Remote multi-color excitation using femtosecond propagating surface plasmon polaritons in gold films

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Abstract: We demonstrate dual-color nonlinear excitation of quantum dots positioned onto a gold film at distances up to 40 μm away from a micrometer sized focused laser spot. We attribute the observed remote nonlinear signal to the excitation of two independent surface plasmon polariton (SPP) modes excited at the laser spot in the gold film, which subsequently propagate in a collinear fashion to a distant site and provide the surface field required for nonlinear excitation of the target. This scheme decouples the illuminating photon flux from surface plasmon mediated nonlinear excitation of the target, which provides more control of unwanted heating effects at the target site and represents an attractive approach for surface-mediated femtosecond nonlinear examinations of molecules.

OCIS codes: (190.4180) Multiphoton processes; (240.4350) Nonlinear optics at surfaces; (240.6680) Surface plasmons.

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1. Introduction

Plasmonically active nanostructures have played a crucial role in improving the sensitivity of molecular spectroscopic measurements. The strong local electric field associated with the plasmon excitation boosts the optical response of molecules that reside close to the surface of the nanomaterial. Metallic nanostructures provide field enhancement factors of multiple orders of magnitude, which raise otherwise weak optical signatures of molecules up to detectable levels [1]. Rather than increasing the power of the excitation light by orders of magnitude, which can introduce severe photodamage to surface substrates, plasmonic nanostructures can deliver sufficient energy for optical excitation to select nanoscopic hotspots only, while the overall photon flux is kept to a minimum. Most notably, the surface enhanced spectroscopy approach has enabled sustained probing of the Raman response of molecules at very low concentrations, down to the single molecule level [2–7].

The success of surface enhanced Raman scattering (SERS) methods suggests that surface enhancement also offers a viable route towards boosting the nonlinear optical signal of molecules. For example, enhancement of the molecular nonlinear response could possibly open the door towards investigating molecules at surfaces with ultrafast nonlinear wave-mixing techniques, including sum frequency generation (SFG) and coherent anti-Stokes Raman scattering (CARS) spectroscopies. Although surface-enhanced nonlinear optical signals from molecular targets have been observed, including nonlinearly excited fluorescence [8], SFG [9] and CARS [10,11], such experiments have been hampered by several factors associated with ultrafast pulsed excitation. First, ultrafast excitation of metallic substrates is accompanied by two-photon induced luminescence [12, 13] and four-wave mixing (FWM) processes [14–16] which introduce a strong background signal that is generally absent under continuous wave excitation conditions. Second, compared to continuous wave excitation, the heating and subsequent heat dissipation kinetics of metallic substrates is different when ultrafast pulse excitation is used. Several studies have shown increased levels of photo-induced melting of metallic nanostructures for pulses in the 100 fs range [17–19]. The unfavorable heating kinetics require a different balancing of the incident photon flux, the ensuing heating effects, and the desired local field enhancement, relative to what is customary in SERS experiments.

Some of the detrimental heating effects in the nanostructure can be controlled by decoupling the site of illumination from the site where the molecular target resides. In this so-called remote excitation scheme, a surface plasmon polariton (SPP) is excited in the metallic substrate, which subsequently propagates the excitation energy to a distant site where coupling to a local surface plasmon mode provides a well-defined excitation spot. This scheme allows the target to be excited by controllable amounts of energy carried by surface fields alone, whereas unwanted direct excitation of dissipative modes of the nanostructure by the illumination field, which is difficult to control on the nanoscale, can be avoided. Remote excitation schemes based on traveling surface polaritons have been successfully employed to focus excitation energy into tapered waveguides in metallic films [20, 21], nanochannels [22], and nanoscopic tips [23, 24]. Recently, this principle has been used in metallic nanowires to probe the SERS [25–27] or fluorescence response [28, 29] of molecules that were located tens of micrometers away from the micrometer-sized excitation site.

In this work, we investigate nonlinear excitation of nano-scale objects in a remote, collinear excitation scheme. Using femtosecond excitation, Gunn et al have shown that SPP propagation in surfaces covered with colloidal nanoparticles enables nonlinearly excited luminescence of the metal colloids at distances up to 100 μm from the focused laser spot, demonstrating the

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feasibility of SPP-assisted remote nonlinear excitation [30, 31]. In the experiments by Gunn et al, the nonlinear excitation was performed with two pulse trains derived from a single coherent light source. However, in the case of collinear excitation with two coherent single-color laser beams, the resulting SPP pulses are not mutually independent but rather constitute a single excitation field. The single color approach is thus unable to examine the question whether nonlinear excitation with two independent SPP modes can be achieved at the site of a remote target. In analogy with free-space nonlinear optical spectroscopy, the success of surface-mediated nonlinear spectroscopy depends on the ability to control the independent delivery of multiple excitation pulses in both space and time. Here we aim to design an assay that enables multi-color nonlinear excitation of targets on the surface by two independent surface plasmon polaritons in a controlled fashion. The collinear excitation scheme examined here is simpler than more advanced excitation schemes, such as counter-propagating SPP modes that have been used for nonlinear surface excitation. [32, 33] In our assay, the direction of the SPP propagation is well defined in order to excite targets at select locations. Using a simple patterned gold film as the substrate, we demonstrate that it is possible to perform dual-color nonlinear excitation of quantum dots at distances of up to 40 μm from the focused laser light.

2. Materials and methods

2.1. Microscope setup

The experimental configuration is sketched in Fig. 1(a). In the experiments reported here, we used the signal (λ_1=730 nm) and idler (λ_2=935 nm) derived from a tunable optical parametric oscillator system (Inspire, SpectraPhysics). The two 80 MHz pulse trains were combined collinearly on a dichroic mirror and spatially shaped with the aid of a pinhole into a thin pencil of light with beam diameter $\sim$0.8 mm. Two translational mirrors controlled the lateral position at which the combined beams enter the back aperture of a high numerical aperture lens (60x, NA 1.42 oil immersion, Olympus), which is mounted on a microscope frame (IX81, Olympus). The high NA objective lens is used both for coupling the free space propagating light into the SPP mode as well as to capture the nonlinear signals generated in the focal plane in an epi-direction detection geometry [34, 35], as shown in Fig. 1(b). The objective lens focused the beams to a micrometer-sized spot, with an adjustable angle of incidence, onto the gold film. The temporal pulse width in the focal plane was 280 fs for the λ_1 beam and 140 fs for the λ_2 beam. The average power at the sample was 3 mW per beam. The epi-detected signals were directed to a short wave pass dichroic mirror (680 nm center wavelength, Chroma) and projected onto an imaging CCD camera (Clara, Andor). Bandpass filters were used to selectively detect the nonlinearly excited fluorescence (λ_{max} =520 - 560 nm), four-wave-mixing contributions (FWM, $\lambda_3 \sim$ 600 nm), or a combination of both at the detector.

2.2. Sample preparation

The sample consisted of a lithographically patterned gold film. To this end, a Cr (1nm) / Au (45 nm) gold film was thermally evaporated onto a No. 1 borosilicate coverslip. A positive-tone photoresist (PR, Shipley 1808, Microchem) was spin coated onto the gold film, and a pattern was imprinted onto the photoresist with a contact mask under 365 nm illumination. The exposed Au and Cr was etched away by a KI (100 g/L) / I2 (50g/L) aqueous solution and a commercial Cr etchant (Aldrich), respectively, resulting in a 'finger' pattern of extensions of variable length (10 - 100 μm) and a fixed width of 3.5 μm, which were spaced by 6.5 μm relative to one another. The photoresist layer was removed by rinsing with acetone. A sketch of the sample is shown in Fig. 1(c).

We have used CdSe quantum dots (QSO-520 and QSO-560, Ocean Nanotech) as a probe for remote wave-mixing. The QD solution was diluted 10 times with toluene and applied onto the

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tips of the gold fingers with a precision injection system (PicoPump, World Precision Instruments). After evaporation of the solvent, small clusters of QDs were formed near the finger tips. The nonlinearly excited fluorescence emitted by these small clusters was used to examine the SPP mediated remote excitation process.

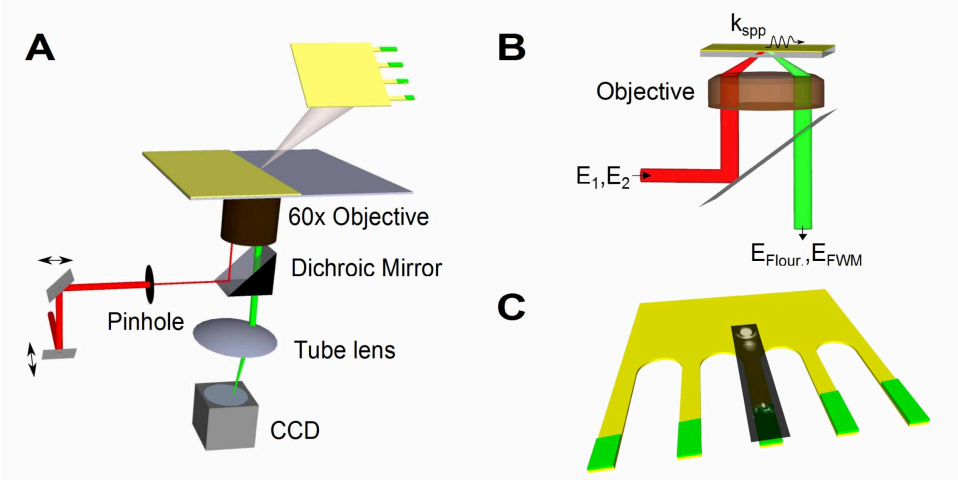

Fig. 1. (A) Schematic of the experimental setup. (B) Geometry of beam focusing and surface plasmon excitation with an objective lens. (C) Sketch of the patterned gold film (yellow) with extensions partially covered with CdSe quantum dots (green). The overlaid image represents actual data showing the FWM signals at the laser spot and the nonlinearly excited fluorescence from the quantum dots.

3. Experimental results

3.1. Surface plasmon polarition propagation in gold films

We first examined SPP excitation in the absence of the QD probe. Representative imaging results for SPP propagation of the incident beams are shown in Fig. 2(a). The excitation beams were p-polarized relative to the gold film and the incident angle matched to the SPP coupling angle in the Kretschmann configuration [36]. The laser spot can be easily seen through the back reflection at the gold surface, which features characteristic diffraction rings. The cone half-angle of the focused beams was 5^o, resulting in a spot size (full width half maximum) of 3.0 μm for the signal beam and 3.7 μm for the idler beam. In addition, the leakage radiation of the SPP mode can be seen [37, 38], evidencing that traveling surface plasmon polaritions can be launched in a well-defined direction. By positioning the focused laser spot in line with the gold fingers, traveling SPP modes were injected into the extensions. An oscillatory modulation of detected radiation along the plasmon propagation direction is observed. This modulation is the result of mutual interference of the leakage radiation and spurious radiation from the fundamental laser beams at the gold interfaces. In addition, the lateral confinement of the waveguide affects the set of allowable propagating modes, and can introduce modulation patterns due to mode interference [39]. For both the 730 nm and the 935 nm laser beam, leakage radiation well over 50 μm away from the excitation spot was observed, indicating that SPP propagation is persistent over such length scales despite lateral confinement effects. When pulse trains were incident with s-polarization, the diffracted laser spot remained whereas the characteristic leakage radiation was no longer observed, confirming the SPP origin of the directional signal.

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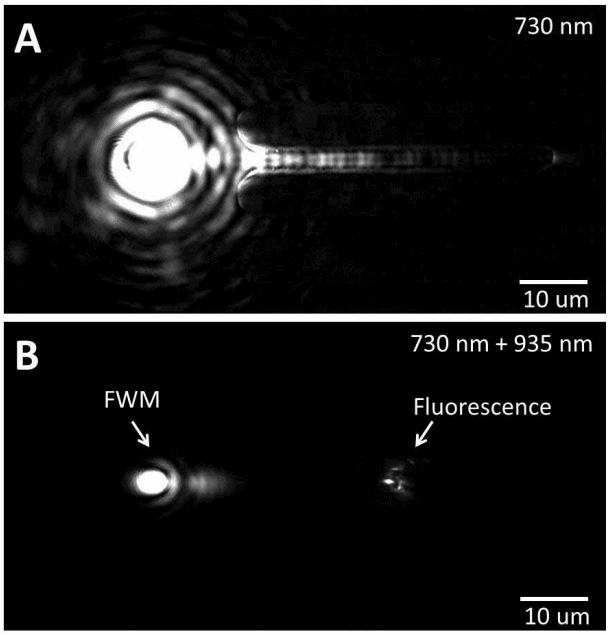

Fig. 2. (A) CCD image showing the laser spot and the leakage radiation of the propagating SPP mode excited by 730 nm p-polarized light. Note that the SPP mode propagates into the gold finger. (B) Image showing the FWM signal at the location of the laser spot, the leakage radiation from a SPP mode at $2\omega_1 = \omega_2$ and the remotely-excited fluorescence from the quantum dots positioned on the gold finger. For this image, the bandpass filter in front of the CCD camera was chosen such that both the fluorescence emission and the FWM radiation was detected.

3.2. Remote nonlinear excitation of quantum dots

When the QDs were applied onto the gold waveguides, a strong emission from the clusters was detected upon launching a propagating SPP mode in the gold finger. Using bandpass filters, we verified that the observed emission was maximum at the wavelength corresponding to the peak of the QD fluorescence. We thus attribute this emission to the fluorescence of the QDs that is excited with twice the plasmon frequency ($2\omega_1$ or $2\omega_2$). Quantum dot fluorescence was observed at a distance of 50 μm from the focused laser spot for the 730 nm beam and up to 80 μm for the 935 nm beam. The presence of the fluorescence signal is explained by the excitation of a propagating SPP mode, which couples to a local mode at the site of the QD perturbation, providing a local surface field for nonlinear excitation of the particle [40]. These results confirm previous observations that SPP mediated nonlinearly excited fluorescence can be observed at distances of tens of micrometers from the excitation spot [20, 30].

We next examined the feasibility of remote dual-color nonlinear excitation by focusing both beams simultaneously onto the gold film in a collinear fashion. Two strong nonlinear contributions can be distinguished, as shown in Fig. 2(b). First, a strong signal at the location of the excitation spot is observed. This signal peaks at the wavelength that corresponds to a FWM contribution at $\omega_3 = 2\omega_1 - \omega_2$. The FWM signal indicates that the spatially and temporally overlapped beams induce a third-order polarization near the interface [41]. Part of the FWM radiation is observed in the direction of the SPP mode. Upon changing the p-polarization of the incident beams to s-polarization, the FWM at the focal spot was retained while the directional FWM disappeared. We attribute the directional FWM to the launching of a SPP of frequency ω_3

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at the site of the laser spot, which subsequently propagates in the film. Because the distribution of incident excitation wave vectors has a finite width, the incident wave vectors can combine to launch a SPP mode with $k_3^{spp} = 2k_1 - k_2$. This mechanism bears similarity to the nonlinear SPP excitation through wave vector matching of weakly focused beams, as demonstrated recently by Renger et al. [41, 42]. Second, for temporally overlapped beams, the fluorescence of the QD cluster is stronger than the sum of the fluorescence contributions from each individual beam. This indicates that the QDs are excited through dual color excitation mediated by the two fundamental SPP modes ($\omega_1 + \omega_2$). We note that the QD signal virtually disappears when detected at wavelengths away from the wavelength of maximum fluorescence, indicating that the QD response is dominated by nonlinearly excited fluorescence under the excitation conditions examined here.

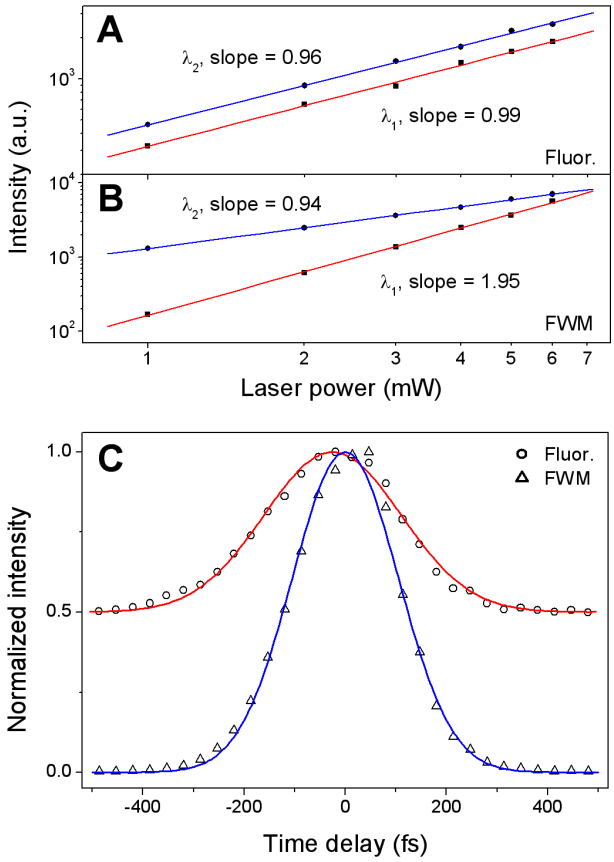

Fig. 3. Power dependence of the nonlinearly excited fluorescence (A) and FWM (B) signals. Both the signals and the laser powers of the fundamental beams (λ_1, λ_2) are plotted on a logarithmic scale. (C) Fluorescence and FWM signals as a function of the time delay between the λ_1 and λ_2 beams. The red and blue curves show Gaussian fits to the nonlinear fluorescence and FWM cross correlations, respectively.

3.3. Characterization of FWM and fluorescence contributions

In Fig. 3, we further examine the nature of the nonlinearly excited fluorescence and FWM contributions. In these measurements, the QDs were placed at a distance of 40 μm from the

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focused laser spot. In Fig. 3(a) and 3(b), the power dependence of the fluorescence and FWM are shown. The fluorescence signal of the QD is linear with the power of both λ_1 and in λ_2 beams, which confirms the nonlinear origin of the signal. The FWM near the launching site shows a quadratic dependence on λ_1 and a linear dependence on λ_2, underlining that the $\omega_3 = 2\omega_1 - \omega_2$ mixing process is responsible for this signal.

In Fig. 3(c), the fluorescence and FWM signals are plotted as a function of the time delay between the excitation beams. At the site of laser excitation, a cross correlation is found that follows the expected third-order FWM profile. At the site of the QD, the fluorescence signal shows the dual color excitation ($\omega_1 + \omega_2$) contribution when the two pulses overlap in time, in addition to the time-delay independent fluorescence contribution from the individual SPP modes (excited at $2\omega_1$ and at $2\omega_2$, respectively). As can be seen from the Figure, the dual-color excitation contribution constitutes about half of the total fluorescence response when the pulses overlap in time. This time-resolved cross correlation contribution to the nonlinear fluorescence signal clearly demonstrates that dual-color excitation of two independent surface fields is achieved at the site of the QD, 40 μm away from the laser excitation site. The observed width of the cross correlations (312 fs and 247 fs for nonlinear fluorescence and FWM correlations, respectively) complies with Gaussian estimates based on the measured pulse widths of the laser beams (314 fs and 243 fs, respectively). A small offset between the nonlinear fluorescence and FWM cross correlations is seen, which is due to the group delay dispersion between the signal and idler beams in the gold film. Under continual fs-excitation of the gold film, surface-mediated fluorescence signals from the QD cluster were observed over a time span of more than 5 hours without any sign of signal loss from the QD or photodamage to the substrate.

3.4. Polarization dependence of remote nonlinear excitation

To investigate whether the wave-mixing is primarily mediated by the SPP excitation, we studied the QD fluorescence as a function of beam polarization. In Fig. 4(a), the polarization orientation of the collinear incident laser beams is changed with an achromatic half-wave plate before entering the microscope. The figure shows that maximum fluorescence is observed for p-polarized beams and that the nonlinear signal disappears for s-polarized light. Note also that the directional FWM signal near the laser spot disappears for s-polarized light, indicating that SPP excitation is responsible for the observation of this nonlinear signal.

Finally, in Fig. 4(b), we examine the dependence of the fluorescence signal as a function of incident angle of the excitation beams. A clear maximum is found in the vicinity of the calculated Kretschmann coupling angle (42.9^o for 730 nm, 42.3^o for 935 nm), providing strong evidence that the SPP excitation is responsible for the nonlinear excitation of the QDs rather than the spurious diffracted laser light at the interface. The width of the angular distribution reflects the angular resolution in the experiment.

4. Discussion

In this work, we studied the feasibility of nonlinearly exciting remote targets with two independent surface plasmon polariton modes. We have used a simple, collinear excitation geometry based on an objective lens that is compatible with most optical microscopy experiments. In this configuration, the excitation light is applied in a light cone with a cone angle of $\sim 5^o$. The finite cone angle enables us to focus the light to microscopic dimensions (several μm), which introduces a clear spatial separation of the SPP launching site and the excitation site of the target. Inherent to this microscopic focusing method, not all the illumination light is efficiently coupled into the propagating SPP mode. However, our experiments show that with mW average powers, sufficient light is coupled into the surface plasmon modes for remote excitation of quantum dots more than 40 μm from the illumination site. The illumination site is positioned in the Au film,

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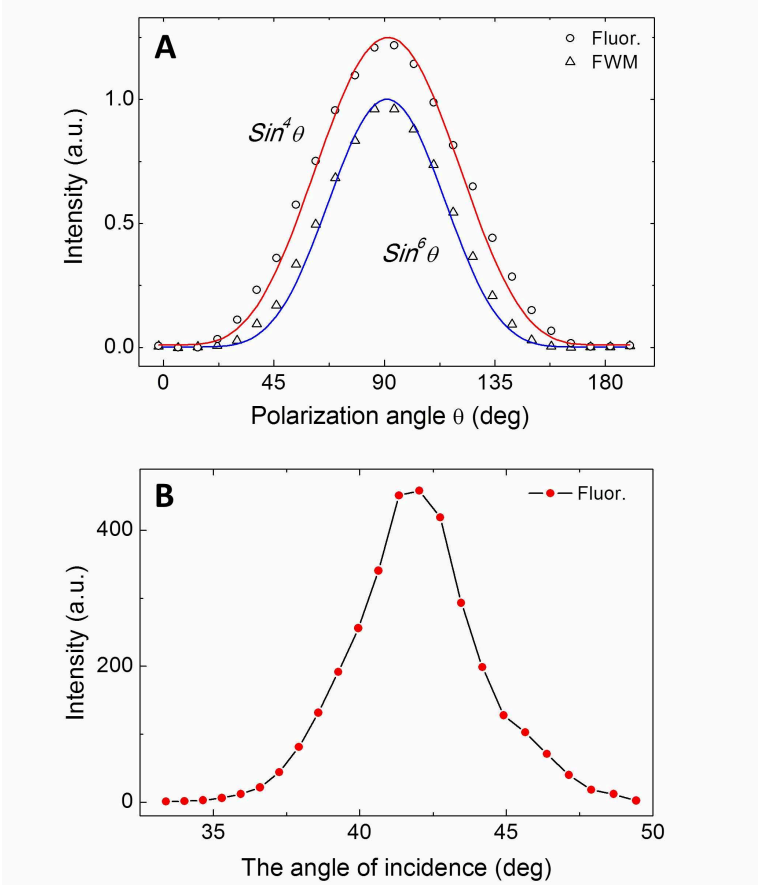

Fig. 4. (A) Nonlinearly excited fluorescence and FWM signals as a function of the polarization orientation of incident laser beams. S-polarized light corresponds to 0 degrees and p-polarized light coincides with 90 degrees in this graph. (B) Fluorescence intensity of the remotely excited quantum dots as a function of incident angle of the collinearly overlapped excitation beams.

away from the waveguide, at a location with limited local mode structure. Therefore, heating of the film is relatively minor, as evidenced by the absence of any photodamage to the substrate, even after 5 hours of continual illumination with two fs laser beams. In addition, the nonlinear FWM or fluorescence signals were extremely stable on the timescale of the experiment (0.1 s and up), and no heating related fluctuations were observed. These observations emphasize the robustness of this surface-mediated excitation approach.

We have carefully examined whether the remote nonlinear excitation is mediated by the SPP modes. The polarization orientation dependence and the incident angle dependence provide very strong evidence that the SPP mode is responsible for the remote nonlinear excitation. Previous work has shown that SPP fields are capable of inducing coherent anti-Stokes Raman scattering (CARS) in liquids near surfaces [43], and four-wave mixing in Si nanostructures placed on gold films [33]. The latter excitation schemes are parametric processes in which the material mediates the generation of a signal field without dissipating the excitation energy. In the present work we have focused on direct nonlinear electronic excitations, where the target is excited through the simultaneous absorption of energy contained in two independent surface

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waves.

Gunn et al. have demonstrated that a SPP mode can remotely generate a surface bound field strong enough to induce a nonlinear electronic excitation in the waveguiding metal itself [30, 31]. Verhagen et al. have successfully shown that a propagating surface field can remotely and nonlinearly excite transitions of ions embedded in the dielectric side of a metal/dielectric interface [20]. Our results build on these previous studies by demonstrating that (1) propagating SPP modes can nonlinearly excite surface bound nanoscale targets located several tens of microns from the SPP launching site, and (2) the target can be remotely excited by two independent surface plasmon fields.

The observed fluorescence signals from the QDs clearly demonstrate that excitations of electronic transitions in nanostructures placed on gold surfaces can be accomplished with surface plasmon fields. The nonlinearly excited fluorescence mediated by two surface plasmon modes is analogous to two-photon excited fluorescence (TPEF) of the QDs. The important difference between TPEF and the fluorescence observed in this work is that the nonlinear excitation is not mediated by photons but by the energy contained in two surface-bound field modes. Our experiments thus suggest that many nonlinear spectroscopy experiments that have traditionally been performed with photons can be replicated with surface plasmon polaritons in a remote excitation scheme. Such controlled SPP excitations may prove useful for sensitive nonlinear spectroscopy of individual targets as small as single molecules.

5. Conclusion

The experiments described here show that two independent and collinear SPP modes of different frequencies, while excited at a remote location, can combine at a distant site to nonlinearly excite selected targets. With distances of 40 μm away from the focus laser spot, excitation of the target is mediated solely by the energy contained in the SPP surface field and is fully decoupled from the illuminating photon flux. While we have used the fluorescence response of QDs as a probe for nonlinear excitation, these measurements indicate that multi-color nonlinear excitation at a distant site is possible, paving the way for more complex nonlinear spectroscopic examinations of targets, including time-resolved nonlinear experiments of molecules.

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