Enhancement of optical processes in coupled plasmonic nanocavities [Invited]

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We present detailed experimental and numerical investigations of resonances in deep nanogroove gratings in metallic substrates. These plasmonic nanocavity gratings feature enhanced fields within the grooves that enable a large enhancement of linear and nonlinear optical processes. This enhancement relies on both localized and propagating surface plasmons on the nanopatterned surface. We show that the efficiency of optical processes such as Raman scattering and four-wave mixing is dramatically enhanced by plasmonic nanocavity gratings. © 2011 Optical Society of America

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1. Introduction

The unique optical properties of metallic nanostructures have recently attracted a great deal of attention, bringing the field of plasmonics [1,2] to the forefront of nanophotonics research. Plasmonic elements have led to applications in optical labeling [3] and chemical and biological sensing [4,5], and more recently have enabled the utilization of nonlinear optical processes at the nanoscale [6–11].

In this paper, we demonstrate that plasmonic nanocavity gratings [11] can be used as substrates for enhancement of different types of optical processes. Plasmonic nanocavity gratings consist of deep periodically arranged grooves patterned into metallic films to create resonant nanocavities [12,13] at desired frequencies. Such structures take advantage of the excitation of surface waves, known as surface plasmon polaritons, via a second order grating to funnel and concentrate the energy into highly localized plasmonic modes of the nanocavities (see Fig. 1).

In the first part of this paper, we will discuss the resonant properties of our plasmonic nanocavity gratings. Supported by finite-difference time-domain simulations (FDTD Lumerical solutions) we show that the maximum field enhancement in the groove is obtained when the structure satisfies a double resonance condition, i.e., when the grating launches surface waves at a wavelength that is also resonant with the localized cavity mode. The second part of this paper is devoted to showing the potential of our structure for enhancing optical processes. We experimentally demonstrate enhanced nonlinear four-wave mixing (4 WM) and Raman scattering in plasmonic nanocavity gratings.

2. Resonances of Coupled Plasmonic Nanocavities

The optical properties of the structure sketched in Fig. 1 can be analyzed by using FDTD simulations. Figures 2(a)–2(c) summarize the resonance properties of plasmonic nanocavity gratings.

Fig. 2(a) shows the intensity, measured in the center of the groove entrance (denoted by the small $x$ in the inset) and normalized by the incident intensity $|E/E_0|^2$, for a single nanocavity. This plot shows that
the resonance wavelength ($\lambda_{cav}$) of the nanocavity is controlled by the depth $d$. Increasing $d$ red-shifts the resonance of the nanostructure. This behavior is explained by considering the nanocavities as truncated vertical metal-insulator-metal waveguides \cite{14} for which the bottom part is replaced by a gold mirror and the upper part is open to the air. This causes the nanocavities to behave as nanoscale Fabry–Perot resonators.

Figure 2(b) presents the calculated position $\lambda_g$ of the maximum of resonance for plasmonic nanogroove gratings as a function of the grating period $\Lambda_g$. Note that for a given $d$ and a fixed incidence angle ($\alpha$), $\Lambda_g$ controls the wavelength of the coupled surface wave, i.e., such that

$$k_0 \sin(\alpha) + q \beta_g = k_g, \quad (1)$$

where $q$ is an integer, $\beta_g = 2\pi/\Lambda_g$, $k_g = n_{eff}k_0$, and $k_0$ are the wave vector of the surface wave and of the free-space wave vector, respectively, and $n_{eff}$ is the effective mode index of the waves propagating along the nanogroove grating surface.

For a given $\Lambda_g$ but at different $d$, we observe that the coupled wavelength changes. This indicates that both $d$ and $\Lambda_g$ contribute to the resonance of the system. In Fig. 2(c), we plot the maximum of the normalized electromagnetic field as a function of $\Lambda_g$. We observe that the maximum field at the groove entrance is obtained when $\Lambda_g$ is such that the grating launches surface waves, which are resonant with the intrinsic mode of the isolated nanocavities, i.e., when $\lambda_{inc} = n_{eff}\Lambda_g = \lambda_{cav}$. In this case, the incident light coupled into the localized nanocavity modes is assisted by surface plasmon polaritons propagating at the surface of the corrugated metallic structure. For practical applications, once the operating wavelength has been determined, the depth of the nanocavities can be chosen. Then, to maximize the field enhancement produced by the structure, for a given incident angle, the grating period must be chosen to launch surface waves that are also resonant with the intrinsic nanocavity modes ($\lambda_{cav}$), i.e., which satisfy Eq. (1) with $k_g = 2\pi n_{eff}/\lambda_{cav}$.

Note that the number of illuminated grooves plays an important role in this coupling process. By increasing the beam waist, a larger number of grooves are simultaneously illuminated, thereby narrowing the resonance and improving the coupling to surface waves.

To better characterize the influence of the geometrical parameter ($w, d, \Lambda_g$) of the patterned structure on the electromagnetic field, we introduce the local field enhancement factor $\eta_{loc}$.

Fig. 3 shows the two different procedures employed to evaluate this local enhancement factor $\eta_{loc}$, for a given frequency, in the air ($\eta_{loc,\text{air}}$) and in
characterized via the $\eta_{\text{in}}$ at each frequency. Because of Purcell enhancement, collimation effect by the structure, and the finite numerical aperture of the microscope objective used for the experiment, there is an enhancement of the collected 4WM signal with respect to one coming from a flat surface [16,17]. To better characterize both this emission enhancement and the coherent scattering of the generated polarization, we introduce the out-coupling enhancement factor ($\eta_{\text{out}}$) of the structure, which quantifies the influence of the environment on the emission of a small volume of polarized medium emitting at a given frequency. This volume is modeled as an electric dipole. The dipole is aligned along $x$, i.e., along the dimension perpendicular to the grooves, and positioned like the monitors used to evaluate $\eta_{\text{in}}$, i.e., within the metal at a distance $h = 5\,\text{nm}$ below the air/metal interface (red crosses in (a) and (b)). We monitor the radiated field and calculate the power $P_{\text{rad}}$, which would be the case of a nanogroove grating is very different (Fig. 4(c)). The dipole source also launches surface waves on the corrugated surface, but as they propagate away from the source they undergo coherent scattering at the grooves. The direction of constructive interference (angle with respect to the normal to the surface) is then determined by Eq. (1). For instance, with grooves of 90 nm depth and 60 nm gap, light is emitted mainly normal to the surface ($= 0$) when the grating period is $\Lambda_g = 300\,\text{nm}$ at $\lambda = 670\,\text{nm}$ and $q = 1$.

The local enhancement factor ($\eta_{\text{in},\text{metal}}$) in the metal and in the gap of the nanocavity is calculated as follows: At the groove entrance at the location indicated by the yellow cross in (a), $\eta_{\text{in},\text{air}} = |E/E_0|$, where the calculated field $E$ is normalized to the incident field $E_0$. In the metal, we must account for the finite penetration, i.e., the skin depth of the electromagnetic field. We therefore define $\eta_{\text{in},\text{metal}} = |E/E_{\text{flat,metal}}|$ where the field $E$ calculated at the location indicated by the red cross in (a) is normalized to the field $E_{\text{flat,metal}}$ of the unpatterned structure (red cross in (b)). Electric field distribution $|E/E_0|^2$ for a nanogroove grating with a width $w = 60\,\text{nm}$, a depth $d = 90\,\text{nm}$ and $\Lambda_g = 560\,\text{nm}$ (c), and for a flat gold surface (d). The incident Gaussian beam has a maximum field amplitude $|E_0|$ and a free space wavelength $\lambda_{\text{free}} = 820\,\text{nm}$.

In the next section, we will make use of these enhancement factors to quantify the influence of the geometrical parameters of the structure ($w$, $d$, and $\Lambda_g$) on the generated nonlinear four wave mixing signal and on the Raman scattering signal.

3. Plasmonic Nanocavity Gratings Enhance Optical Processes

A. Four-Wave Mixing

Noble materials have intrinsically large nonlinear coefficients, notably their third order susceptibility $\chi^{(3)}$, which, for example, for gold films can be about 10 times higher than that of LiNO$_3$ ([15]). We have previously reported that an enhanced 4WM signal can be obtained in gold plasmonic nanocavities [11]. In the following, we would like to elaborate on the method used to design the plasmonic structure for 4WM and the role of $\eta$ in the enhancement of this nonlinear process. Since the nonlinear material used for this experiment is the gold itself, for simplicity we will omit the subscript “metal” in the next section. In this process, two photons at $\omega_1$ interact with a photon at $\omega_2$ to generate a nonlinear polarization at $\omega_{4\,\text{WM}}$ such that $\omega_{4\,\text{WM}} = 2\omega_1 - \omega_2$. This nonlinear process, known as degenerate up-converted 4WM, occurs in the vicinity of plasmonic structures where the fields exhibit plasmonic enhancement and where the generated nonlinear polarization undergoes coherent scattering by the structure. The plasmonic field enhancement experienced by each beam can be directly characterized via the $\eta_{\text{in}}$ at each frequency.
After defining enhancement factors at each frequency, we can estimate the overall enhancement of such a complex nonlinear process by defining the local 4 WM enhancement factor: $\text{EF}_{\text{local}} = \eta_{\text{in},1}^2 \eta_{\text{in},2}^2 \eta_{\text{out},4\text{WM}}^2$.

Since the $\eta$’s are obtained using either point monitors or point sources, the $\text{EF}_{\text{local}}$ is a local value. This local $\text{EF}_{\text{local}}$ can also be obtained by $\text{EF}_{\text{local}} = \frac{P_{4\text{WM,flat.local}}}{P_{4\text{WM,flat.local}}}$ where $P_{4\text{WM,flat.local}}$ are the powers collected at $\omega_{4\text{WM}}$ when the patterned and unpatterned gold structures, respectively, are illuminated by two beams at frequencies $\omega_1$ and $\omega_2$, considering only an infinitesimal volume of gold where the nonlinear polarization is generated. The infinitesimal volume, modeled by a single dipole, is centered around the location of the red cross monitor in Fig. 3 and around the source in Fig. 4. The overall 4 WM enhancement could be in principle calculated by summing the 4 WM fields generated by each volume element of the gold structure, normalized to the result of the same summation for a flat surface. However, performing such a summation with FDTD simulations remains challenging. We therefore cannot directly compare the overall 4 WM enhancement to $\text{EF}_{\text{local}}$. However, we expect that the dependence on the geometrical parameters is similar for both local and overall enhancements, especially because our experiments have been performed with a relatively high NA microscope objective—the incident beam has a $\sim1 \mu$m waist size—for which the volume of interaction is limited to the waist of the beam, thereby limiting interference effects which might occur when considering a spatial distribution of sources for the 4 WM polarization.

Figure 5 shows $\eta_{\text{in},1}^2$ and $\eta_{\text{in},2}^2$ as a function of $d$ and $\Lambda_g$, respectively. These colorplots enable us to quantify the combined effect of localized surface plasmons and surface waves on the field enhancement and on the in-coupling process. $\eta_{\text{in},1}^2$ vs. $d$ exhibits a maximum when there exists a resonant mode at $\lambda_{\text{inc}}$, i.e., when $d$ is such that $\lambda_{\text{inc}} = \lambda_{\text{cav}}$. At the same time, $\eta_{\text{in},2}^2$ vs. $\Lambda_g$ exhibits a maximum when the surface waves at $\omega_{\text{inc}}$ are efficiently excited, i.e., when $\Lambda_g$ is such that $\lambda_{\text{inc}} = \frac{n_{\text{eff}} m \Lambda_g}{\sin \theta}$ ($m$ is an integer). The same arguments also apply for $\eta_{\text{in},2}^2$ vs. $d$ and $\Lambda_g$, but since the incident frequency is different, the double resonance condition is reached for a different set of geometrical parameters. The maxima in Fig. 5 correspond to $m = 1$.

We can also display the calculated $\eta_{\text{out},4\text{WM}}$ as a function of $d$ and $\Lambda_g$ (Fig. 6). This plot enables us to observe again the role of both nanocavity modes and the surface waves on the field enhancement in the out-coupling process. As for the in-coupling mechanism, $\eta_{\text{out},4\text{WM}}$ vs. $d$ exhibits a maximum when there exists a nanocavity mode at $\lambda_{\text{dipole}}$, i.e., when $d$ is such that $\lambda_{\text{dipole}} = \lambda_{\text{cav}}$. Also here, at the same time, $\eta_{\text{out},4\text{WM}}$ vs. $\Lambda_g$ exhibits a maximum when the surface waves at $\lambda_{\text{dipole}}$, are efficiently converted into photons that are able to reach the detector, i.e., when $\Lambda_g$ is such that $\lambda_{\text{dipole}} = m n_{\text{eff}} \Lambda_g$ ($m$ is an integer). The maxima in Fig. 6 correspond to $m = 1$, $m = 2$, and $m = 3$, respectively. Because $\eta_{\text{in},1}$ appears at the fourth power in the expression for $\text{EF}_{\text{local}}$. It is clear that the maximum enhancement factor of the whole nonlinear process would occur for devices designed to maxmize $\eta_{\text{in},1}$. To do so, we fabricated and measured arrays of nanocavity gratings that achieve localized resonance at $\omega_1$, i.e., for 90 nm deep nanocavities (see Fig. 5(a)).

Fig. 7 shows a schematic of the experimental setup used to measure the enhanced 4 WM signal. Mode-locked laser pulse-trains at 820 nm ($\lambda_1$) are generated by an optical parametric oscillator (Levante Emerald, APE-Berlin) synchronously pumped by a frequency doubled Nd:YVO4 laser (picoTRAIN, High-Q $\lambda = 532$ nm, 7 ps pulse duration, 76 MHz repetition rate). Additionally, the pump laser provides another output at 1064 nm ($\lambda_2$). Since many of the optical components inserted along the beam paths are polarization-sensitive, we fixed the polarization of both beams and mounted the sample on a rotation stage to align the polarization of both laser beams perpendicular to the grooves (for such incident polarization, the coupling between incident TE to TM surface waves is maximized [18]). The two beams are spatially and temporally overlapped before being sent into an inverted Olympus FV 300 confocal microscope through a scanning module. The scanning module is composed of two mirrors acting on two spatial dimensions and enables us to scan the sample along $x$ and $y$. Light is focused onto the sample using a 40× objective (0.75 NA). For such an objective, the scanning area is about 350 µm by 350 µm. The generated 4 WM light

![Fig. 5](image-url)  (Color online) (a),(b) Calculated local enhancement factor $\eta_{\text{in},1}$ at $\omega_1$ and $\eta_{\text{in},2}$ at $\omega_2$ (b) as a function of $d$ and $\Lambda_g$ for normally incident monochromatic laser beams focused on the nanocavity grating. The simulated groove width is $w = 60$ nm. In (a) and (b) the incident free space wavelength is 820 nm and 1064 nm, respectively.

![Fig. 6](image-url)  (Color online) Calculated local enhancement factor $\eta_{\text{out},4\text{WM}}$ at $\omega_{4\text{WM}}$ as a function of $d$ and $\Lambda_g$. The simulated groove width is $w = 60$ nm. In our experiment, we only considered the up-converted four wave mixing signal which results in light generation at 667 nm. The dipole used for this simulation is emitting at this wavelength noted $\lambda_{\text{dipole}}$ in the text.
Nonlinear signal at for a fixed depth and width of the mW pump laser beam at 90° presents the results obtained on the surface of the metal. To avoid any oxidation of the Ag, a continuous thermally conductive layer is deposited after the liftoff, and a second evaporation helps with thermal management and prevents damage to the structure by creating a continuous thermally conductive layer.

Figure 8(a) presents the experimental measurements of the 4WM enhancement as a function of the grating period \( \Lambda_g \) for a fixed depth and width of the nanocavities \( (d = 90 \text{ nm}, w = 80 \text{ nm}) \). Each mark in Fig. 8(a) corresponds to the detected 4WM signal from a few grooves (ranging between 2 to maximum 10 depending \( \Lambda_g \)), averaged over the corresponding grating and normalized by that of a flat gold interface to express the enhancement factor \( \text{EF}_{\text{measured}} = P_{\text{4WM measured}} / P_{\text{4WM flat measured}} \). We remark that the maximum enhancement occurs for \( \Lambda_g = 560 \text{ nm} \), i.e., when \( \eta_{\text{in metal}} \) is maximum (see Fig. 5(a)).

\[ \eta_{\text{in metal}} = \eta_{\text{in metal}} \left( \frac{\eta_{\text{out}}}{\eta_{\text{in} 1}} \right)^2. \]

We also remark that the local maximum of the 4WM signal at \( \Lambda_g \approx 320 \text{ nm} \) corresponds to the position of the peak of the calculated out-coupling coefficient \( \left( \eta_{\text{out} \cdot 4 \text{WM}} \right)^2 \). The validity of the previous argument that local enhancement factors can help to understand the total enhancement factor of the nonlinear process is confirmed by comparing the position of the maximum of the calculated local nonlinear polarization with that of the maximum of the 4WM signal as a function of \( \Lambda_g \). As was expected with the simulation, a maximum of nonlinear four wave mixing enhancement, of about 2000, occurs for plasmonic nanocavity gratings exhibiting a double resonance condition at \( \lambda_1 \). We recall that the measured 4WM enhancement results from the summation of the 4WM fields generated by each volume element of the gold structure and therefore may differ from the multiplication of the local enhancement factors in Figs. 8(b) and 8(c).

### B. Surface Enhanced Raman Scattering

Figure 9 presents the results obtained on the surface enhanced Raman scattering (SERS) measurements from a self-assembled monolayer of benzene-thiol molecules adsorbed on silver-based plasmonic nanocavity gratings. Figure 9(a) sketches the experiment: a ~5 mW pump laser beam at 532 nm with an incident polarization perpendicular to the grooves is focused onto the structure using the 20x microscope objective of a Witec confocal Raman microscope. The Raman scattered (Stokes) signal and the reflected pump beam are collected together via the same objective. The Raman signal is separated from the pump light by a filter and then directly fed in a spectrometer to acquire the Raman spectrum. For this experiment, the plasmonic structure is specifically designed in silver (Ag) to avoid non-desirable interband transitions that take place in gold for our pumping wavelength of 532 nm. To avoid any oxidation of the Ag...
surface, the structure is dipped for half a day into the benzenethiol solution immediately after the e-beam evaporation. Measurements were performed immediately after removing the structure from the benzenethiol solution. Figure 9(b) is an example of an FDTD simulation showing the pump intensity distribution in the vicinity of a plasmonic nanocavity grating in silver for parameters fulfilling the previously discussed double resonance condition considering an incident pump wavelength of 532 nm. In this case, this condition occurs for $d = 40 \text{ nm}$, $\Lambda_g = 330 \text{ nm}$ (we also choose $w = 30 \text{ nm}$). The corresponding spectrum is shown in Fig. 9(c). Figure 9(b) shows the intensity distribution at this double resonance condition and shows that molecules placed at the entrance of the grooves experience maximum local intensity enhancement, about $\eta^2_{532 \text{ nm}} > 1.5 \times 10^3$. For small Raman shift, both the pump and the Stokes electric fields are enhanced in the nanocavities and by essentially the identical factor given the vicinity of the Stokes and pump frequencies, leading to a rough estimation of the maximum SERS enhancement $\text{EF} = \eta^4$ of about $2.25 \times 10^6$. Figure 9(d) presents the experimental enhancement of the Raman scattering signal as a function of Raman shift in wavenumbers for several $\Lambda_g$ and for a fixed depth $d = 40 \text{ nm}$. The experimental enhancement of the Raman signal is determined by normalizing the Raman signal obtained from the nanocavity grating with that of a pure benzenethiol solution taking into account the number of molecules in each case [19]. A maximum surface enhanced Raman signal—about $8 \times 10^8$—occurs for the period $\Lambda_g = 330 \text{ nm}$. As it has been often reported in similar SERS experiments [20], the measured enhancement is higher than the one expected using field enhancement as the unique mechanism for Raman signal enhancement. Chemical effects, which have been reported to be on the order of $10^2$, can explain the mismatch between our measurements and the numerical simulations [21] and also explain the broad underlying continuum in SERS signal observed in Fig. 9(c) around 1300 cm$^{-1}$ wavenumber. The maximum SERS enhancement occurs for a grating period for $\Lambda_g = 330 \text{ nm}$, but it remains high for slightly larger period than the one providing the maximum $\eta_{532 \text{ nm}}$ because even for small Raman shift, the best compromise for both pump and Stokes enhancement ($\eta_{\text{pump}}^2\eta_{\text{Stokes}}^2$) have to be considered. We also notice that no Raman signal is observed when the incident polarization is chosen parallel to the grooves axis.

4. Conclusion
We demonstrated that a metallic film patterned with periodically arranged resonant nanocavities can enhance both degenerate 4WM and Raman scattering processes by several orders of magnitude. We expect that this technique is broadly applicable to other nonlinear processes, such as second and third harmonic generation, and linear processes such as absorption and fluorescence. Further investigation of nonlinear optical processes at the nanoscale may lead to the development of highly sensitive nonlinear spectroscopy techniques such as surface-enhanced stimulated Raman scattering and coherent anti-stokes Raman scattering.

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References