Plasmon excitation on flat graphene by spolarized beams using four-wave mixing

Jin Tao,^{1,2,5} Zhaogang Dong,^{3,5} Joel K. W. Yang,^{3,4,6} and Qi Jie Wang^{1,2,7}

 ¹OPTIMUS, Photonics Centre of Excellence, School of Electrical and Electronic Engineering, Nanyang Technological University, 50 Nanyang Ave, 639798, Singapore
 ²CDPT, Centre for Disruptive Photonic Technologies, School of Physical and Mathematical Sciences, Nanyang Technological University, 637371, Singapore
 ³Institute of Materials Research and Engineering, A*STAR (Agency for Science, Technology and Research), 3 Research Link, 117602, Singapore
 ⁴Singapore University of Technology and Design, 20 Dover Drive, 138682, Singapore
 ⁵J. T. and Z. D. contributed equally to this work.
 ⁶joel_yang@suid.edu.sg
 ⁷ qjwang@ntu.edu.sg

Abstract: Graphene plasmons have received significant attention recently due to its attractive properties such as high spatial confinement and tunability. However, exciting plasmons on graphene effectively still remains a challenge owing to the large wave-vector mismatch between the optical beam in air and graphene plasmon. In this paper, we present a novel scheme capable of exciting graphene surface plasmons (GSPs) on a flat suspended graphene by using only *s*-polarized optical beams through fourwave mixing (FWM) process, where the GSPs fields were derived analytically based on the Green's function analysis, under the basis of momentum conservation. By incorporating the merits of nonlinear optics, the presented scheme avoids any patterning of either graphene or substrate. We believe that the proposed scheme potentially paves the way towards an efficient pure optical excitation, switching and modulation of GSPs for realizing graphene-based nano-photonic and optoelectronic integrated circuits.

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1. Introduction

Plasmonic structures allow electromagnetic waves to be guided, manipulated and confined to the sub-wavelength scales, enabling wide applications in integrated photonic circuits [1–3], light harvesting [4], to metamaterials [5] and biochemical sensing [6]. Recently, graphene

surface plasmons (GSPs) have attracted tremendous interests due to its unique properties [7–19]. For example, unlike conventional metal-based plasmons, GSPs can be tuned *in situ* by a bias voltage applied on a field-effect transistor (FET) [20] in less than a nanosecond [21]. In addition, it has an unprecedented spatial confinement even down to one fortieth of the free-space wavelength, and such a spatial confinement has been verified by experiments [7, 8]. Moreover, graphene exhibits a relatively large conductivity, which translates into long optical relaxation times (τ ~100 fs), and thus it could potentially provide a large plasmon wave propagation distance [22]. These properties make graphene as a promising platform for plasmonic applications in the infrared frequency regime.

Despite these promising GSPs capabilities, methods to efficiently excite GSPs by freespace optical beams are on demand, where such a challenge is due to the large wave-vector mismatch between GSPs and optical beams. In recent experimental demonstrations so far, a sharp atomic force microscope (AFM) metallic tip that acts as a resonant optical antenna to mimic a vertically-polarized dipole, was used for launching GSPs [7, 8, 11]. Another approach is to use grating coupling method, for example the patterned silicon gratings placed beneath the graphene layer [23, 24] or graphene grating created by its elastic vibration due to the flexural wave or electrically generated surface acoustics [25, 26]. While, the verticaldipole method needs the AFM tip contact with graphene surface which could change the properties of the graphene, and the grating coupler method could suffer from scattering of plasmons on the patterned edges. Terahertz surface plasmon excitation by the nonlinear difference frequency generation in graphene and topological insulators have been theoretical studied [27]. Moreover, all these approaches for exciting GSPs requires the polarization state of the incident optical field to be *p*-polarized incidence as is also the case for other plasmonic materials, such as gold and silver [28]. In this case, a fundamental question of interest arises whether it is possible to excite plasmons using *only s-polarized* light.

In this paper, we present a novel scheme that is capable of exciting GSPs on a *flat* suspended graphene by using *only s-polarized* optical beams through nonlinear four-wave mixing (FWM) process. We present the detailed theoretical derivations by using the Green's function analysis, which enables us to obtain the required conditions of third-order susceptibility tensors for plasmon excitation on graphene. The proposed scheme provides a new route for graphene plasmon excitation with a potential for pure optical switching and modulation of GSPs.

2. Scheme for exciting graphene surface plasmons using four-wave mixing

The proposed scheme for exciting GSPs using FWM process is shown in Fig. 1, where two *s*-polarized optical beams (i.e. the electric field polarized along *y*) are with the oscillation frequencies of ω_1 and ω_2 , respectively. The corresponding incident angles are denoted as θ_1 and θ_2 , where the incident angle θ is measured with respect to the surface normal direction clockwise. The graphene layer is suspended in air and the dielectric environment surrounding graphene in this case is denoted as $\varepsilon_1 = \varepsilon_2 = 1$. Because the nonlinear FWM process involves three incident photons, the oscillation frequencies of the resultant optical beams will be either $2\omega_1 - \omega_2$ or $2\omega_2 - \omega_1$. Here, to simply the analysis, we focus on one of the oscillation frequencies without the loss of generality, where

$$\omega_{\rm spp} = 2\omega_{\rm l} - \omega_{\rm 2} \tag{1}$$

Nonlinear FWM process has been used to excite surface plasmon polaritons on gold film using two *p-polarized* optical beams [29, 30], where the detailed analytical expressions of the required third-order nonlinear susceptibility is difficult to obtain due to the 3D nature of bulk gold. In comparison, graphene has an atomic layer thickness, which simplifies the analysis significantly. This simplification enables us to investigate the novel excitation schematic, i.e. pure *s-polarized* incident condition.



Fig. 1. Scheme for exciting GSPs by using FWM process. The incident optical beams from free-space are having the oscillation frequencies of ω_1 and ω_2 , respectively, where the incidence angles are denoted as θ_1 and θ_2 . The figure illustrates the resonant incident angles (blue arrows) and the direction of GSPs propagation (purple arrow).

Figure 2 presents the dispersion curve of GSP with a Fermi energy level of $E_f = 0.4 \text{ eV}$ (solid red line), where the in-plane GSP wave vector is given as

$$k_{\rm spp}(\omega_{\rm spp}) = \varepsilon_0 \frac{\varepsilon_1 + \varepsilon_2}{2} \frac{2i\omega_{\rm spp}}{\sigma(\omega_{\rm spp})}.$$
 (2)

This expression was obtained by solving the dispersion relation of GSPs [22]. Here, σ is the optical conductivity calculated using random-phase approximation (RPA) [31], and the detailed expression of σ is given by Eq. (13) (see Appendix for details). The in-plane dielectric constant of graphene is characterized by a dielectric function of $\varepsilon_{x,y} =$ $2.5+i\sigma(\omega)/(\varepsilon 0\omega t)$, and the out-of-plane component is $\varepsilon_z = 2.5$, which is based on the dielectric constant of graphite [32]. We can see that the GSPs wave vector is much larger than the one of the free-space optical beams with the same oscillation frequency. In order to excite GSPs with free-space optical beams, the momentum mismatch has to be satisfied. Based on the conservation of momentum as shown in Fig. 2, we have

$$\mp \operatorname{Re}\left\{k_{\rm spp}\left(\omega_{\rm spp}\right)\right\} = 2k_1\sin\theta_1 - k_2\sin\theta_2 \tag{3}$$

where the upper sign of $k_{spp}(\omega_{spp})$ is corresponding to a solution of $\theta_2 > \theta_1$, and the lower sign is corresponding to $\theta_1 > \theta_2$.

In order to satisfy the momentum conservation condition as specified by Eqs. (1) and (3), the relationship between θ_1 and θ_2 are solved numerically as shown in Fig. 3, where the incident optical beam has the free-space wavelengths of $\lambda_1 = 40 \,\mu\text{m}$ and $\lambda_2 = 25 \,\mu\text{m}$ respectively. From Fig. 3, one can see that within the solutions of the angular regions, the incident angles can be tuned by adjusting the Fermi energy levels, which principally enable to realize the functions of ultrafast electrically controlled switches.



Fig. 2. Dispersion curve of GSPs with the Fermi energy level of $E_{\rm f} = 0.4$ eV (solid red line).

Dashed line represents the light line in free-space, where $k_f = (\pi n)^{1/2}$ is the Fermi wave vector. The carrier mobility used is $\mu = 10000 \text{ cm}^2/(\text{V}\cdot\text{s})$. The GSP dispersion curve is lying beyond the light line, which prohibits the plasmon to be excited by a single incident beam. The vectorial sum of three incident photons, as shown solid line in pink and purple, make it possible to couple light into GSPs in the red line.



Fig. 3. Relationship between the incident angles of θ_1 and θ_2 for exciting GSPs using FWM with different Fermi energy levels of graphene. The incident wavelengths are $\lambda_1 = 40 \ \mu m$ and $\lambda_2 = 25 \ \mu m$.

3. Derivation of nonlinear optical field distribution for exciting graphene plasmon

In this subsection, we shall present the detailed analytical investigation for exciting GSPs using FWM with only *s*-polarized optical beams. The electric field components for the two incident optical beams with the oscillation frequencies of ω_1 and ω_2 are written as:

$$E_{1,y} = E_1 e^{ik_{x1}x} e^{ik_{z1}z} e^{-i\omega_0 t}$$

$$E_{2,y} = E_2 e^{ik_{x2}x} e^{ik_{z2}z} e^{-i\omega_2 t} , \qquad (4)$$

where E_1 and E_2 are the electric field amplitude of the incident waves. k_x and k_z vectors are determined by the angle of incidence θ according to $k_{x1,2} = \omega_{1,2} \sin \theta / c$ and $k_{z1,2} = \omega_{1,2} \cos \theta / c$.

The nonlinear polarization at the FWM frequency ω_{spp} , i.e. $P_i(\vec{r})$, due to the two incident optical beams on graphene itself can be expressed as

$$P_{i}(\vec{r}) = \chi_{(3),iyyy} E_{1,y} E_{1,y}^{*} E_{2,y}^{*}(\vec{r}),$$
(5)

where $\chi_{(3),iyy}$ denotes a component of third-order susceptibility tensor. At the FWM frequency of $2\omega_1-\omega_2$, the beam at the oscillation frequency " ω_1 " contributes two photons, where the other beam at the oscillation frequency " ω_2 " contributes one photon. Similarly, at the FWM frequency of $2\omega_2-\omega_1$, the condition will be vice versa.

The electric field distribution at the FWM frequency can be calculated from the current source based on the Green's function $\vec{G}(\vec{r},\vec{r'})$ as [28]

$$\vec{E}(\vec{r}) = i\omega\mu\mu_0 \int_V \vec{G}(\vec{r},\vec{r'})\vec{j}(\vec{r'})dV', \qquad (6)$$

where the current source is given by (see Eq. (14) in Appendix for details)

$$\vec{j}(\vec{r'}) = -i\omega \vec{P}(\vec{r'}). \tag{7}$$

After inserting Eq. (5) and Eq. (7) into Eq. (6), we obtain

$$\vec{E}(\vec{r'}) = i\omega\mu\mu_0 \iiint_{yyz} \vec{G}(\vec{r},\vec{r'})\vec{j}(\vec{r'})dx'dy'dz'$$

$$= i\omega\mu\mu_0 \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \vec{G}_0(\vec{r},\vec{r'})[\hat{a}_x\chi_{_{(3),yyy}} + \hat{a}_y\chi_{_{(3),yyy}} + \hat{a}_z\chi_{_{(3),yyy}}]E_1^2E_2^* \qquad (8)$$

$$\times e^{i[2k_{x_1}-k_{x_2}]x'}e^{i[2k_{z_1}-k_{z_2}]z'}e^{-i\omega_{yp}t}\delta(z'-z_0)dx'dy'dz',$$

where we use $\delta(z'-z_0)$ here to represent the 2D dimension characteristic of graphene. \hat{a}_x , \hat{a}_y and \hat{a}_z are unit vectors along x, y and z directions, respectively. Substituting the Green's function as shown in Eq. (17) into Eq. (8), we can obtain the analytical expression for the GSPs field:

$$\vec{E}(\vec{r}) = -\frac{\omega\mu\mu_{0}}{2} \begin{bmatrix} M_{xx}(k_{x},k_{y}=0)\chi_{(3),xyyy} + M_{xz}(k_{x},k_{y}=0)\chi_{(3),zyyy} \\ M_{yy}(k_{x},k_{y}=0)\chi_{(3),yyyy} \\ M_{zx}(k_{x},k_{y}=0)\chi_{(3),xyyy} + M_{zz}(k_{x},k_{y}=0)\chi_{(3),zyyy} \end{bmatrix}$$

$$\times e^{i(2k_{x1}-k_{x2})x} e^{ik_{zxyp}(k_{x},k_{y}=0)z} \times E_{1}^{2}E_{2}^{*}e^{-i\omega_{xyp}t},$$
(9)

where M_{xx} , M_{xz} , M_{zx} , M_{zz} are the components of matrix \overline{M} (see Eq. (18) in Appendix for details). The optical fields generated at the FWM frequency have two sets of independent fields:

- a) One is transverse electric (TE) field component consisted of E_y , H_x , and H_z , which is not a surface mode wave.
- b) The other one is the transverse magnetic (TM) field component consisted of E_x , E_z , and H_{y_2} which is corresponding to the GSPs mode.

As shown in literature [22], for graphene surface plasmon field for z>0, we have

$$E_{x} = A e^{ik_{x,spp}x} e^{-ik_{z,spp}z}, E_{y} = 0, E_{z} = B e^{ik_{x,spp}x} e^{-ik_{z,spp}z},$$
(10)

with $k_v = 0$, where A and B are the electric field amplitude.

By comparing Eqs. (9) and (10), we can obtain relation for the M matrix components in order for the FWM process to satisfy the GSPs condition:

$$\frac{M_{xx}(k_x, k_y = 0)\chi_{(3), xyyy} + M_{xz}(k_x, k_y = 0)\chi_{(3), zyyy}}{M_{xx}(k_x, k_y = 0)\chi_{(3), zyyy} + M_{zz}(k_x, k_y = 0)\chi_{(3), zyyy}} = \frac{A}{B} = D.$$
(11)

After submitting the M matrix components in to Eq. (11), we obtain the condition for GSPs excitation by *s*-polarized beams as:

$$[k_{z1,\text{spp}}^{2} + Dk_{x}k_{z1,\text{spp}}]\chi_{(3),xyyy} = [Dk_{x}^{2} + k_{x}k_{z1,\text{spp}}]\chi_{(3),zyyy},$$
(12)

where $k_x = k_{spp}(\omega_{spp})$. We can get the numerical relationship between $\chi_{(3),xyyy}$ and $\chi_{(3),xyyy}$, as plotted in Fig. 4 with the monolayer graphene of having different Fermi energy levels. By introducing an elastic or plastic deformation to graphene, its symmetry class can be changed and thus the values of the third-order susceptibility might be able to be tuned for experimental realization of the required susceptibility values [33].



Fig. 4. The relationship between the two components of the $\chi_{(3),yyy}$ and $\chi_{(3),yyy}$ with different monolayer graphene Fermi energy levels of $E_t = 0.2$ eV, 0.4 eV, 0.6 eV and 0.8 eV.

Figures 5(a) and 5(b) show the electric field wavefront distributions of E_y with for the pump lasers with the incident wavelengths of 40 µm and 25 µm, and under the incidence angles of 50° and 25.2° respectively, where the ratio of $\chi_{(3),xyyy}$ over $\chi_{(3),xyyy}$ is 0.014 as calculated in Fig. 4. The location of the monolayer graphene is labeled by the dash lines. Figure 5(c) shows the calculated electric field distribution of E_z for the GSPs, as excited by the FWM process. One can see that the GSPs has a wavelength of 47.8 µm, which is less than half of the wavelength of light in free space. In addition, the electric field is tightly confined on the graphene surface.



Fig. 5. (a)-(b) Electric field wavefront distribution of E_y for the two pump lasers with incident wavelength of 40 µm and 25 µm, and incident angles of 50° and 25.2°, respectively. (c) Electric field distribution of E_z for the excited GSPs on a monolayer graphene sheet with a Fermi energy level of $E_f = 0.4 \text{ eV}$. The ratio of $\chi_{(3),xyyy}$ / $\chi_{(3),zyyy}$ is 0.014.

We have also investigated the third-order susceptibility tensors relation for multilayer graphene with N>1. Here, the optical conductivity for N-layer graphene is $N\sigma$ [34, 35]. In Fig. 6, the relationship between the two components of the $\chi_{(3),xyyy}$ and $\chi_{(3),xyyy}$ for monolayer (N = 1), bilayer (N = 2), and four-layer (N = 4) graphene with a Fermi energy level of $E_f = 0.4 \text{ eV}$ is shown. We can see that the proposed scheme is also working for the multi-layer graphene as well.



Fig. 6. Relationship between the two components of $\chi_{(3),xyyy}$ and $\chi_{(3),xyyy}$ for monolayer (N=1), bilayer (N=2), and four-layer graphene (N=4) with a Fermi energy level of $E_f = 0.4$ eV.

Lastly, we would like to mention that GSPs could also be excited by FWM at *p*-polarized incidence condition, where the required conditions could be derived similarly by using the theoretical framework as formulated in Eqs. (4)-(9). The detailed investigation on the *p*-polarized incidence condition might be beyond the scope of the current manuscript and will

be reported elsewhere. In addition, we also would like to mention a bit on the experimental feasibility, where the required laser power for exciting the four-wave mixing process of graphene optoelectronics is in the level of several hundred μW [36].

4. Conclusions

In conclusion, we have proposed a scheme capable of exciting plasmons on a *flat* suspended graphene through the FWM process. Based on the analytical derivations, we have shown it is possible to excite surface plasmons on graphene sheet by only *s-polarized* optical beams with certain incident angles over a broadband frequency and the graphene surface plasmon are tunable by varying the electrical gating, or graphene doping. The proposed concept contributes a new possibility for the study of graphene surface plasmons, and this scheme can also be used for pure optical modulation and switching applications in the infrared regime.

Appendix

The optical conductivity of graphene can be calculated with random-phase approximation (RPA) [31, 37]:

$$\sigma(\omega_{\rm spp}) = \frac{2ie^2k_{\rm B}T}{\pi\hbar^2(\omega_{\rm spp} + i\tau^{-1})}\ln\left[2\cosh\left(\frac{E_{\rm f}}{2k_{\rm B}T}\right)\right] + \frac{e^2}{4\hbar}\left\{\frac{1}{2} + \frac{1}{\pi}\arctan\left(\frac{\hbar\omega_{\rm spp} - 2E_{\rm f}}{2k_{\rm B}T}\right) - \frac{i}{2\pi}\ln\left[\frac{(\hbar\omega_{\rm spp} + 2E_{\rm f})^2}{(\hbar\omega_{\rm spp} - 2E_{\rm f})^2 + (2k_{\rm B}T)^2}\right]\right\},$$
(13)

where k_B is the Boltzmann constant, *T* is the temperature, τ is the carrier relaxation time, $E_f = \hbar V_f (\pi n)^{1/2}$ is the Fermi energy level, *n* is the charge carrier concentration, $V_f = 10^6$ m/s is the Fermi velocity, and μ is the carrier mobility in graphene. The carrier mobility used is $\mu = 10000 \text{ cm}^2/(\text{V}\cdot\text{s})$ in all calculations.

The relation between current source and the polarization components [28]

$$\vec{j}(\vec{r'}) = -i\omega\varepsilon_0[\varepsilon(\vec{r'}) - \varepsilon_{ref}(\vec{r'})]\vec{E}(\vec{r'})$$

$$= -i\omega\varepsilon_0\Delta\varepsilon(\vec{r'})\vec{E}(\vec{r'}) \qquad (14)$$

$$= -i\omega\vec{P}(\vec{r'}).$$

The detailed derivation for the electric field term in Eq. (5) is shown below:

$$E_{1,y}E_{1,y}E_{2,y}^{*} = E_{1}^{2}e^{i2k_{x1}x}e^{i2k_{z1}z}e^{-i2\omega_{l}t} \times E_{2}^{*}e^{-ik_{x2}x}e^{-ik_{z2}z}e^{i\omega_{2}t}$$

$$= E_{1}^{2}E_{2}^{*}e^{i[2k_{x1}-k_{x2}]x}e^{i[2k_{z1}-k_{z2}]z}e^{-i(2\omega_{l}-\omega_{2})t}$$

$$= E_{1}^{2}E_{2}^{*}e^{i[2k_{x1}-k_{x2}]x}e^{i[2k_{z1}-k_{z2}]z}e^{-i\omega_{spp}t}.$$
(15)

By substituting Eq. (15) into Eq. (5), we obtain,

$$P_{i}(\vec{r}) = \chi_{{}_{(3),jyy}} E_{1}^{2} E_{2}^{*} e^{i[2k_{x1}-k_{x2}]x} e^{i[2k_{z1}-k_{z2}]z} e^{-i\omega_{spp}t} , \qquad (16)$$

$$P_{x}(\vec{r}') = \chi_{(3),xyy} E_{1}^{2} E_{2}^{*} e^{i(2k_{x1} - k_{x2})x'} e^{i(2k_{z1} - k_{z2})z'} e^{-i\omega_{spp}t}, \qquad (16.a)$$

$$P_{y}(\vec{r'}) = \chi_{(3)_{yyyy}} E_{1}^{2} E_{2}^{*} e^{i[2k_{x1}-k_{x2}]x'} e^{i[2k_{z1}-k_{z2}]z'} e^{-i\omega_{spp}t}, \qquad (16.b)$$

$$P_{z}(\vec{r'}) = \chi_{_{(3),zyyy}} E_{1}^{2} E_{2}^{*} e^{i[2k_{x1}-k_{x2}]x'} e^{i[2k_{z1}-k_{z2}]z'} e^{-i\omega_{yp}t'}.$$
 (16.c)

The Green's function is expressed as [28]

$$\vec{G_0}(\vec{r},\vec{r'}) = \frac{i}{8\pi^2} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \vec{M}(k_x,k_y) e^{ik_x(x-x')} e^{ik_y(y-y')} e^{-ik_{z1}^{\rm opp}(z-z')} dk_x dk_y,$$
(17)

and the M matrix is given as

$$\begin{aligned} \overrightarrow{M}(k_x, k_y = 0) &= \frac{1}{k_{1,spp}^2 k_{z1,spp}(k_x, k_y = 0)} \begin{bmatrix} k_{1,spp}^2 - k_x^2 & 0 & \mp k_x k_{z1,spp} \\ 0 & k_{1,spp}^2 & 0 \\ \mp k_x k_{z1,spp} & 0 & k_x^2 \end{bmatrix} \\ &= \begin{bmatrix} M_{xx} & 0 & M_{xz} \\ 0 & M_{yy} & 0 \\ M_{zx} & 0 & M_{zz} \end{bmatrix}. \end{aligned}$$
(18)

It can been seen that some terms in matrix \overline{M} have two different signs. This sign difference originates from the absolute values $|z - z_0|$. The supper sign corresponds to $z > z_0$ and the lower sign to $z < z_0$. As graphene is an anisotropic materials, the relation of the wavevector in both direction is given by:

$$k_x^2 \varepsilon_x + k_z^2 \varepsilon_z = \left(\frac{\omega}{c}\right)^2 \varepsilon_x \varepsilon_z.$$
(19)

By substituting Eqs. (17)-(18) in to Eq. (8), we have

$$\begin{split} \vec{E}(\vec{r}) &= i\omega\mu\mu_{0} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \frac{i}{8\pi^{2}} \int_{-\infty}^{+\infty} \overline{M}(k_{x},k_{y})e^{ik_{x}(x-x)}e^{ik_{y}(y-y')}e^{-ik_{z1}^{spp}z} \\ &\times [\hat{a}_{x}\chi_{(3),xyyy} + \hat{a}_{y}\chi_{(3),yyyy} + \hat{a}_{z}\chi_{(3),zyyy}]E_{1}^{2}E_{2}^{*}e^{i[2k_{x1}-k_{x2}]x'}e^{-i\omega_{app}t}dk_{x}dk_{y}dx'dy' \\ &= i\omega\mu\mu_{0} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \frac{i}{8\pi^{2}} \overline{M}(k_{x},k_{y})e^{ik_{x}x}e^{-ik_{x}x'}e^{ik_{y}y}e^{ik_{z}^{spp}z} \\ &\times [\hat{a}_{x}\chi_{(3),xyyy} + \hat{a}_{y}\chi_{(3),yyyy} + \hat{a}_{z}\chi_{(3),zyyy}]E_{1}^{2}E_{2}^{*}e^{i[2k_{x1}-k_{x2}]x'}e^{-i\omega_{app}t}dk_{x}dk_{y}dx'dy' \\ &= -\frac{\omega\mu\mu_{0}}{4\pi} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \overline{M}(k_{x},k_{y})e^{ik_{x}x}e^{-ik_{x}x'}e^{ik_{z}^{spp}(k_{x},k_{y}=0)z} \\ &\times [\hat{a}_{x}\chi_{(3),xyyy} + \hat{a}_{y}\chi_{(3),yyyy} + \hat{a}_{z}\chi_{(3),zyyy}]E_{1}^{2}E_{2}^{*}e^{i[2k_{x1}-k_{x2}]x'}e^{-i\omega_{app}t}dk_{x}dx', \end{split}$$

where

$$\int_{-\infty}^{+\infty} e^{i[2k_{x1}-k_{x2}]x'} e^{-ik_{x}x'} dx' = 2\pi \delta[2k_{x1}-k_{x2}-k_{x}].$$
(21)

Then, we can obtain:

$$\vec{E}(\vec{r}) = -\frac{\omega\mu\mu_0}{4\pi} \int_{-\infty}^{+\infty} \vec{M}(k_x, k_y = 0) e^{ik_x x} e^{ik_z^{\text{app}}(k_x, k_y = 0)z} [\hat{a}_x \chi_{(3), xyyy} + \hat{a}_y \chi_{(3), yyyy} + \hat{a}_z \chi_{(3), zyyy}] \times E_1^2 E_2^* 2\pi \delta [2k_{x1} - k_{x2} - k_x] e^{-i\omega_{\text{app}}t} dk_x = -\frac{\omega\mu\mu}{2} \vec{M}(k_x = 2k_{x1} - k_{x2}, k_y = 0) e^{i(2k_{x1} - k_{x2})x} e^{ik_z^{\text{app}}(k_x = 2k_{x1} - k_{x2}, k_y = 0)z} \times [\hat{a}_x \chi_{(3), xyyy} + \hat{a}_y \chi_{(3), yyyy} + \hat{a}_z \chi_{(3), zyyy}] \times E_1^2 E_2^* e^{-i\omega_{\text{app}}t}.$$
(22)

By submitting Eq. (18) in to Eq. (22), we have the analytic expressions for the optical field at the FWM frequency:

$$\vec{E}(\vec{r}) = -\frac{\omega\mu\mu_{0}}{2} \begin{bmatrix} M_{xx}(k_{x},k_{y}=0) & 0 & M_{xz}(k_{x},k_{y}=0) \\ 0 & M_{yy}(k_{x},k_{y}=0) & 0 \\ M_{zx}(k_{x},k_{y}=0) & 0 & M_{zz}(k_{x},k_{y}=0) \end{bmatrix}$$

$$\times e^{i(2k_{x1}-k_{x2})} e^{ik_{zxpp1}(k_{x}=2k_{x1}-k_{x2},k_{y}=0)z} \times \begin{bmatrix} \chi_{(3),xyyy} \\ \chi_{(3),zyyy} \\ \chi_{(3),zyyy} \end{bmatrix} \times E_{1}^{2}E_{2}^{*}e^{-i\omega_{xpy}t}$$

$$\vec{E}(\vec{r}) = -\frac{\omega\mu\mu_{0}}{2} \begin{bmatrix} M_{xx}(k_{x},k_{y}=0)\chi_{(3),xyyy} + M_{xz}(k_{x},k_{y}=0)\chi_{(3),zyyy} \\ M_{yy}(k_{x},k_{y}=0)\chi_{(3),yyyy} \\ M_{zx}(k_{x},k_{y}=0)\chi_{(3),zyyy} + M_{zz}(k_{x},k_{y}=0)\chi_{(3),zyyy} \end{bmatrix}$$

$$\times e^{i(2k_{x1}-k_{x2})}e^{ik_{z,xpp}(k_{x},k_{y}=0)z} \times E_{1}^{2}E_{2}^{*}e^{-i\omega_{xpp}t}.$$
(23)

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