Surface-mediated four-wave mixing of nanostructures with counterpropagating surface plasmon polaritons

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We demonstrate that four-wave mixing (FWM) signals from individual Si nanoparticles can be generated by the surface fields of traveling surface plasmon polariton modes. We have chosen a counterpropagating excitation scheme in which the nanoparticle is exposed only to surface excitation fields and not to direct laser illumination. We show that background-free, surface-mediated FWM of nanoparticles can be acquired, and that the resulting nonlinear radiation is coherent. © 2011 Optical Society of America

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The recent surge in nanomaterial fabrication has put renewed emphasis on the development of sensitive techniques for the characterization of nanoscopic systems. Nonlinear optical methods have recently been shown to be attractive probes for the magnitude and dynamics of optical excitations in nanomaterials. Among such nonlinear methods, FWM constitutes a sensitive method for interrogating the material's third-order optical response. When combined with optical microscopy, FWM offers an avenue toward examining the fundamental properties of ultrafast nanoparticle excitations at the single particle level, including exciton-exciton interactions, phonon coupling, and scattering at lattice defects [1].

Whereas the optical response of larger nanostructures produces detectable signals, more significant demands are put on the sensitivity of the technique when zooming into progressively smaller nano-objects, including single molecular compounds. In this regard, surface-enhanced FWM may provide the sensitivity improvement needed to bring the coherent nonlinear optical properties of nanosized systems into view. Surface-enhanced coherent anti-Stokes Raman scattering (SE-CARS) experiments have recently provided evidence that the local field of localized surface plasmons can boost the nonlinear optical signals from molecular compounds [2,3].

SE-CARS experiments thus far have been far from straightforward. The metallic tips and colloidal particles used in these studies exhibit localized surface plasmon modes that are generally not well characterized, and complicate the experiment in terms of local heating and FWM background generation in the metal [2,4]. Compared to the electric fields of highly localized surface plasmon resonances, the surface fields associated with traveling surface plasmon polaritons (SPP) on planar metal surfaces are typically weaker. However, SPP excitations provide a much higher degree of experimental controllability and, therefore, offer an opportunity to systematically interrogate the physics of surface-enhanced FWM. Recent FWM studies have shown that nonlinear SPP waves can be generated and probed in a controlled fashion at metallic surfaces [5–7]. In this approach, incident frequencies ω_1 and ω_2 induce a polarization at the metal surface of frequency $2\omega_1 - \omega_2$, which can produce propagating SPP modes at this new frequency. Moreover, the scattering of the FWM surface field at surface structures can be used as a microscopic contrast mechanism for visualizing surface morphology [8]. These studies allude to the possibility to employ well-defined SPP modes as surface excitation fields for probing the $\chi^{(3)}$ properties of nanosized targets.

To utilize the controllability of SPP modes for surface-mediated FWM of (nonmetallic) nanostructures placed on a planar metallic surface, the driving frequencies ω_1 and ω_2 need to set up a nonlinear polarization in the nanostructure rather than in the metal alone. Evidence that surface waves can induce a third-order polarization in a material in contact with the metal surface has previously been provided by macroscopic CARS experiments [9]. In this work, we aim to answer the question whether a detectable third-order polarization can be established in individual nanostructures driven by two SPP modes of fundamental frequencies ω_1 and ω_2. We will provide evidence that the $\chi^{(3)}$ of the nanomaterial can be probed through excitation by surface waves alone, and that the resulting radiation is coherent.

To study whether the third-order polarization in the nanostructure can be driven solely by the SPP surface fields, we have adopted a remote excitation scheme that avoids direct excitation by the freely propagating driving fields. This scheme is sketched in Fig. 1(a). Two femtosecond laser beams, at center wavelengths $\lambda_1 = 726\,\text{nm}$ and $\lambda_2 = 942\,\text{nm}$, with a pulse width of 370 fs and 160 fs, respectively, are derived from an optical parametric oscillator (Inspire, Spectra Physics). The laser beams are focused by a high numerical aperture lens (60×, NA 1.42 oil, Olympus) to ~3 μm diameter spots that are separated by ~20 μm. The average power for each beam at the sample is 10 mW.

The sample consists of a borosilicate glass coverslip with a 45 nm thick gold layer. The angle of incidence of the two beams is tuned to the Kretschmann angle to couple part of the freely propagating light into a propagating SPP mode at the gold/air interface [5]. In this particular geometry, two counterpropagating SPP modes, of wave vector $k_i^{\text{spp}} \approx (\omega_i/c)\{\epsilon(\omega_i)/[\epsilon(\omega_i)+1]\}^{1/2}$ [10], are launched at the fundamental excitation frequencies ω_i with $i = 1, 2$. Here ϵ is the dielectric function of gold and c is the speed of light. The excitation geometry is sketched in Fig. 1(b).

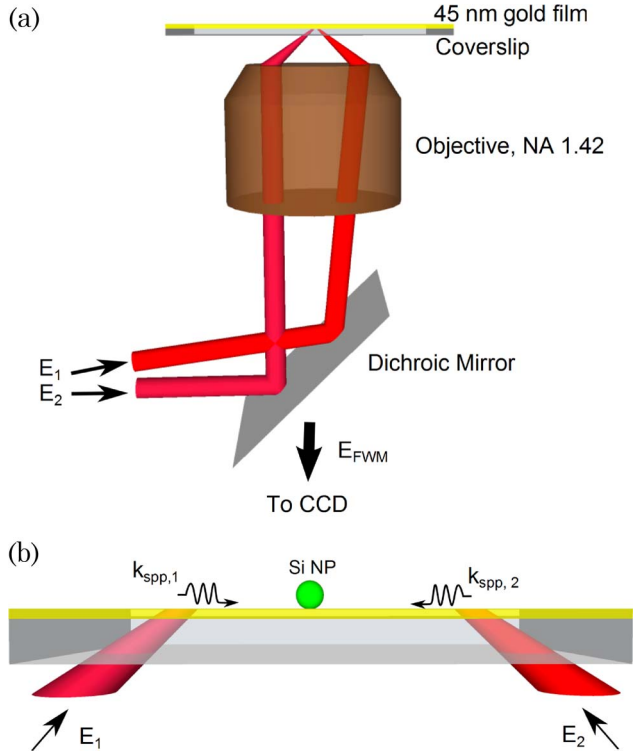

Fig. 1. (Color online) Schematic of the experiment. (a) Beam configuration for objective-based focusing of incident fields E_1 and E_2. (b) Excitation configuration. Two counterpropagating surface plasmon polaritons are launched into an Au film. The Si nanotarget is placed onto the gold surface in between the launching spots.

The nanosized Si targets (Meliorum Technologies) are placed on the surface in between the focal spots in an area devoid of direct illumination. FWM ($2\omega_1-\omega_2$; $\lambda_{\mathrm{FWM}} = 591$ nm) at the target can only take place through temporal and spatial overlap of the counterpropagating surface waves rather than through direct excitation of the particle with freely propagating light. The FWM emission is detected in the epidirection and separated from the incident light with a dichroic mirror (SWP 680 nm, Chroma). A CCD camera (Clara, Andor) equipped with a bandpass filter (590 nm, Semrock) is used to capture an image of the FWM emission from the nanoparticle with an image integration time of 100 ms.

In Fig. 2(a), a CCD image of the focused beam spots onto the Au film is shown. The weak tails in between the excitation spots are due to the leakage radiation of the counterpropagating SPP modes. Figure 2(b) depicts the FWM radiation at 591 nm observed at the target site. As can be seen from the figure, the nanotargets are not directly exposed to the excitation light.

To further investigate the nature of the observed FWM signal, we have examined its power dependence. Figure 3(a) shows that the signal scales quadratically with the λ_1 beam and approximately linearly with the λ_2 beam, in concert with the expected power dependence of the FWM signal. Whenever the overlap of the excitation beam is temporally offset, the signal disappears, as shown in Fig. 3(b). In addition, the FWM is strongest when the incident beams are p-polarized, as illustrated in Fig. 3(c). When the polarization of either beam is independently

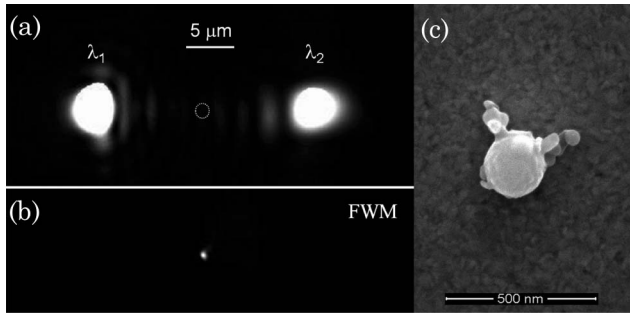

Fig. 2. (a) CCD image of the focused laser spots on the gold film. Dotted circle indicates the location of the nanoparticle. (b) CCD image of the FWM radiation from the nanoparticle. (c) SEM image of a 200 nm Si nanoparticle.

changed from p to s, the FWM signal vanishes accordingly. This latter observation confirms that surface-bound fields are responsible for excitation of the nanoparticles.

The observed FWM radiation can arise either from a surface field driven, third-order polarization in the particle, or from an evanescent FWM field, which may linearly scatter at the target site [8]. To investigate the origin of the signal, we have examined the dependence of the signal on the $\chi^{(3)}$ properties of the particle. We find that the signal strongly depends on the size of the Si nanoparticle. We consistently observe that ~200 nm diameter Si particles produce much stronger FWM signals than ~50 nm

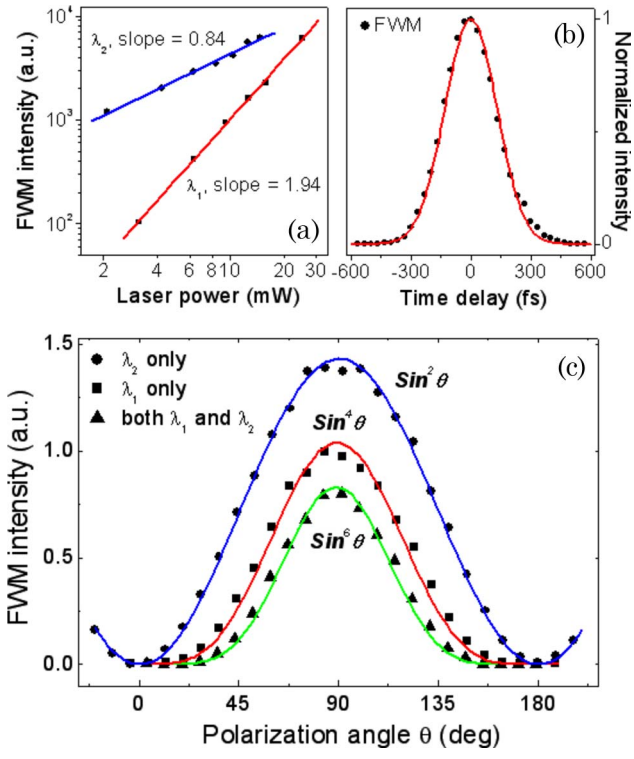

Fig. 3. (Color online) (a) Power dependence of the FWM radiation from the Si nanoparticle. Solid lines are linear fits. (b) FWM signal as a function of the time delay between E_1 and E_2. The solid curve is the calculated cross-correlation based on the pulse widths of the individual beams (assuming Gaussian pulses). (c) Dependence of the FWM signal as a function of the polarization orientation E_1 (squares), E_2 (circles), or both (triangles). Solid curves are fits with the functions indicated.

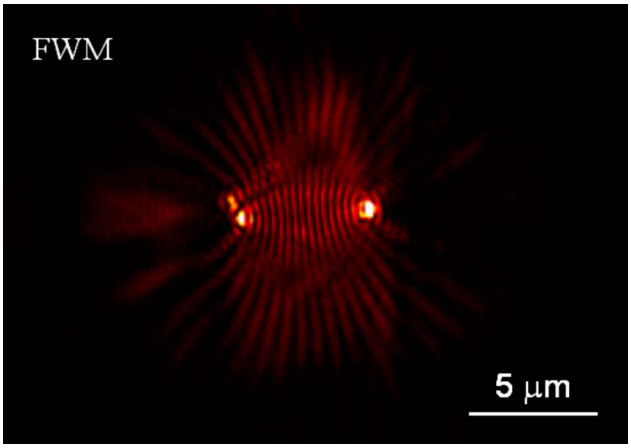

Fig. 4. (Color online) Interference of two surface plasmon modes emanating from two spatially offset nanoparticles.

sized particles. In addition, the signal from ~200 nm polystyrene beads is more than 3 orders of magnitude weaker than the signal from similarly sized Si particles. These observations are in accordance with the much higher $\chi^{(3)}$ of Si compared to the $\chi^{(3)}$ of polystyrene [1,11]. Since the strength of the FWM signal is dictated by the size and the nonlinear susceptibility of the nanomaterial, we conclude that the nonlinear polarization in the nanoparticle, which is driven by the surface fields of the fundamental SPP modes, constitutes a major contribution to the observed FWM radiation. We note that the FWM signal was stable on the time scale (0.1 s to several hours) of the experiment, indicating the absence of any photothermal fluctuations. A given particle could be visualized day after day, with similar FWM results.

Finally, in Fig. 4, we provide evidence that the surface-enhanced FWM emission from Si nanoparticles is coherent. Here two nanotarget sites are simultaneously excited by the fundamental surface waves within the area (width ~40 μm) where the SPP waves temporally overlap. FWM emission from each spot can be seen. In addition, part of the FWM radiation couples back into the Au film, forming propagating SPP modes at the FWM frequency. In between the two radiating spots, the two counterpropagating nonlinear surface waves mutually interfere, as observed through the SPP leakage radiation. The experimentally measured oscillation period of $0.29 \pm 0.01\,\mu$m is close to the expected periodicity of $0.28\,\mu$m as calculated from the interference of two surface waves with $k_{\mathrm{FWM}}^{\mathrm{spp}}$. The observed interference pattern indicates that the FWM radiation produced by the nanotargets is coherent.

In summary, we have performed surface-mediated FWM measurements by using two counterpropagating SPP waves for driving a third-order polarization in nanoparticles placed on gold surfaces. This remote excitation scheme enabled us to investigate the ability of surface waves to act as a source for FWM signals from nanotargets in a reproducible and background-free fashion. Our experiments indicate that pure surface-wave-induced FWM signals in individual nanoparticles can be achieved and that the ensuing radiation from the nanoparticles is coherent. We expect that the remote excitation scheme employed here will offer a convenient strategy to perform controlled surface-enhanced FWM experiments on nanoscopic objects and molecular structures, including vibrational CARS of surface-bound molecules at low copy numbers.

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