating that it is not the plasmonic field enhancement which fluctuates but the nonlinear polarizability ($\chi^{(2)}$) of the emitting species.

DOI: 10.1103/PhysRevB.80.161407 PACS number(s): 78.66.Bz, 78.30.−j, 78.55.Mb, 78.60.Fi

Temporal fluctuations in the response of a nanoscale light source to an incident optical field provide intricate information on the physics of the system and its surroundings. Common examples of fluctuations include blinking in the light emission of single atoms,[1,2] molecules,[3] or quantum dots.[4] While strong fluctuations in the emission of nanoscale objects can be understood in terms of saturation processes in two-level systems, it is not immediately obvious whether size limitations should impact quasiclassical nonlinear light scattering such as second-harmonic (SH) generation (SHG). We probe the nonlinear response of individual metal nanoparticles by amplifying the local electric (optical) field in the hot spot of a rough silver film.[5,6] Nonlinear optical characterization of plasmon-mediated surface enhancement has attracted particular attention because of the increasing use of surface-enhanced Raman scattering (SERS), the most prominent application of plasmonic field amplification.[7–12] Fluctuations in single molecule SERS have been reported,[9,11,12] which are thought to arise from changes in the interaction of the analyte molecule with the regions where largest field enhancement occurs—the hot spots. The same mechanism which enhances Raman scattering can also be probed by SHG[9,13–17] and nonlinear optical processes such as multiphoton luminescence and stimulated Brillouin scattering which lead to spectral continuum emission (CE).[5,18] Using these nonlinear responses, we distinguish between the nonlinear susceptibilities $\chi^{(2)}$ and $\chi^{(3)}$ of a small particle in a hot spot. Whereas the $\chi^{(3)}$ response appears constant with time, $\chi^{(2)}$ exhibits strong temporal fluctuations reminiscent of blinking in single quantum emitters.

We examined the nonlinear optical response of silver nanoparticle films which have previously allowed reproducible single molecule SERS spectroscopy.[19,20] The silver films are grown in a solution-based Tollens silver mirror reaction on glass, leading to fractal silver nanoparticle arrangements approximately 30 nm thick.[19] Figure 1 summarizes the main optical characteristics of such a silver film. A scanning electron micrograph of a sample illustrates the distribution of positions and sizes of nanoparticles in the right-hand inset of panel C. The film is mounted in high vacuum ($<10^{-6}$ mbar) beneath a fluorescence microscope objective (numerical aperture 0.55) and excited under wide-field illumination at an angle of ~30° by infrared radiation from a tunable Ti:sapphire laser (80 MHz, 140 fs pulse length, ~15–60 kW/cm^2 cw intensity). Figure 1(A) illustrates a typical emission pattern from the metal film under excitation at 1070 nm. Spatially discrete emission is observed as diffraction-limited bright spots. Placing a slit over the image (dashed lines in A) and directing the light through a spectrometer enables emission spectroscopy (B), spatially resolved along the vertical axis of the microscope image. The image in B and the graph in C show the corresponding spectrum of the bright spot in panel A, which appears broad with a narrow peak superimposed at 535 nm (the spectrum is trun-

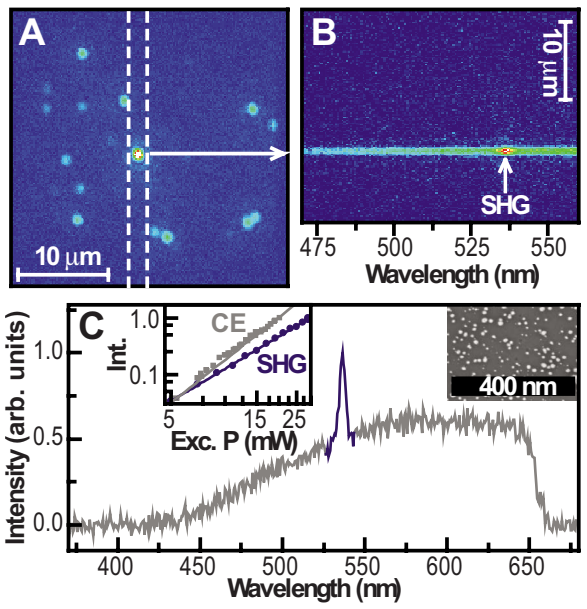

FIG. 1. (Color online) Nonlinear optical emission from a fractal silver nanoparticle film. (A) Real-space image of surface-plasmon localization and hot spot emission (seen as diffraction-limited spots) under pulsed excitation at 1070 nm. Placing a slit in the image (dashed lines) and dispersing the light through a spectrometer provides spatially resolved spectral information along the vertical axis (B). (C) Hot spot emission spectrum, truncated at 660 nm by a short-pass filter. The spectrum consists of a broad CE and a narrow peak at half the excitation wavelength which is due to SHG. A scanning electron micrograph of a typical nanoparticle sample is shown in the inset, as are the nonlinear excitation power dependencies of CE ($\propto I^{2.6}$, gray) and SHG ($\propto I^2$, blue/black).

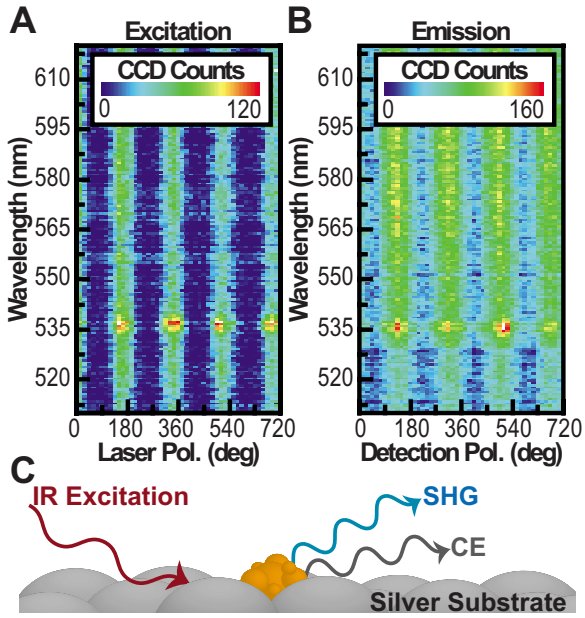

FIG. 2. (Color online) Spectrally resolved polarization anisotropy of the excitation and emission of single hot spots. (A) Modulation of the polarization of the exciting laser leads to a periodic change of both CE (broad) and SHG (537 nm) intensity (5 s time resolution). (B) The emission of the hot spot is dipolar, following a similar modulation as in excitation. (C) CE and SHG must arise from the same hot spot. We propose that the two nonlinear optical phenomena originate from a small particle located within the hot spot.

cated at 660 nm by a short-pass filter). The peak arises from SHG of the incident 1070 nm radiation whereas the broad emission results from CE.[20] Within the excitation densities under consideration, SHG and CE depend nonlinearly on excitation intensity as shown in the left-hand inset of panel C.

Metal films constitute nonlinear optical materials where the second-order response is due to the structural and field discontinuities present at the surface,[6] which break inversion symmetry as required for a $\chi^{(2)}$ process. SHG resulting from this nonzero interface $\chi^{(2)}$, which has been shown to occur from metal clusters as small as 1 nm,[21,22] can be enhanced by surface roughening.[5] A particle exhibiting SHG must coincide spatially with a plasmonic hot spot. Consequently, the density of optical hot spots in Fig. 1(A) is over 10 000 times *lower* than the density of silver nanoparticles seen in the inset of Fig. 1(C).

To probe the origin of nonlinear hot spot emission, we vary the polarization planes of the exciting laser and the detector in Figs. 2(A) and 2(B), respectively. Both excitation and emission show a high degree of linear polarization (a more complete characterization of the polarization state is provided in the *supporting information*[23]). In excitation, the intensity modulation of the SHG line follows that of the broad white light background. This demonstrates that both CE and SHG report on the same enhanced incident field since a hot spot will only couple to the light field of a certain polarization. However, the hot spot radiates at a different wavelength so that the polarization in emission does not report on the plasmonic enhancement, but rather on the orientation of the electronic polarization created within the hot spot. The dipolar nature of the spot emission suggests the polarizable species is situated *within* the hot spot which couples to the enhanced *fundamental* excitation field. We therefore propose that both SHG and CE arise from a small silver particle located within the hot spot region of large field enhancement, as sketched in Fig. 2(C).

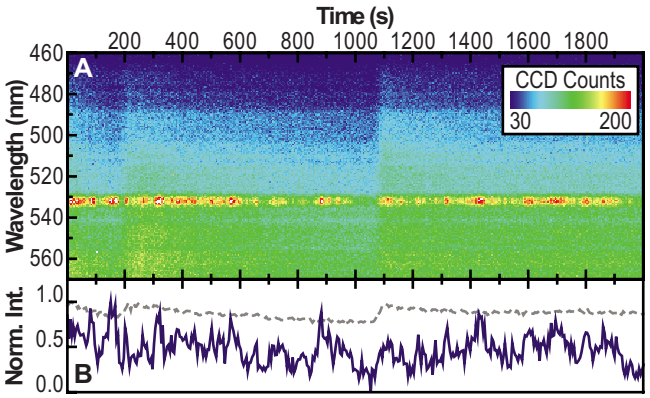

FIG. 3. (Color online) Temporal fluctuations of SHG from a single hot spot. (A) Emission trace recorded with 5 s resolution, showing that the SHG peak at 532 nm is not constant in intensity with time, reminiscent of blinking in the emission of single molecules or nanoparticles. (B) Temporal evolution of the SHG (blue/black) and CE (gray) intensity from the same hot spot.

It is important to note that $\chi^{(2)}$ of nanometer-sized metal particles actually *increases* with decreasing particle size due to the growing contribution of quantum chaotic rather than purely electrodynamical effects as the surface to bulk ratio rises.[22] This increase in nonlinear response counteracts the decrease of overall SHG due to the reduction in number of atoms involved.[22] In conjunction with the electric-field enhancement due to the hot spot we can therefore detect SHG from single nanometer-sized metal particles. In contrast, much larger particles, which may have significantly greater $\chi^{(2)}$, will not fit into a plasmonic hot spot and therefore appear mute in the experiment. Evidence for the presence of a small silver particle as the polarizable species in the hot spot comes from a striking spatial anticorrelation between single molecule SERS and CE.[20] We recently demonstrated that SERS preferentially occurs from hot spots which do not exhibit CE, suggesting a physical difference between hot spots responsible for CE and SERS.[20] As CE and SHG indicate the presence of a small metal particle at the focus of the hot spot, a likely origin of the SERS-CE anticorrelation is absorption of the locally enhanced optical field by the interstitial metal particle. If a particle is present in the hot spot, a single molecule will simply not fit into it: single molecule SERS cannot occur.

Remarkably, $\chi^{(2)}$ (SHG) and $\chi^{(3)}$ (CE) processes display very different physical characteristics. Figure 3 illustrates the temporal evolution of single-particle SHG and CE. Whereas CE is virtually constant with time, displaying two subtle jumps at 200 and 1080 s along with a gradual decrease in intensity due to photodegradation, the SHG peak fluctuates strongly in intensity. The fluctuations are reminiscent of blinking of single quantum systems,[1–4] suggesting micro-

scopic temporal variations in $\chi^{(2)}$ of the optically active nanoparticle in the hot spot. Clearly, it is not the field enhancement of the hot spot which is changing, as this would give rise to correlated intermittency of SHG and CE. We note that photoexcitation of rough silver films is known to lead to the formation and photomodification of emissive silver nanoclusters.[24,25] The occasional jumps to higher CE intensities most likely arise from two-photon-induced growth of the silver particle in the hot spot which increases the bulk volume and thus $\chi^{(3)}$.

$\chi^{(2)}$ fluctuations do not appear to be sensitive to external perturbations. The fluctuations are not modified by temperature (between 5 and 300 K), pressure (up to atmospheric pressure), and hot spot density (controlled by the growth time of the SERS substrates). The independence of the phenomenon on pressure and temperature, and the lack of correlation between CE and SHG fluctuations, rather suggests that it is not a physical rearrangement of material in the hot spot which gives rise to SHG blinking. In addition, we did not observe any systematic change in fluctuations over an order-of-magnitude increase in excitation intensity. We conclude that the polarizable species in the hot spot must experience random variations in $\chi^{(2)}$, but not in $\chi^{(3)}$.

In contrast to $\chi^{(3)}$, $\chi^{(2)}$ only arises in materials of broken inversion symmetry. Bulk silver has a face-centered-cubic lattice with inversion symmetry. Consequently, the dipolar $\chi^{(2)}$ response of the silver nanoparticle is limited to surface SHG originating from only a few atomic layers of the silver particle where inversion symmetry is broken. On the other hand, $\chi^{(3)}$ should have significant bulk contributions. Due to the large surface to bulk ratio and the presence of discrete electronic states, small metal clusters are prone to charging, which can impact the optical[26] and transport[27] properties. Indeed, metal nanoparticles do not display purely metallic behavior on nanometer length scales, as evidenced by the absence of plasmon resonances, and may even exhibit molecular-like electronic structure with discrete rather than continuous metallic states.[26] A possible scenario for the origin of SHG blinking lies in spontaneous changes in the local charge distribution within or in the vicinity of the radiating particle. These changes will lead to a fluctuation of both the magnitude and the polarization of SHG (surface sensitive), while leaving the CE (bulk sensitive) virtually unchanged. Support for this proposition of a temporally varying charge distribution which controls $\chi^{(2)}$ comes from considerations of polarization-resolved SHG blinking. Figure 4 illustrates the fluctuations in hot spot emission intensity for simultaneous detection parallel and perpendicular to the polarization plane of excitation. The transient reveals uncorrelated fluctuations in the two polarization planes of the SH radiation (marked by the shaded regions in panels A and B). No strong polarization fluctuations are observed in CE (C and D). We conclude that the effective components of the $\chi^{(2)}$ tensor vary independently with time, suggesting a local rearrangement of static polarization without physical movement of the particle (which would affect CE). Localized charges on or in the vicinity of the emitting particle could account for this effect. A complete characterization of the SHG polarization state in the framework of Stokes parameters is given in the *supporting information*[23] and demonstrates further subtle fluctuations in the SH radiation while the CE remains constant in time.

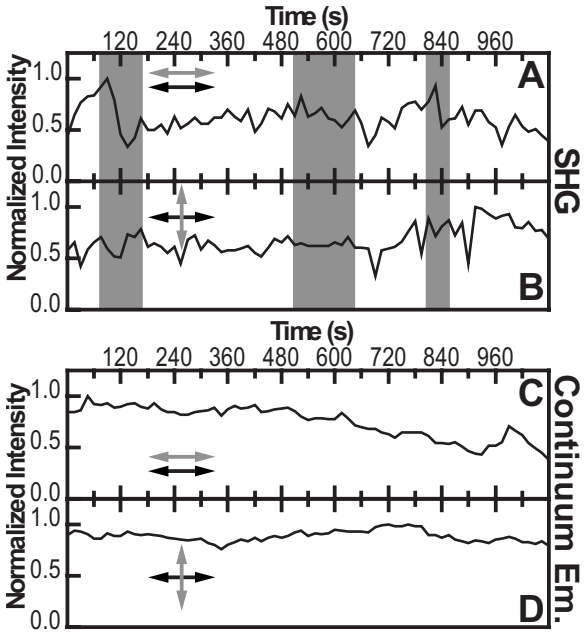

FIG. 4. Polarization dependence of SHG intermittency and CE from a single hot spot. The parallel (A) and orthogonal (B) polarization components of SHG with respect to the incident laser polarization (black arrows) are only weakly correlated, particularly in the shaded regions (measurement resolution 10 s). The simultaneous CE does not display any substantial fluctuations in either polarization channel (C and D), besides a gradual intensity decay due to photodegradation. A complete analysis of the polarization state is given in the *supporting information* (Ref. 23).

SHG offers a powerful microscopic technique to image processes at interfaces.[6] As the method is applied to ever smaller objects, it is critical to realize that the nonlinear optical response can exhibit discreteness and intermittency—in analogy to blinking in luminescence.[1–4] The conceptual difference to luminescence blinking lies in the fact that luminescence requires real states, whereas scattering involves virtual levels. As such, intermittency in nonlinear light scattering constitutes an unexpected phenomenon. The observation of temporal fluctuations in spatially discrete surface-enhanced SHG illustrates that the intrinsic $\chi^{(2)}$ of a nanostructure such as a nanoparticle cannot be meaningfully quantified although it can be readily detected.

We are grateful to the Petroleum Research Fund (Grant No. 46795) and the National Science Foundation (Grant No. 0748473) for financial support, as well as to the David & Lucile Packard Foundation. We thank R. Polson for assistance in acquiring the SEM image.

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