Impact of nonlocal response in plasmonic metasurfaces on four-wave mixing

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Abstract
We report the impact of nonlocal response in metallic nanostructures on four-wave mixing (FWM) process in nonlinear plasmonic metasurfaces which consist of Au nanostructures coupled with Au film spaced by an ultrathin dielectric film. When the dielectric film is linear and FWM only from the Au nanostructures, the FWM efficiency of around two orders of magnitude enhancement is obtained when the nonlocal effect of Au, not the traditionally local Drude model of Au, is considered. However, when the dielectric film is nonlinear and FWM from the Au nanostructures is negligible, the almost half FWM response from the nonlinear metasurface under the nonlocal, not the local model, of Au is confirmed. These results are both ascribed to the different local electric field distributions near the surface of Au nanostructures and in the gap at the local and nonlocal response of Au. The results have an important significance to design ultra-compacted integrated nonlinear optical devices or to explain the experimental measurements of nonlinear response involving plasmonic nanostructures of ultra-small gaps.

1. Introduction
Four-wave mixing (FWM), as a parametric third-order optical nonlinear process, has widespread and important applications in frequency conversion, correlated photon pairs generation, nonlinear imaging, switching, amplification and comb generation [1–6]. However, as a third-order nonlinear optical effect, FWM process in subwavelength nanostructures is quite weak and the efficiency is extremely low [7]. Large input intensities are essentially required to get the feasible FWM signals, which indeed limits its practical applications. In order to overcome the weak nature of third-order optical nonlinearity of materials, various optical resonators are designed to boost the FWM process by confining or slowing the light in extreme small volumes. For example, dispersion engineered waveguides [8, 9], photonic crystal waveguides [10, 11], waveguides integrated with 2D materials [12, 13], micro-rib resonators [14, 15], Fabry–Perot cavity [16], and various plasmonic nanostructures [17–20]. Among these methods, the plasmonic nanostructures have attracted enormous attention since the electromagnetic waves can be extremely confined into deep subwavelength volumes, and thus the local field can be dramatically enhanced to strength the light–matter interaction [17]. The resonance wavelength in the plasmonic nanostructures can be flexibly tuned by changing the shape, the coupling gap, and dielectric environment of plasmonic nanostructures, which can realize the efficient FWM in a broadband. FWM efficiency was reported to be enhanced up to sixteen to nineteen orders in the plasmonic nanowires coupled with silver films [20].

The coupled plasmonic nanostructure, i.e. two or more metallic nanostructures close to each other with the coupled near electric-field, is one of the most efficient plasmonic configurations for nonlinear optics, due to the extremely enhanced local field between the gaps [21–23]. The gap between the metallic nanostructures is a critical parameter which effects the plasmonic resonance frequency and the confinement of electromagnetic wave. It is traditionally considered that the local field enhancement in the gap could exponentially increase with the decrease of gap to enhance the light–matter interaction. However, recent
The research process shows that, as the nanoscale feature size of plasmonic systems is below 20 nm, the classical theoretical description based on Drude or Drude–Lorentz model of metals becomes discrepancy with the experimental observations [24]. The spatial nonlocal effect of dielectric response in conducting materials becomes not negligible, and the effect of nonlocality in the metallic structures can limit the field enhancement [24–27]. When the gap of coupled metallic nanostructures is less than 0.5 nm, the quantum tunneling effect is probably involved and the local field enhancement is further dramatically reduced comparing with the classical local effect [28–31]. Besides the linear optical response, the nonlinear optical properties, such as harmonic generation, optical bistability, in gap-plasmon nanostructures have been studied [32–35].

In this paper, we investigate how the nonlocal effects in the plasmonic structures influence the FWM efficiency from the metallic nanostructure itself and nonlinear dielectrics between the gap, respectively. A metasurface consisting of Au grating and Au film spaced by a layer of dielectric film is designed and studied. Compared with the results obtained from classical electromagnetic theory, the dramatical enhancement of FWM from metallic nanostructures, while the reduction of FWM from nonlinear dielectrics, is obtained when the nonlocal effect of Au is considered due to the changed local field distribution.

2. Geometry, materials and numerical method

The geometry of the designed nonlinear metasurface is depicted in figure 1(a). The thickness of bottom metallic film is designed as 200 nm, which is much larger than the skin depth of Au to ensure no light transmission. Periodic Au nanostrips are supposed to be infinite along z-direction, and the periodicity along x-direction is denoted as \( P = 100 \) nm. The width and height of an Au nanostrip is designed as \( L_a = 55 \) nm and \( H_a = 40 \) nm, respectively. The thickness of the ultrathin dielectric material is \( g = 1 \) nm.

Experimentally, such ultrathin gap has been feasibly prepared by atomic layer deposition method [24, 36]. The Au nanostrips were then fabricated on the dielectric films by electron-beam lithography (EBL) technique. The mature process for EBL is clearly described in reference [24]. Briefly, a positive electron-beam resist, poly(methyl methacrylate) (PMMA) was spin coated on the ultrathin dielectric film and baked, and then was exposed by EBL system according to the designed pattern. The exposed PMMA was removed by the standard MIBK:IPA developer, and the Au films with a designed thickness was then deposited by electron-beam evaporation or sputtering. Finally, the unexposed PMMA was lift-off, followed by a rinse and blow dry to obtain the samples.

Two transverse magnetic polarized waves of different wavelengths \( \lambda_1 \) and \( \lambda_2 \) (angular frequency \( \omega_1 \) and \( \omega_2 \)) shine on the metasurface in the \( x-o-y \) plane. The angles of incidence are \( \theta_1 \) and \( \theta_2 \), respectively. The generated light of new frequency \( \omega_3 \) via the degenerate FWM process satisfying \( \omega_3 = 2\omega_1 - \omega_2 \) is concerned.

Assuming a time-harmonic propagation and undepleted pump approximation, the linear optical response from the metasurface can be obtained by solving the wave equation deduced from classical...
where \( k_o \) is the wavevector of incident light, \( \mu_0 \) is the vacuum permeability, \( \mathbf{E}_o \) is the fundamental electric field, and \( \mathbf{P}_o \) is the polarization at position \( r \). For the classical local model, the polarization at position \( r \), i.e. \( \mathbf{P}_o (r) \), is induced by the local field \( \mathbf{E}_o (r) \), and \( \mathbf{P}_o (r) = \mathbf{D}_o (r) - e_0 \varepsilon_o \mathbf{E}_o (r) \) with the electric displacement field \( \mathbf{D}_o (r) = \varepsilon_0 \varepsilon (\omega, \mathbf{r}) \mathbf{E}_o (r) \), where \( \varepsilon (\omega, \mathbf{r}) \) is the permittivity of materials. For the isotropy dielectric materials, \( \varepsilon (\mathbf{r}, \omega) = \varepsilon_0^s \). For the Au, the classical local Drude model gives \( \varepsilon (\mathbf{r}, \omega) = \varepsilon_b (\omega) - \omega_p^2 / (\omega^2 + i\omega\gamma) \), where \( \varepsilon_b (\omega) \) is the frequency-dependent background dielectric constant from the bound changes, \( \gamma \) is the damping frequency of \( 1.07 \times 10^{14} \) rad s\(^{-1} \), and \( \omega_p = \sqrt{n_0e^2/\varepsilon_0 m_e^*} \) is the plasma frequency with \( n_0 \) the electron density, \( e \) the electron charge, and \( m_e^* \) the effective electron mass. For Au, \( n_0 = 5.8 \times 10^{22} \) cm\(^{-3} \), and \( m_e^* = m_e \) with \( m_e \) the mass of electron, and thus \( \omega_p = 1.36 \times 10^{16} \) rad s\(^{-1} \). \( \varepsilon_b (\omega) \) is determined by \( \varepsilon_b (\omega) = \varepsilon_{\text{exp}} (\omega) + \omega_p^2 / (\omega^2 + i\omega\gamma) \) \([37, 38]\), where \( \varepsilon_{\text{exp}} (\omega) \) is the measured dielectric constant of Au \([39]\).

When the gap between the plasmonic nanostructures is small enough and the spatial nonlocality of dielectric in the metal is not negligible, the hydrodynamic Drude model becomes the rather exact model of the permittivity of metal, i.e. \( \varepsilon (\mathbf{k}_o, \omega) = \varepsilon_b (\omega) - \omega_p^2 / (\omega^2 + i\omega\gamma - \beta^{2}\mathbf{k}_o^2) \), where \( \beta = \sqrt{3/5} \nu_f \) is the parameter of nonlocality with the Fermi velocity \( \nu_f = 1.39 \times 10^6 \) m s\(^{-1} \), and \( \mathbf{k}_o \) is frequency dependent propagation vector. The polarization in the metal considering the nonlocal effect is written as \([32]\),

\[
\beta^{2}\nabla \cdot (\nabla \cdot \mathbf{P}_o) + (\omega^2 + i\omega\gamma)\mathbf{P}_o = -\frac{n_0e^2}{m_e}\mathbf{E}_o. \tag{2}
\]

The FWM process can be described by the nonlinear wave equation \([7]\),

\[
\nabla \times \nabla \times \mathbf{E}_{12} - k_{12}^2 \mathbf{E}_{12} = \mu_0 \Omega^2 \mathbf{P}_{12} + \mu_0 \Omega^2 \mathbf{P}_{NL}, \tag{3}
\]

where \( \Omega = \omega_3 \) is the angular frequency of generated new light, \( \mathbf{P}_{12} \) and \( \mathbf{P}_{NL} \) is the linear and nonlinear polarization at \( \Omega \). \( \mathbf{P}_{12} \) has the same form as \( \mathbf{P}_o \) as mentioned above. \( \mathbf{P}_{NL} \) is expressed as \([20]\),

\[
\mathbf{P}_{NL} = \varepsilon_0 \chi^{(3)} (\Omega; \omega_1, \omega_2) \mathbf{E} (\omega_1) \mathbf{E} (\omega_2) \mathbf{E}^* (\omega_3) \tag{4}
\]

By solving the wave equation (1) using finite elements method (FEM) via the commercial software Comsol multiphysics, the linear optical response, for example, the reflectance, the local electric field, and surface charge etc can be obtained. The settings are described in details as in reference \([34]\). The separately solved electric fields \( \mathbf{E} (\omega_1) \) and \( \mathbf{E} (\omega_2) \) are taken into the equation (4) to get the nonlinear polarization of FWM, then the nonlinear wave equation (equation (3)) can be finally solved.

The linear refractive index \( n_0 \) of dielectric material is assumed to be 1.8 (the corresponding relative permittivity \( \varepsilon_1^d \) is around 3.24), which is a typical value for oxides or polymers. The value of \( n_0 \) mainly affects the resonance wavelengths but will not change the conclusions on nonlinear responses. The
third-order nonlinear susceptibility $\chi^{(3)}$ of Au is $2 \times 10^{-19} \text{ m}^2 \text{ V}^{-2}$ [7]. When the FWM from Au nanostructures is considered, the $\chi^{(3)}$ of dielectric material is assumed to be negligible compared with that in Au, such as Al$_2$O$_3$ [22], CaF$_2$ [40] of $\chi^{(3)} \sim 10^{-23} \text{ m}^2 \text{ V}^{-2}$. When the FWM from nonlinear dielectric material in the gap is considered, an isotropic dielectric of a large $\chi^{(3)}$ is chosen. Note that for the isotropic materials, Au or dielectrics, we have $\chi^{(3)} = \chi_{xxxx}^{(3)} = \chi_{yyyy}^{(3)} = \chi_{zzzz}^{(3)} = \chi_{xxyy}^{(3)} + \chi_{xyxy}^{(3)} + \chi_{xyyx}^{(3)}$, and $\chi_{xxyy}^{(3)} = \chi_{xyxy}^{(3)} = \chi_{xyyx}^{(3)}$ is assumed [41]. The nonlinear materials, such as SrTiO$_3$ films [42], nonstoichiometric SiC [43] or SiO$_x$C$_y$ films [44], transition-metal oxides (Cr$_2$O$_3$, Mn$_3$O$_4$ etc) [45], nitrogen-enriched TiO$_2$ films [46], Si quantum dots doped Si-rich SiN$_x$ films [47], P-toluene sulphonate [48], possess large $\chi^{(3)} \sim 10^{-17} \text{ m}^2 \text{ V}^{-2}$, and the component $\chi_{iiii}^{(3)} (i = x, y, z)$ is assumed to be $4 \times 10^{-18} \text{ m}^2 \text{ V}^{-2}$ [20].

3. Results and discussion

The linear reflectance spectra of the metasurface at the different incident angles is shown in figure 1(b). The fundamental and second-order resonance wavelength of the plasmonic gap mode at the normal incidence is around 1672 nm and 947 nm, respectively, when the classical local Drude model of Au is considered. When the nonlocal effect of Au is involved due to the ultrathin gap, the resonance wavelength blueshifts to 1550 nm and 866 nm, respectively. Such trend has been reported as in references [25, 33]. There is a slightly blueshift when the angle of incidence increases whenever the local or nonlocal model of Au is considered, respectively. The electric field distributions at the fundamental and second-order resonance plasmonic gap mode considering the local and nonlocal effects of Au at the normal incidence are shown in figures 2(a)–(d), respectively. The maximum enhancement factor is around 206 and 196 at the local Drude and nonlocal model of Au at the fundamental resonance mode, respectively, and is around 115 and 88 at the second-order resonance mode, respectively. It is obvious that the enhancement factor considering
Figure 4. Reflected FWM CE from Au nanostructures as the function of incident wavelengths under the (a) local and (b) nonlocal model of Au, respectively. Both excitation lights are at normal incidence. (c) and (d) is the distribution of FWM electric field $|E(\omega_3)|$ of units $\text{V m}^{-1}$ at the maximum FWM efficiency in (a) and (b), respectively.

Figure 5. The dependence of FWM power from Au nanostructures on the incident angles of $\theta_1$ and wavelength $\lambda_1$ at local and nonlocal effect of Au, respectively. The nonlocal effect is smaller than that at the traditional local model, owing to the screening effect of electron–electron interaction [33]. The induced charge density $n = \nabla \cdot P_\omega/e$ at the nonlocal model of Au at the fundamental and second-order resonance mode is shown in figures 3(a) and (b), respectively. The line profile of charge distribution near the metal–dielectric interface along the labeled lines is shown in figures 3(c) and (d), respectively. Different from the induced charge distributing on the metal–dielectric interface under the classical local mode, the induced charge varies inside the metal of order of Thomas–Fermi screening length $\lambda_{TF} = v_f/\omega_p = 0.1 \text{ nm}$ at the nonlocal model of Au, which explains the different electric field distribution and further the FWM behavior under the two models.
Figure 6. The dependence of reflected FWM intensity from Au nanostructures on the incident intensity of $I_1$ and $I_2$ at the (a) local and (b) nonlocal model of Au, respectively.

Figure 7. Reflected FWM CE from nonlinear dielectric film in the gap as the function of incident wavelengths under the (a) local and (b) nonlocal model of Au, respectively. Both excitation lights are at normal incidence. (c) and (d) is the distribution of FWM electric field $|E(\omega_3)|$ of units V m$^{-1}$ at the maximum FWM efficiency in (a) and (b), respectively.

We next focus on the FWM results. We first study the FWM from pure Au nanostructures with a linear dielectric as the spacer. The two incident waves have equal intensities $I_1 = I_2 = 13.3$ MW cm$^{-2}$ if not specified in the article. The FWM conversion efficiency (CE) is defined as $\eta = P_{\text{swm}} / [P_1^2P_2]$, where $P_{\text{swm}}$ is the generated FWM power, $P_1$ and $P_2$ are the power of incident lights [49]. The dependence of the reflected FWM CE on the fundamental wavelengths $\lambda_1$ and $\lambda_2$ at the normal incidence considering the classical local and nonlocal model of Au is shown in figures 4(a) and (b), respectively. In the two scenarios, the maximum FWM CE both occurs when the fundamental and second-order resonance modes are just the incident fundamental waves. It is understandable that the local fields are mostly concentrated at the two resonance modes. The maximum FWM CE from the nonlinear metasurface when the nonlocal effect of Au is considered is around two orders of magnitude larger than that from the nanostructure considering the traditional local Drude of Au. It is ascribed to the penetrated field into the Au nanostructures which will
enhance the FWM response as the bulk third-order nonlinear process, as the enhanced third harmonic generation when considering the nonlocal field. The distribution of FWM electric field $|E(\omega_3)|$ at the maximum FWM CE in figures 4(a) and (b) under the local and nonlocal model of Au is shown in figures 4(c) and (d), respectively. The dependence of FWM CE from the nonlinear metasurface on the incident angle considering local and nonlocal mode of Au is calculated as shown in figure 5. For simplicity, we fix the $\lambda_2 = 1672 \text{ nm}$ and $1550 \text{ nm}$ under the local and nonlocal model of Au with the normal incidence, and just change the angle of incidence $\theta_1$ and wavelength $\lambda_1$. The results show that the maximum FWM response also occurs at the respective second-order plasmonic mode when the incident angle varies, and the FWM CE some decreases with the increase of incident angle due to the decrease of local electric field (not shown here). Note that the change of FWM CE is within one order of magnitude when $\theta_1$ varies from $0^\circ$ to $45^\circ$, indicating that the FWM from the nonlinear metasurface is relatively insensitive to the incident angles, as reported in reference [20].

The reflected FWM intensity can be flexibly controlled by varying the incident intensity of fundamental waves, as shown in figures 6(a) and (b), considering local and nonlocal model of Au, respectively. When $I_1$ ($I_2$) varies, $I_2$ ($I_1$) is set to be 100 MW cm$^{-2}$. The FWM intensity is a square function of $I_1$ and a linear function of $I_2$, as expected by equation (4). Below the damage threshold of Au and dielectric layer, the generated intensity of FWM can be arbitrarily increased.

We next investigate the FWM from nonlinear dielectric thin film between the gap. Under the same configuration of FWM from Au nanostructures, the dependence of FWM CE on the fundamental wavelengths $\lambda_1$ and $\lambda_2$ at normal incidence considering the classical local and nonlocal model of Au is shown in figures 7(a) and (b), respectively. First, the same conclusion as that obtained in the aforementioned FWM from Au nanostructures is, the maximum FWM CE also occurs at the fundamental and second-order resonance modes of fundamental waves due to the mostly enhanced local fields at these modes. Different from the FWM in pure Au nanostructures that the nonlocal effect of Au produces much larger FWM response, the maximum FWM CE from the nanostructure of nonlocal model of Au is around a half of that when considering the local effect of Au. That is because that the more enhanced local field at the resonance gap mode appears within the local model than the nonlocal model of Au. Comparing the FWM CE from the bare dielectric film of the same thickness on the Au film (the FWM CE is around $1.1 \times 10^{-23} \text{ W}^{-2}$), the FWM CE from the nonlinear metasurface is enhanced by $10^{11}$. The distribution of FWM electric field $|E(\omega_3)|$ at the maximum FWM CE in figures 7(a) and (b) under the local and nonlocal model of Au is shown in figures 7(c) and (d), respectively. The dependence of FWM CE from the metasurface on the angles of incidence considering local and nonlocal mode of Au is shown in figure 8. The same configuration is used as that to study the FWM from Au nanostructures, i.e. the $\lambda_2$ is fixed at the fundamental resonance mode of the metasurface and the waves incident at normal incidence, then to change the angle of incidence $\theta_1$ and wavelength $\lambda_1$. The same conclusions are observed as those obtained above. The reflected FWM intensity which is controlled by varying the incident intensity of fundamental waves under local and nonlocal model of Au is shown in figures 9(a) and (b), respectively. The same settings are used as for figure 6, i.e. when $I_1$ ($I_2$) varies, $I_2$ ($I_1$) is set to be 100 MW cm$^{-2}$. The quadric and linear

![Figure 8. The dependence of FWM CE from nonlinear dielectric film in the gap on the incident angles of $\theta_1$ and wavelength $\lambda_1$ at local and nonlocal effect of Au, respectively.](image)
relation of $I_1$ and $I_2$ with FWM is also satisfied. Finally, we point out that under this case when the optical nonlinearity of dielectric is considered, the nonlinear response from the Au is negligible and the overall FWM response is almost kept even both of the nonlinearity of Au and dielectric are considered simultaneously.

4. Conclusions

We investigate the influence of nonlocal effect of plasmonic nanostructures on the FWM nonlinear process. The Au-nanostrips coupled with Au-film spaced with the ultrathin dielectric film of plasmonic gap modes is performed as the model to demonstrate our goals. Different from the previous study on second- or third-order harmonic generation within the nonlocal model of metal, the two excitation waves at the fundamental and second-order plasmonic gap modes are simultaneously used to study the nonlocal effect on the nonlinear process. The significantly enhanced FWM from the Au nanostructures of linear dielectric spacer, while reduced FWM from nonlinear dielectric films, due to the nonlocal effect of Au are confirmed. Our study has an important significance for the design ultra-compacted integrated nonlinear optical devices or the explanation of experimental measurements. We finally note that, in this article, the gap of 1 nm is used for the study, and the more obvious influences of nonlocal effect of Au is expected with the further reduction of the gap. When the gap reduced to sub-nanometer, the quantum effect related the electron tunneling will be involved to further affect the nonlinear process in the more complicated way.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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