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Optical second harmonic generation from plasmonic nanoshells using the nonlocal hydrodynamic model

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A B S T R A C T

In this paper, we investigate the linear and nonlinear optical response of spherical plasmonic nanoshells within the nonlocal hydrodynamical model for conduction electrons. The optical absorption and surface second-harmonic generation (SHG) associated with metallic core-shell nanoparticles is studied on the basis of the hydrodynamic Drude model. The influence of nonlocality on the optical SHG is investigated. We show that nonlocal effects can be applied to boost SHG from plasmonic nanoshells. It is found that the surface SHG radiation from the surface of nanoshells can be achieved by symmetry-breaking and is sensitive to nonlocality of the electron response. It is also shown that nonlocal effects lead to enhancement and shift of the resonant wavelengths of the optical absorption and SHG in metal nanoshells. Keywords: Optical absorption, Second harmonic generation, plasmonic nanoshell, nonlocal effects.

1. Introduction

Understanding linear and nonlinear optical properties of nanoplasmonic structures and metallic systems is essential to design of plasmonic devices at the nanoscale. Optical properties of plasmonic materials are important for many practical applications which the plasmon resonances of material match with the spectral regions of interest [1]. For this purpose, metallic nanostructures are ideal candidates for linear and nonlinear optics due to the large local electromagnetic fields associated with the excitations of nanoparticle where are known as plasmons [2]. On the other hand, nanometer-sized metallic structures which support plasmon resonances at optical and near-optical frequencies can be engineered to have optimum desired optical response in the field of nanoplasmonics. The plasmonic resonance peaks strongly depend on the material, geometry, size and host medium and can be highly tunable and manipulated [3,4]. Additionally, plasmonic nanoshells where provide good possibility to tune the surface plasmon resonance (SPR), are much more suited for many applications than single nanoparticles.

In particular, when the dimensions of nanoparticle is small, the coupling between plasmons in metal nanoparticles cannot be fully described using a local model and nonlocality effects play an important role [2]. Nonlocal response is a semiclassical effect which emerges in nanoplasmonics at few-nanometer length scales [5]. In the nonlocal treatment, the dielectric function is frequency- and wavevector-dependent [6], and this nonlocal dielectric function couples the surface excitations to bulk-plasmon modes [7]. Nonlocality that arises from the electron-electron interactions and results in the spatial dispersion of the dielectric response in material play an important role in nano-optics and plasmonics [8]. The hydrodynamic model allows to consider nonlocal effects to study the optical response such as the optical absorption. For example, the nonlocal polarizability for a single hydrodynamic sphere and nonlocal optical response in metallic nanostructures has been investigated by using the nonlocal hydrodynamic model which is associated with additional dynamics of the electron gas in metals [9–11]. Furthermore, the nonlocal hydrodynamic electron model can be applied to simulate nonlinear optical interactions such as second harmonics generation (SHG) [12–14], and plasmonic nanoparicles show unique resonances due to nonlocal response in the hydrodynamic Drude model [9].

Since interaction of light with plasmonic nanostructures exhibits novel optical phenomena, in this study, our aim is to investigate optical response of metal nanoshells with spherical structure by taking into account nonlocal effects due to the strong electron confinement. We theoretically investigate the nonlocality effect on the linear and nonlinear optical response of metal nanoshells with core-shell geometry owing to their unrivalled optical response, and because nonlinear optical materials such as plasmonic nanoparticles are the vital components of future optoelectronic technologies. On the other hand, we study the impact of the nonlocal dielectric response on the optical absorption and SHG, because the nonlocal response is important for small particles at the nanometer scale.

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2. Model and theory

The nonlocal polarizability of a small metallic sphere within the theory of the nonlocal hydrodynamic model was first discussed in Ref. [10]. In order to obtain an expression for nonlocal ploarizability of a nanoshell, suppose a plasmonic core-shell nanostructure placed in a background medium of dielectric constant ε_h and illuminated by an electromagnetic wave as shown in Fig. 1. By taking into account the nonlocal effects for a hydrodynamic core-shell nanoparticle and without going into the full details, the general solutions of the electric scalar potential and free-electron density in different regions, the core, the shell and environment can be written as:

$$\begin{cases} n_c = \sum_{\ell m} (A_{\ell m} j_\ell(k_{NL} r)) Y_{\ell m}(\theta,\varphi), & n_s = 0 \\ \phi_c(r,\theta,\varphi) = \sum_{\ell m} \left(B_{\ell m} r - A_{\ell m} \frac{e}{\varepsilon_0 \varepsilon_\infty k_{NL}^2} j_\ell(k_{NL} r) \right) Y_{\ell m}(\theta,\varphi), & \\ \phi_s(r,\theta,\varphi) = \sum_{\ell m} \left(E_{\ell m} r + F_{\ell m} r^{-2} \right) Y_{\ell m}(\theta,\varphi), & \\ \phi_h(r,\theta,\varphi) = \sum_{\ell m} \left(C_{\ell m} r + D_{\ell m} r^{-2} \right) Y_{\ell m}(\theta,\varphi), & \\ \psi_c = \frac{1}{i\omega - \gamma} \left(\varepsilon_0 \omega_p^2 \phi_c - e\beta^2 n_c \right), & \end{cases} \quad (1)$$

where $n_{c(s)} (= n_{core(shell)})$, β, k_{NL}, ϕ and ψ are the free-electron density of core (shell), the nonlocal parameter obtained from Thomas-Fermi theory, the nonlocal longitudinal wave vector, the electric and current scalar potentials, respectively. Also, $j_\ell(x)$ and $Y_{\ell m}(\theta,\varphi)$ are the spherical Bessel function of the first kind of order ℓ and the spherical harmonics, respectively. Note that for a free electron gas, at high frequencies ($\omega \gg \gamma$), $\beta^2 = \frac{3}{5} v_f^2$ represents the dynamic pressure [15], where v_F is the Fermi velocity.

Here, the unknown coefficients A_{lm}, B_{lm} , C_{lm}, D_{lm}, E_{lm} and F_{lm} are found by applying the appropriate boundary conditions at the interfaces,

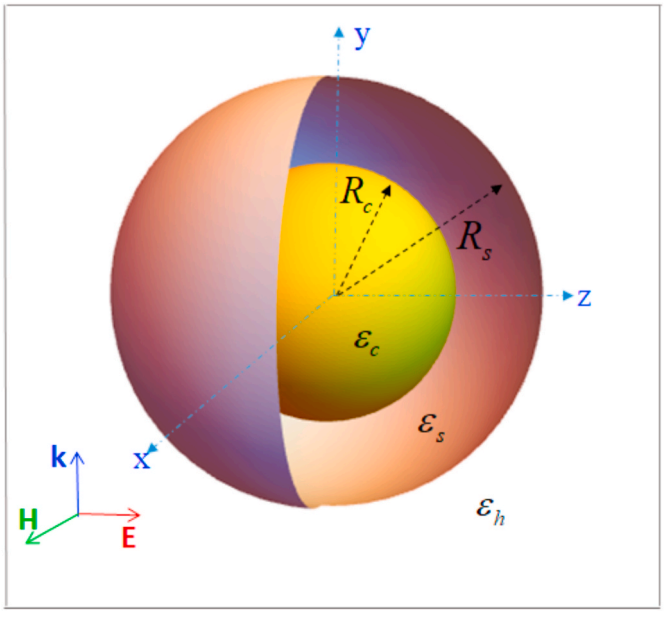

Fig. 1. Schematic view of the core-shell metal nanoparticles with spherical structure illuminated by a plane wave. The incident electric field is parallel to the z-axis and the particle is placed in a homogeneous host medium with permittivity ε_h. Also, R_c and R_s are the core radius and the shell radius, while ε_c and ε_s denote the dielectric functions of the core and shell, respectively.

and a single additional boundary condition which states that the normal component of the free-electron current density must vanish [9]. Since, the electric field directed in the $\hat{e}_z$ direction, $\mathbf{E} = E_0 \hat{e}_z$. Then $\phi_h = -E_0 r\cos\theta$ as $r \to \infty$ which excludes all orders of (ℓ,m) in Eq. (1) except (ℓ, m) = (1,0), and this demands that $C_1 = -E_0$. However, the remaining coefficients, A_1, B_1 , D_1, E_1 and F_1 are determined by replacing the equations in the boundary conditions, and applying additional boundary condition [10].

2.1. Optical absorption of nanoshells: effect of nonlocal response

Since the dipole moment depends on the polarizability and the incident field, the relation between the induced dipole moment and the electric field is defined as

$$\vec{p} = \varepsilon_0 \varepsilon_h \alpha \vec{E} \quad (2)$$

However, after some algebric calculations the exact expression of the nonlocal nanoparticle polarizability can be written as

$$\alpha_{NL} = \frac{4\pi D_1}{\varepsilon_h E_0} \quad (3)$$

In the local treatment which nonlocal effects are neglected, the dielectric function of a metal nanoparticle is frequency-dependent and determined by the Drude formula, $\varepsilon(\omega) = \varepsilon_\infty - \omega_p^2/(\omega^2 + i\gamma\omega)$, in which in the nonlocal theory the dielectric function is a function of frequency and the wavevector **k** [6,11]. However, the hydrodynamic Drude model, which is an approach to take into account the nonlocal effects of the conduction electrons in metal nanoparticles, is described by the nonlocal response function given by Refs. [16,17]:

$$\varepsilon(k,\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\gamma\omega - \beta^2 k^2} \quad (4)$$

where ω_p, γ, ε_∞, β and k are the plasma frequency of metal, the collision frequency of free electrons or damping rate, the high-frequency part of the dielectric function, the spatial dispersion parameter or strength of nonlocality and the wavevector, respectively. Note that quantum mechanical effects should be considered when the diameter is reduced below 10 nm (diameters smaller than 10 nm) [18].

In our calculations, metallic nanoshells composed of noble metals such as gold (Au) and silver (Ag), because they support localized surface plasmon resonances. However, the appropriate parameters for Ag and Au can be found in Refs. [19,20].

Fig. 2 shows the calculated optical absorption spectra of nanoscale core-shell particles for Au core/Ag shell and Ag core/Au shell nanoparticles with local and nonlocal contributions for comparison. This figure shows the nonlocal polarizability of a plasmonic nanoshell placed in a embedding medium with $\varepsilon_h = 2.5$. This figure compares the results for the local and nonlocal optical effects of a plasmonic nanoshell and the difference between local and nonlocal responses is clearly observed. The optical absorption spectrum is characterized by two resonance peaks which corresponds to dipolar plasmon the SPR frequency. As shown in Fig. 2a and 2b, a significant frequency shift is seen and this results demonstrate that compared with the local response, nonlocal effects produce a strong shift in the plasmon wavelength [21].

Let us investigate the influence of the shell thickness and the core size of the metallic nanoshell on the behavior of the optical absorption when $n_{core} \neq 0$. As can be observed from Fig. 3, the absorption highly depends on the radius of the core and shell of the particle. When the shell radius is 7 nm and the core radius increases, the first absorption peak is shifted toward longer wavelengths, whereas the second peak is shifted toward short wavelengths as seen in Fig. 3a. But this behavior is different for the second case where the shell radius changes as seen in Fig. 3b. A strong shift for both resonance wavelengths is observed with decreasing the shell thickness due to plasmon hybridization [21]. The optical absorption increases as the particle size increases. However, besides the shell

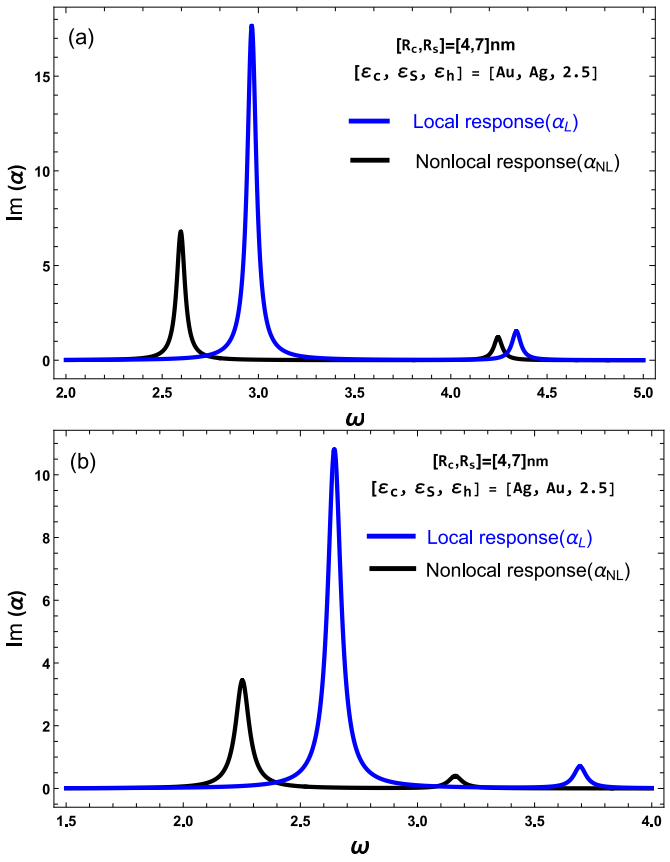

Fig. 2. Normalized imaginary part of the local and nonlocal polarizability as a function of photon energy for Au core/Ag shell and Ag core/Au shell nanoparticles of R_c = 4nm and R_s = 7nm.

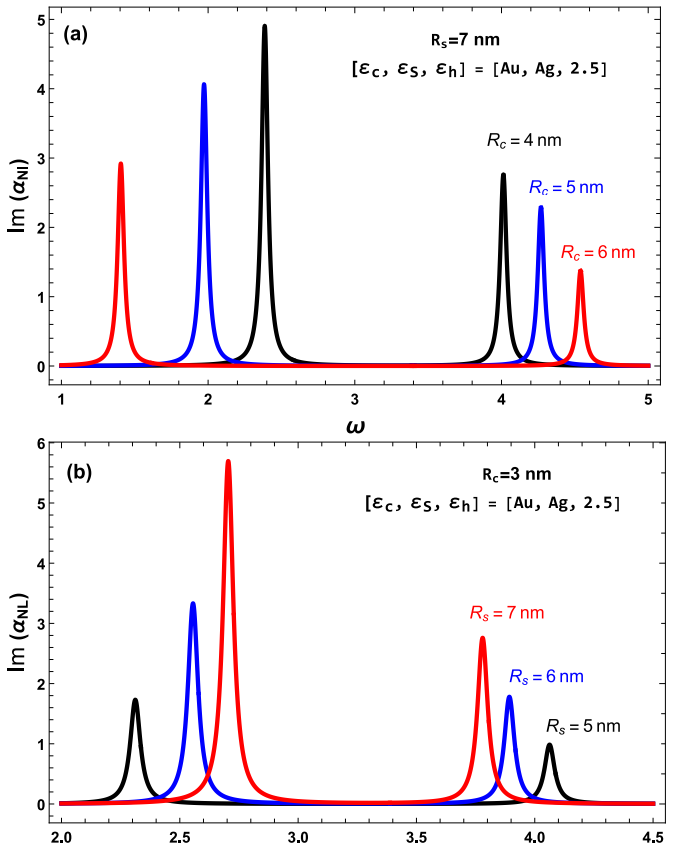

Fig. 3. Normalized imaginary part of nonlocal polarizability as a function of photon energy for Au core/Ag shell and Ag core/Au shell nanoparticles for different particle sizes.

thickness, the core radius strongly can affect the position and amplitude of the absorption peaks because the plasmon resonance of metal nanoshells is strongly sensitive to the particle size. The spectral range becomes smaller as the particle size increases, in which the spectral range becomes wider with increasing the core radius. This means that the spectral position of the absorption resonance peaks can be tuned by varying the radius of core or shell, and therefore the absorption wavelengths of can be significantly engineered by changing and controlling the size of nanoshell.

2.2. *Nonlinear optical response of nanoshells: effect of nonlocal response on SHG*

In addition to optical properties, nonlinear optical properties play an important role in photonics, ultrahigh-resolution spectroscopy, frequency conversion systems, bioimaging and sensing [14,22]. Recently, nonlinear optics at plasmonic nanomaterials and nanoscale systems have attracted attention because of its potential wide applications [13,23,24]. In fact, resonant properties of plasmonic nanostructures give them decisive advantage for the generation of high intensity nonlinear signals at the nanoscale [25]. The interaction between plasmonic nanoparticles with light leads to a strong electric fields in the adjacent nanomaterial, and nonlinear response is directly related to the surface plasmon resonances of metallic nanoparticles. When a plasmonic nanoparticle illuminated by a monochromatic plane-wave light field oscillating at the frequency ω, new light-wave fields such as the second-harmonic wave at the frequency 2ω, are excitated due to field interaction with medium [26]. Second harmonic generation (SHG), which is a second-order nonlinear process arises from volume and surface contributions, is the lowest order frequency mixing nonlinear optical process which have been observed in metallic nanostructures and two photons combine to create a photon at double frequency [27–31].

SHG from surface is a non-destructive nonlinear optical technique and has shown great potential for applications in biosensors and surface spectroscopy [32,33]. Since SHG is extremely sensitive to surface roughness conditions, it can occur at the surface or at the interface between two different centrosymmetric media where the inversion symmetry is broken and therefore conditions for frequency doubling is achieved. Additionally, the nonlinear optical response of the electrons in metal can be described by hydrodynamic model which gives a fairly accurate description of linear and nonlinear processes occurring at the surface of metallic structures [34]. Since free-electron plasma in metals and plasmonic nanoparticles acts as the source of the optical nonlinearity, therefore the nonlinear surface contribution is strongly related to the response of the electrons [15,34].

In plasmonic nanostructures, when the wavelength of the incident light matches the resonant wavelength of a localized surface plasmon resonance an enhancement of the intensity of the SHG radiation is observed [30]. However, in the case of metallic nanostructures which provide strong field enhancement near the surfaces and interfaces, the intensity of the SHG radiation is defined as [35,36].

$$I(2\omega) \propto \omega^2 \eta^{SHG}(\omega) \tag{5}$$

where $\eta^{SHG}(\omega)$ denotes the parameter characterizing the enhancement of local field on the surface of metal nanoshell and has the form

$$\eta^{SHG}(\omega) = \left| L^2(\omega) L(2\omega) \right|^2 \tag{6}$$

where, $L(\omega)$ and $L(2\omega)$ are the local field factors at the fundamental and

SHG frequencies, respectively. Also, $L(\omega)$ denotes the enhancement of incident field at the fundamental frequency while $L(2\omega)$ denotes the enhancement of second-harmonic response [37].

Fig. 4 shows the normalized SHG intensity spectra for Au core/Ag shell and Ag core/Au shell nanoparticles with the contribution of local and nonlocal effects for comparison. In nanoscale systems the SHG radiation is sensitive to nonlocality of the electron response [13]. This figure clearly compares the results for the surface SHG radiation in plasmonic nanoshells by taking into account the local and nonlocal effects. The SHG is resonantly enhanced by SPRs in metallic nanoparticles due to the strong local field enhancement around the metal nanoparticles, while the spectral position of SPR depends on the particles size [38]. However, in addition to the local effects, SHG can be strongly affected by the nonlocal effects as can be observed from Fig. 4. It is worth noting that optical nonlinearities at nanoscale can be significantly affected by the nonlocal effects, while these effects usually are small in the linear optical response [25]. We also observe two plasmonic resonant wavelengths red-shifted when the core is silver and the shell is gold. Also, for Au core/Ag shell nanoparticle, the spectral window is broader than the spectral range of Ag core/Au shell nanoparticle. Consequently, strength and spectral width of the second harmonic resonances are influenced by the composition of nanoparticle.

The sensitivity of SHG signal on the nanoshell size by taking into account nonlocal effects for Au core/Ag shell and Ag core/Au shell particles is calculated and shown in Fig. 5. As obvious from this figure, the SHG signal intensity increases with increasing particle size which is in good agreement with experimental results [39–41]. Since the plasmon wavelength depends on the particle size, the plasmon resonances become stronger as the size of nanoparrticle increases, therefore there is

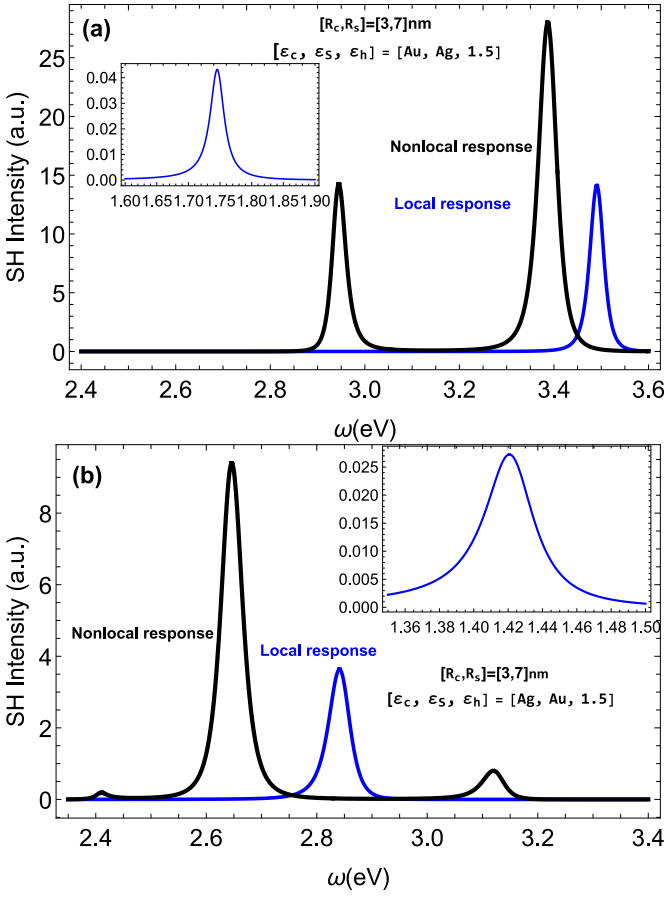

Fig. 4. Normalized SH intensity from the surface of Au core/Ag shell and Ag core/Au shell nanoparticles as a function of photon energy with local and nonlocal theories for comparison.

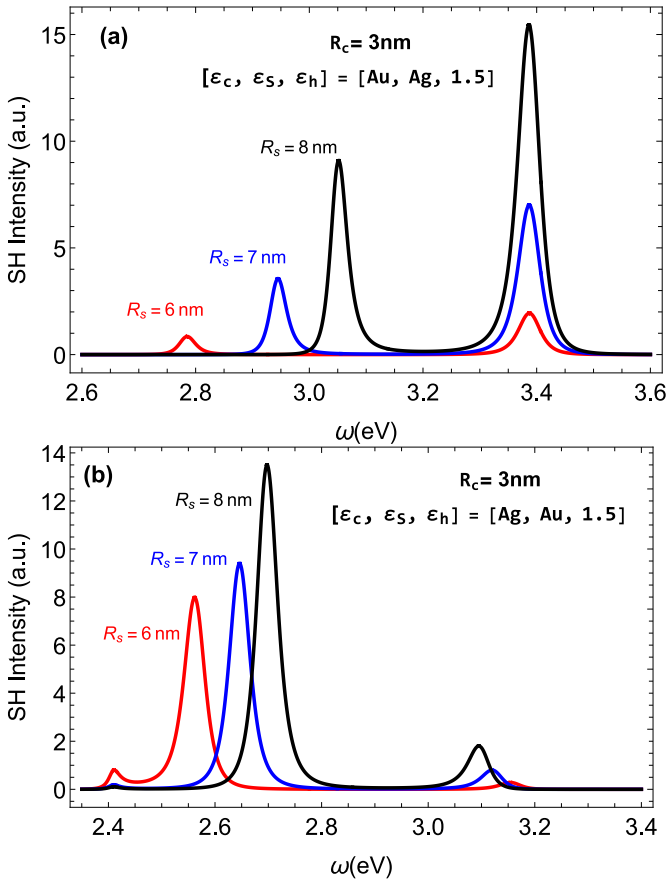

Fig. 5. Normalized SH intensity from the surface of Au core/Ag shell and Ag core/Au shell nanoparticles as a function of photon energy for different particle sizes.

a enhancement of the second harmonic signal. The first resonance peak at low frequency blue-shifts as the shell thickness increases, while the position of the second resonance peak at high energy is fixed. Both intensity and wavelength of the SHG are sensitive to the shell thickness [37]. Further, a large enhancement of SHG at surface plasmon resonant frequencies and the position of resonant frequencies can be obtained by choosing proper of the particle size as evident of this figure. However, the SHG regime can be controlled and adjusted at certain wavelengths by varying the shell thickness [42], where provides an extremely sensitive tool to biological sensing and study of the adsorption of different molecules and molecular interactions at interfaces and surfaces [33,39].

3. Conclusion

In summary, we have investigated the influence of nonlocality on the optical absorption and SHG in plasmonic nanoshells in the framework of hydrodynamic model. A comparison between local and nonlocal response and their impact on the optical absorption and SHG has been done. In other words, we have shown the nonlocal effects play an important role in determining the magnitude and the resonant frequencies of both SHG and optical absorption. We have also demonstrated the optical absorption and the second harmonic resonant wavelengths can be adjusted in a wide range by a hydrodynamic core-shell nanoparticle. In addition to optical absorption, we have demonstrated the SHG resonances of metallic nanoparticles can be tuned by varying the core size and the thickness of the shell. The SHG intensity increases with the particle size and the spectral range changes which may help to design and improve nonlinear plasmonic sensors such as sensing based on SHG.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] U. Guler, V.M. Shalaev, A. Boltasseva, Mater. Today 18 (2015) 227.
[2] M. Pelton, G. Bryant, Introduction to Metal-Nanoparticle Plasmonics, John Wiley &Sons, Hoboken, New Jersey, 2013.
[3] S. Kawata, V.M. Shalaev, Nanophotonics with Surface Plasmons, Elsevier, Amsterdam, 2007.
[4] S.A. Maier, Plasmonics: Fundamentals and Applications, Springer, New York, 2007.
[5] T. Christensen, W. Yan, S. Raza, A.-P. Jauho, N. Asger Mortensen, M. Wubs, ACS Nano 8 (2014) 1745.
[6] S.G. Kosionis, A.F. Terzis, V. Yannopapas, E. Paspalakis, J. Phys. Chem. C 116 (2012) 23663.
[7] R. Rojas, F. Carloadn, R. Fuchs, Phys. Rev. B 37 (1988) 6799.
[8] Y. Huang, L. Gao, Prog. In Electromagnetics Research 133 (2013) 591.
[9] S. Raza, G. Toscano, A.-P. Jauho, M. Wubs, N.A. Mortensen, Phys. Rev. B 84 (2011), 121412(R).
[10] S. Raza, W. Yan, N. Stenger, M. Wubs, N. Asger Mortensen, Optic Express 21 (2013) 27344.
[11] S. Raza, S.I. Bozhevolnyi, M. Wubs, N.A. Mortensen, J. Phys. Condens. Matter 27 (2015) 183204.
[12] M. Corvi, L. Schaich, Phys. Rev. B 33 (1986) 3688.
[13] P. Ginzburg, A.V. Krasavin, G.A. Wurtz, A.V. Zayats, ACS Photonics 2 (2015) 8.
[14] A. Hille, et al., J. Phys. Chem. C 120 (2016) 1163.
[15] A.V. Krasavin, P. Ginzburg, A.V. Zayats, Laser Photon. Rev. 12 (2018) 1700082.
[16] S. Raza, T. Christensen, M. Wubs, S.I. Bozhevolnyi, N.A. Mortensen, Phys. Rev. B 88 (2013) 115401.
[17] J.R. Maack, N.A. Mortensen, M. Wubs, Europhys. Lett. 119 (2017) 17003.
[18] J.A. Scholl, Ai L. Koh, J.A. Dionne, Nature 483 (2012) 421.
[19] P.B. Johnson, R.W. Christy, Phys. Rev. B 6 (1972) 4370.
[20] P.R. West, S. Ishii, G.V. Naik, N.K. Emani, V.M. Shalaev, A. Boltasseva, Laser Photon. Rev. 4 (2010) 795.
[21] C. David, F. Javier GarcÃ-a de Abajo, J. Phys. Chem. C 115 (2011) 19470.
[22] N.M. Jassim, Advances in Research 7 (2016) 1–17.
[23] N.C. Panoiu, W.E.I. Sha, D.Y. Lei, G.-C. Li, J. Optic. 20 (2018), 083001.
[24] L. Bonacina, P.-F. Brevet, M. Finazzi, M. Celebrano, J. Appl. Phys. 127 (2020) 230901.
[25] A.V. Krasavin, P. Ginzburg, G.A. Wurtz, A.V. Zayats, Nat. Commun. 7 (2016) 11497.
[26] G. Wang, Q. Guo, Eur. Phys. J. B 63 (2008) 219.
[27] G. Bachelier, J. Butet, I. Russier-Antoine, C. Jonin, E. Benichou, P.-F. Brevet, Phys. Rev. B 82 (2010) 235403.
[28] P. Ginzburg, A. Krasavin, Y. Sonnefraud, A. Murphy, R.J. Pollard, S.A. Maier, A. V. Zayats, Phys. Rev. B 86 (2012), 085422.
[29] J. Butet, I. Russier-Antoine, C. Jonin, N. Lascoux, E. Benichou, P.-F. Brevet, J. Phys. Chem. C 117 (2013) 1172.
[30] J. Butet, P.-F. Brevet, O.J.F. Martin, ACS Nano 9 (2015) 10545.
[31] B.C. Yildiz, M.E. Tasgin, M.K. Abak, S. Coskun, H.E. h Unalan, A. Bek, J. Optic. 17 (2015) 125005.
[32] S.M. Anderson, B.S. Mendoza, Frontiers in Materials 4 (2017) 1–7.
[33] R.J. Tran, K.L. Sly, J.C. Conboy, Annu. Rev. Anal. Chem. 10 (2017) 11.1–11.18.
[34] C. CiracÃ±, E. Poutrina, M. Scalora, D.R. Smith, Phys. Rev. B 85 (2012), 201403 (R).
[35] B. Metzger, L. Gui, J. Fuchs, D. Floess, M. Hentschel, H. Giessen, Nano Lett. 15 (2015) 3917.
[36] N. Daneshfar, Z. Noormohamadi, Appl. Phys. A 126 (2020) 55.
[37] J. Zhu, Nanotechnology 18 (2007) 225702.
[38] C. Hubert, L. Billot, P.-M. Adam, R. Bachelot, P. Royer, J. Grand, D. Gindre, K. D. Dorkenoo, A. Fort, Appl. Phys. Lett. 90 (2007) 181105.
[39] S.-H. Jen, G. Gonella, H.-L. Dai, J. Phys. Chem. 113 (2009) 4758.
[40] M. Mutailipu, M. Zhang, H. Wu, Z. Yang, Y. Shen, J. Sun, S. Pan, Nat. Commun. 9 (2018) 3089.
[41] M. Mutailipu, M. Zhang, B. Zhang, L. Wang, Z. Yang, X. Zhou, S. Pan, Angew. Chem. Int. Ed. 57 (2018) 6095.
[42] S.A. Scherbak, A.A. Lipovskii, J. Phys. Chem. C 122 (2018) 15635.