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**ABSTRACT:** We develop an electromagnetic theory of surface enhanced Raman scattering (SERS) from coated nanoparticles with spherical anisotropy in the quasistatic limit. The multipolar polarizability of the spherically coated nanoparticle is derived on the basis of the first-principles approach, and then we employ the Gersten—Nitzan model to investigate SERS from molecules adsorbed on the coated nanoparticles. It is found that the introduction of spherical anisotropy into the core or the shell provides a novel approach to tailor the surface plasmon resonant frequencies and enhanced SERS peaks. In addition, the dependence of the SERS spectra upon the size is addressed. Our investigation can be applied in prospective stimulated Raman scattering schemes in nano-optics and plasmonics when a certain extent of anisotropy is involved.



# **1. INTRODUCTION**

Surface-enhanced Raman scattering (SERS) has attracted much attention since  $1974^1$  due to its wide potential applications. For instance, SERS plays an important role in the modern sensing such as molecular detection and nanoparticle-based biosensor<sup>2</sup> since the discovery of extremely strong single-molecule SERS in silver nanoparticle aggregates.<sup>3,4</sup> The key mechanism of the SERS is related to the electromagnetic enhancement at the position of the single-molecule near plasmonic nanoparticles.<sup>5–7</sup> Besides the electromagnetic effect, the chemical adsorption of the metal interface<sup>8</sup> and some quantum effects<sup>9</sup> lead to additional enhancement of the SERS.

As far as the electromagnetic enhancement of SERS is concerned, Leung et al.  $^{10,11}$  adopted the Gersten $-\rm Nitzan\ model^7$  to investigate the effect of substrate temperature on SERS spectra. They observed the possibility of sustaining SERS even at elevated temperatures. By taking into account the interplay between electromagnetic effects and the molecular dynamics, Xu et al.<sup>12,13</sup> gave a general study of SERS near two Ag nanoparticles. Halas et al.<sup>14-17</sup> adopted nanoshells or nanoshell dimers to control the SERS through the adjustment of the dimension of the core or the shell. Simovski<sup>18</sup> theoretically studied the cavity resonance and the plasmon resonance in silica core-silver shell and revealed the significant increase of Raman gain when  $\varepsilon$ -near-zero metamaterial shell was considered. Recently, Tian and co-workers<sup>19</sup> reported an approach of shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS), in which the Raman signal amplification is provided by gold nanoparticles with an ultrathin silica or alumina shell. The coating of metallic nanoparticle is helpful to overcome the instability of spectra of singlemolecule SERS and even enhance the SERS.<sup>20</sup> Moreover. metallic nanoshells are believed to be adaptive subwavelength optical devices because their surface plasmon resonances can

be tuned from the visible region to the near-infrared one by changing the relative dimensions of the core and shell layers.<sup>21</sup>

In view of the fact that the enhancement of SERS can be realized by the choice of the core-shell structure and by the suitable adjustment of physical parameters of the core (or the shell), it is interesting to investigate the effect of anisotropic parameters on the SERS enhancement. Now, spherical anisotropy is introduced for the first time into the parameters of both the core and the shell. Spherical anisotropy indicates that the tensors for dielectric functions are assumed to be radially anisotropic; i.e., the dielectric functions are uniaxial in spherical coordinates with values  $\varepsilon_{ir}$  along the radial direction and  $\varepsilon_{it}$  along the tangential direction [i = c (or s) stands for the core (or the shell), respectively]. Actually, such spherical anisotropy has already been taken into account to realize the invisibility for Pendry's cloak,<sup>22</sup> the optical bistability,<sup>23</sup> the enhancement of second and third harmonic generations of nondilute suspensions of coated nanoparticles,<sup>24</sup> peculiar light scattering,<sup>25</sup> the electromagnetic transparency,<sup>26</sup> the optical nonlinearity enhancement,<sup>27</sup> etc. Incidentally, spherical anisotropy was indeed found in phospholipid vesicle systems<sup>28</sup> and in cell membranes containing mobile charges.<sup>29,30</sup> Furthermore, such spherically anisotropic materials can be easily established from graphitic multishells.<sup>31</sup>

We investigate the SERS for a molecule adsorbed on a metallic nanopaticle with spherical anisotropy in the quasistatic limit. Under an inhomogeneous electric field induced by the emission of the molecule, higher-order multipolar moments should be considered. In this regard, we present a first-principles approach

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**Figure 1.** Schematic figure describing the physical process of SERS and the geometry of the coated nanoshell with the molecule adsorbed on the surface.

to model multipolar moments induced by the coated particles with spherical anisotropy. On the basis of the Gersten–Nitzan model,<sup>7</sup> one can take one step forward to investigate the SERS from a molecule adsorbed on such coated nanoparticles. We show that the introduction of spherical anisotropy may be helpful to achieve significant enhancement of SERS signals and adjust the surface plasmon resonant frequencies in a wide frequency band.

The paper is organized as follows. In section 2, we present the first-principles approach to establish the potential distributions of the coated nanoparticles and derive the multipolar moments. Then, the dependence of SERS enhancement ratio on spherical anisotropy is given on the basis of the Gersten—Nitzan model. In section 3, numerical results for two types of coated particles (spherical anisotropy occurring to the core or the shell) are illustrated and discussed. Moreover, the equations governing the surface plasmon resonant frequencies in the presence of spherical anisotropy are derived. The paper is summarized with discussion and conclusion in section 4.

# 2. THEORETICAL FORMULATION

We consider the Raman scattering from a molecule adsorbed on a coated nanoparticle with spherical anisotropy, as shown in Figure 1. For simplicity, the molecule adsorbed on the surface is described by an electric dipole with the dipole moment  $\mathbf{p}$ oriented normal to the nanoshell surface at a distance d from the surface. The coated sphere consists of the core of radius a and the coating shell of radius b. The size of the structure is assumed to be sufficiently small so that the quasistatic approximation could be utilized. Without any loss of generality, both the core and the shell are assumed to have the anisotropic dielectric tensor defined in spherical coordinates,

$$\vec{\varepsilon}_{i} = \begin{pmatrix} \varepsilon_{ir} & 0 & 0\\ 0 & \varepsilon_{it} & 0\\ 0 & 0 & \varepsilon_{it} \end{pmatrix}$$
(1)

where the  $\varepsilon_{ir}$  and  $\varepsilon_{it}$  are the dielectric components perpendicular and parallel to the surface of the core (i = c) and the shell (i = s), respectively. Note that spherical anisotropy described by eq 1 can be transformed from the uniaxial Cartesian anisotropy.<sup>32</sup>

**Potential Function Due to Spherical Anisotropy.** For the anisotropic material, the displacement **D** is related to the local field **E** by  $\mathbf{D} = \varepsilon_0 \vec{\varepsilon} \cdot \mathbf{E}$ . In the quasistatic limit, we arrive at the

Laplace equation describing the electrostatic potential,

$$\nabla \cdot (\vec{\varepsilon} \cdot \nabla \phi) = 0 \tag{2}$$

In the spherical coordinates, eq 2 can be expressed as

$$\frac{\varepsilon_{\rm ir}}{\varepsilon_{\rm it}} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \phi}{\partial r} \right) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \phi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial}{\partial \varphi} \left( \frac{\partial \phi}{\partial \varphi} \right) = 0$$
(3)

From eq 3, we know that  $\phi$  is independent of  $\phi$  due to the spherical symmetry and written as

$$\phi(r,\theta) = \sum_{n=0}^{\infty} R_n(r) \Theta(\theta)$$
(4)

Substituting eq 4 into eq 3, one obtains the radial function  $R_n$ ,

$$\frac{\varepsilon_{\rm ir}}{\varepsilon_{\rm it}} \frac{\partial}{\partial r} \left[ r^2 \frac{\partial R_n(r)}{\partial r} \right] - n(n+1)R_n(r) = 0 \tag{5}$$

On the other hand, we have Legendre polynomials for the part  $\Theta$ , i.e.,  $\Theta(\theta) \equiv P_n(\cos \theta)$ . It can be shown that  $R_n$  varies along with the radius:  $R_n(r) = Ar^{\nu_{in}} + Br^{-(\nu_{in}+1)}$  (for the subscript in, i labels the core or the shell, and *n* is the index labeling the order), where

$$\nu_{in}^{2} + \nu_{in} = \frac{\varepsilon_{it}}{\varepsilon_{ir}} n(n+1)$$

$$(n = 0, 1, 2, ...)$$
(6)

which must be fulfilled for all n = 0, 1, ... In view of the fact  $v_{in} > 0$ , we get

$$\nu_{in} = -\frac{1}{2} + \sqrt{\frac{1}{4} + \frac{\varepsilon_{it}}{\varepsilon_{ir}}n(n+1)}$$
(7)

As a consequence, the potential for the radially anisotropic material takes the form

$$\phi(r,\theta) = \sum_{n=0}^{\infty} (A_n r^{\nu_{in}} + B_n r^{-\nu_{in}-1}) P_n(\cos \theta) \quad (i = c, s) \quad (8)$$

Multipole Polarizability of a Coated Nanosphere with Spherical Anisotropy. With appropriate boundary conditions applied to our model (see Figure 1), the electrostatic solution to the Laplace equation can be obtained. The potentials of the core,  $\phi_c$ , the shell,  $\phi_s$ , and the host medium,  $\phi_{m}$ , are<sup>33,34</sup>

$$\phi_{c} = -\frac{p}{4\pi\varepsilon_{0}\varepsilon_{m}}\frac{1}{R_{mo}^{2}} + \sum_{l=1}^{\infty}A_{l}r^{\nu_{cl}}P_{l}(\cos\theta)$$

$$\phi_{s} = -\frac{p}{4\pi\varepsilon_{0}\varepsilon_{m}}\frac{1}{R_{mo}^{2}} + \sum_{l=1}^{\infty}\left(B_{l}r^{\nu_{sl}} + \frac{C_{l}}{r^{\nu_{sl}+1}}\right)P_{l}(\cos\theta)$$

$$\phi_{m} = -\frac{p}{4\pi\varepsilon_{0}\varepsilon_{m}}\frac{1}{R_{mo}^{2}} + \frac{p}{4\pi\varepsilon_{0}\varepsilon_{m}}\sum_{l=1}^{\infty}$$

$$-(l+1)\frac{r^{l}}{R_{mo}^{l+2}}P_{l}(\cos\theta) + \sum_{l=1}^{\infty}\frac{D_{l}}{r^{l+1}}P_{l}(\cos\theta) \quad (9)$$

where  $\varepsilon_{\rm m}$  is the dielectric constant of the host medium assumed to be 1 for vacuum, and  $A_b B_b C_b$ , and  $D_l$  are the coefficients to be determined. The multipolar moment  $D_l$  is expressed as<sup>33</sup>

$$D_{l} = p(l+1) \frac{b^{2l+1}}{(b+d)^{l+2}} \Delta_{l}$$
(10)

where  $\Delta_l$  is the multipole polarizability factor of the coated nanosphere, and  $\alpha_l = \Delta_l b^{2l+1}$  is the *l*th pole polarizability

$$\alpha_{l} = \frac{a^{2\nu_{sl}+1}P_{l} - b^{2\nu_{sl}+1}Q_{l}}{a^{2\nu_{sl}+1}M_{l} + b^{2\nu_{sl}+1}N_{l}}b^{2l+1}$$
(11)

with

$$\begin{split} P_l &= (l\varepsilon_m + \varepsilon_{\rm sr} + \varepsilon_{\rm sr}\nu_{\rm sl})(\varepsilon_{\rm cr}\nu_{\rm cl} - \varepsilon_{\rm sr}\nu_{\rm sl})\\ Q_l &= (l\varepsilon_m - \varepsilon_{\rm sr}\nu_{\rm sl})[\varepsilon_{\rm cr}\nu_{\rm cl} + \varepsilon_{\rm sr}(1+\nu_{\rm sl})]\\ M_l &= (-\varepsilon_{\rm cr}\nu_{\rm cl} + \varepsilon_{\rm sr}\nu_{\rm sl})[(l+1)\varepsilon_m - \varepsilon_{\rm sr}(1+\nu_{\rm sl})]\\ N_l &= (\varepsilon_m + l\varepsilon_m + \varepsilon_{\rm sr}\nu_{\rm sl})[\varepsilon_{\rm cr}\nu_{\rm cl} + \varepsilon_{\rm sr}(1+\nu_{\rm sl})] \end{split}$$

SERS Enhancement Ratio. We consider the molecule adsorbed on the surface of the coated nanoparticle, and discuss in detail how the SERS signal can be enhanced and tailored by spherical anisotropy in the nanoparticle. The mechanism of the SERS is mainly related to the electromagnetic enhancement at the position of the single molecule near nanoparticles.<sup>34</sup> In detail, it includes two processes such as the excitation of the molecule and the emission from the molecule. The first process is that when the electric field is introduced into a SERS active system, plasmonic resonance in the coated nanoparticle amplifies the local field around the molecule, resulting in the scattered electric field  $E_s$ . For the second process, the enhanced field  $E_s$  interacts with the molecule to produce Raman scattering  $E_R$ , which in turn interacts again with the nanoparticle to produce a SERS signal  $E_{SERS}$  (see Figure 1).

In the Gersten-Nitzan model,<sup>7</sup> Raman cross section at the frequency  $\omega$  from a dipole-coated spherical system is expressed in terms of the induced polarizability ( $\Delta \alpha$ ) for the molecule due to the change of nuclear coordinate (*C*),<sup>35</sup>

$$\sigma_{\text{Raman}} = \frac{8\pi}{3} \left(\frac{\omega}{c}\right)^4 (\Delta C)^2 \left(\frac{\partial \alpha}{\partial C}\right)^2 \times \left|\frac{1}{1 - \alpha G} \left[1 + \frac{2\alpha_1}{(b+d)^3}\right]\right|^4$$
(12)

where  $\alpha$  is the molecular polarizability (taken as 10 Å<sup>3</sup>),  $\alpha_1$  is the dipole polarizability of the coated nanosphere, and the "image-field factor" *G* for a radially oriented molecular dipole is given as a function of  $\alpha_b$ 

$$G = \sum_{l} \frac{(l+1)^2}{(b+d)^{2(l+1)}} \alpha_l$$
(13)

The SERS enhancement ratio, defined as the ratio between  $\sigma_{\text{Raman}}$  in eq 12 and the one in the absence of the coated sphere, is written as

$$R = \left| \frac{1}{1 - \alpha G} \left[ 1 + \frac{2\alpha_1}{\left(b + d\right)^3} \right] \right|^4 \tag{14}$$

# 3. NUMERICAL RESULTS AND DISCUSSION

We consider two typical cases: (1) a spherically anisotropic core with a metallic shell (case A); (2) a metallic core with a spherically anisotropic shell (case B). To give quantitative comparison with its isotropic counterpart and to demonstrate the role of anisotropy, we keep the geometric average of dielectric



**Figure 2.** SERS enhancement ratio *R* in case A (spherically anisotropic core and metallic nanoshell) as a function of the normalized incident frequency  $\omega/\omega_{\rm p}$  at three different anisotropy ratios  $\varepsilon_{\rm ct}/\varepsilon_{\rm cr} = 1/8$  (red dashed line), 1 (solid line), and 8 (blue dotted line). Other parameters are *b* = 10 nm, *a* = 5.0 nm, and *d* = 1.0 nm. The equivalent permittivity of the anisotropic core  $\varepsilon_{\rm ec}$  as a function of the anisotropic ratio  $\varepsilon_{\rm ct}/\varepsilon_{\rm cr}$  is plotted in the inset.

components  $\varepsilon_i \equiv 2\varepsilon_{it}/3 + \varepsilon_{ir}/3$  unchanged for anisotropic core (i = c) or shell (i = s), while  $\varepsilon_{it}/\varepsilon_{ir}$  is varied.<sup>27</sup>

SERS Enhancement Ratio *R* for Case A. In this case, the anisotropic core is characterized by two dielectric elements  $\varepsilon_{\rm cr}$  and  $\varepsilon_{\rm ct}$ . We tune  $\varepsilon_{\rm ct}/\varepsilon_{\rm cr}$  while keeping  $\varepsilon_{\rm c} = 9/4$ .<sup>27</sup> The silver shell is of the Drude form,

$$\varepsilon_{\rm sr} = \varepsilon_{\rm st} = \varepsilon_{\rm s} = 1 - \frac{\omega_{\rm p}^2}{\omega^2 + i\omega\gamma}$$
 (15)

where the plasmon frequency for Ag is  $\omega_{\rm p} = 1.36 \times 10^{16} \, {\rm s}^{-1}$ , and the damping constant accounting for interface scattering has the following form:  $\gamma = \gamma_{\rm f} + Av_{\rm f}/(b-a)$ , with  $\gamma_{\rm f} = 2.56 \times 10^{13} \, {\rm s}^{-1}$ ,  $v_{\rm f} = 1.39 \times 10^6 \, {\rm m/s}$ , and  $A = 1.^{36}$ 

In Figure 2, the SERS enhancement ratio R is shown for case A (i.e., a spherically anisotropic core with a metallic shell) as a function of the normalized frequency  $\omega/\omega_{\rm p}$ . We find that there exist two surface plasmonic resonant modes: (1) the symmetric low-frequency dipole mode at  $\omega_{1-}$  and (2) the antisymmetric high-frequency dipole mode at  $\omega_{1+}$ . It is known that the SERS enhanced peak at  $\omega_{1+}$  results from the antibonding resonance, which is an antisymmetric coupling between the surface charge oscillations on two interfaces at r = a and r = b, while the other enhanced peak at low frequency  $\omega_{1-}$  corresponds to symmetric coupling.<sup>37</sup> For an isotropic core, the SERS enhancement for the symmetric mode ( $R \approx 3.6 \times 10^5$ ) at  $\omega_{1-} \approx 0.48 \omega_p$  is found to be about 1 order in magnitude larger than that of the antisymmetric mode  $(R \approx 1.4 \times 10^4)$  at  $\omega_{1+} \approx 0.77 \omega_p$ . This is consistent with previous observations on SERS from metallic nanoshells with isotropic nonlocal response.<sup>35</sup> When spherical anisotropy is introduced into the core (see the lines for  $\varepsilon_{\rm ct}/\varepsilon_{\rm cr} = 1/8$  and 8), both low and high resonant frequencies  $\omega_{1-}$  and  $\omega_{1+}$  exhibit the blue-shift in comparison with the isotropic cases. In addition, the SERS enhancement for the symmetric mode becomes strong, while the one for the asymmetric mode is damped as spherical anisotropy is introduced. Especially, the antisymmetric plasmon modes are more sensitive to the change of spherical anisotropy. Actually, in the quasistatic limit, from the expression of the polarizability for l = 1 (see eq 11), we can regard the anisotropic core as an isotropic core with the equivalent permittivity  $\varepsilon_{ec}$  =  $\varepsilon_{\rm cr} v_{\rm c1} = 27(-1/2 + (1/4 + 2\varepsilon_{\rm ct}/\varepsilon_{\rm cr})^{1/2})/[4(2\varepsilon_{\rm ct}/\varepsilon_{\rm cr} + 1)],$ 



**Figure 3.** Near-field distributions for Ag nanoshell with an anisotropic core at (a) the low frequency for  $\varepsilon_{ct}/\varepsilon_{cr} = 1/8$ , (b) the high frequency for  $\varepsilon_{ct}/\varepsilon_{cr} = 1/8$ , (c) the low frequency for  $\varepsilon_{ct}/\varepsilon_{cr} = 8$ , and (d) the high frequency for  $\varepsilon_{ct}/\varepsilon_{cr} = 8$ .

which is a nonmonotonic function of  $\varepsilon_{ct}/\varepsilon_{cr}$  and has a maximal value 9/4 when  $\varepsilon_{cr} = \varepsilon_{ct}$  (i.e., isotropic case as shown in the insert of Figure 2). In other words, the equivalent permittivity of the anisotropic core  $(\varepsilon_{\rm ct}/\varepsilon_{\rm cr}\neq 1)$  is always smaller than that of the isotropic core with  $\varepsilon_{ct} = \varepsilon_{cr} = \varepsilon_c = 9/4$ . As a consequence, when we take spherical anisotropy into account, the induced charge on the interface between core and the shell will be increased compared to the isotropic case, resulting in enhanced restoring forces and large resonant energies (blue shift of the surface plasmonic resonant modes).<sup>38</sup> Moreover, the antisymmetric mode at  $\omega_{1+}$  is mainly dominated by the contribution from the plasmons on the interface between the core and the shell (r = a), while the symmetric mode at  $\omega_{1-}$  is mainly relevant to the plasmon resonance on the interface between shell and the host (r = b). Therefore, once we vary the spherical anisotropy of the core, the SERS spectrum at the high frequency  $\omega_{1+}$  changes more significantly than the one at low frequency  $\omega_{1-}$ .

To understand the physical insight of the SERS enhancement ratio, we adopt the plasmon hybridization model.<sup>37,38</sup> Note that the equivalent permittivity for the anisotropic case is smaller than the value for isotropic core. Hence, compared to the SERS enhancement with isotropic core, the strength of the SERS enhancement of our current model at symmetric plasmon resonance frequency  $\omega_{1-}$  will be increased, while the strength at the antisymmetric resonant frequency  $\omega_{1+}$  will be decreased. Similar conclusions have been made for isotropic metallic nanoshells on the basis of the time-dependent density function method.<sup>38</sup> Therefore, when the radially anisotropic core is considered, it is possible to realize large enhancement in wide SERS spectra.

Local fields at two surface resonant frequencies are illustrated in Figure 3. It is evident that for low-frequency resonance (corresponding to symmetric modes) (Figure 3a,c), the local electric fields near the outer interface (r = b) are slightly enhanced, while for high-frequency resonance (corresponding to antisymmetric modes) (Figure 3b,d), the electric fields in the shell region (particularly the area close to inner surface r = a) are enhanced. Numerical results clearly demonstrate that the symmetric mode is associated with the plasmons on the outer surface of the nanoshell, while the antisymmetric mode is associated with the plasmons on the inner surface. In addition, when  $\varepsilon_{\rm ct}/\varepsilon_{\rm cr} < 1$ (Figure 3a,b), the electric fields in the center of the core are greatly enhanced, which is quite different from the uniform field distribution in an isotropic core. It is because the electric field has the form  $r^{\nu_{cl}-1}$  in the core and  $\nu_{cl}$  is less than 1 for  $\varepsilon_{ct}/\varepsilon_{cr} < 1$ (eq 7), resulting in a large enhancement near the center of the core. Moreover, we find that the localization pattern inside the anisotropic core is dominated by the anisotropic ratio  $\varepsilon_{\rm ct}/\varepsilon_{\rm cr}$ 



**Figure 4.** Two surface plasmon frequencies (black filled circles) and corresponding maximal values of enhancement ratio *R* (solid lines) as a function of  $\varepsilon_{ct}/\varepsilon_{cr}$  for (a) low-frequency symmetric mode and (b) high-frequency antisymmetric mode. The frequencies and the SERS enhancement are computed for case A with damping as used in Figure 2, by applying the numerical search program for the peak positions and the peak magnitude in SERS spectra. The resonant frequencies determined ideally from eq 16 for *l* = 1, which involves no damping in the Drude material (silver in this case), is given by the red dotted line. Parameters are the same as in Figure 2.

rather than the modes. However, once the anisotropic ratio is fixed, the symmetric mode and the antisymmetric mode will contribute to the field enhancement at outer and inner interfaces, respectively.

In what follows, we study the effect of spherical anisotropy ratio  $\varepsilon_{ct}/\varepsilon_{cr}$  on the resonant frequencies and the corresponding maximal SERS enhancement. First, we derive the analytical formulas governing the ideal resonant frequencies for case A by using the undamped Drude model (i.e.,  $\gamma = 0$  in eq 15). In this connection, the poles of eq 11 yield the following quadratic equation for the surface resonant frequencies of *l*th order

$$[EF + X(l+1)(\varepsilon_{\rm m} - 1)(l - \varepsilon_{\rm cr}\nu_{cl})]y^{2} + [X(l+1)(2l - \varepsilon_{\rm cr}\nu_{cl} - l\varepsilon_{\rm m}) + E(l+1) - Fl]y + H = 0$$
(16)

where  $X = (a/b)^{2l+1}$ ,  $E = l + \varepsilon_m + l\varepsilon_m$ ,  $F = l + 1 + \varepsilon_{cr}\nu_{cb}$ ,  $H = l(l+1)[1 - (a/b)^{2l+1}]$ , and  $(y)^{1/2} = \omega_l/\omega_p$  is the *l*th-multipole resonance frequency normalized by the bulk plasmon of the metal. If there is no spherical anisotropy in the core, i.e.,  $\varepsilon_{cr} = \varepsilon_{cb}$  the solutions to eq 16 can be reduced to eq A3 in Chang's work.<sup>36</sup> From eq 16, we are able to predict two physical solutions for antisymmetric (higher frequency  $\omega_{l+}$ ) and symmetric (lower frequency  $\omega_{l-}$ ) modes.

The dependence of resonant frequencies ( $\omega_{1+}$  and  $\omega_{1-}$ ) and the corresponding maximal enhancement R on the anisotropy ratio  $\varepsilon_{ct}/\varepsilon_{cr}$  are shown in Figure 4. For the low-frequency symmetric mode  $\omega_{1-}$  (Figure 4a), the maximum of SERS enhancement  $R_{max}$  is increased evidently once spherical anisotropy for the core is taken into account. In other words, the



**Figure 5.** SERS enhancement ratio *R* in case A (radially anisotropic core and metallic nanoshell) at various core radii *a*. Other parameters are  $\varepsilon_{ct}/\varepsilon_{cr} = 1/4$  and b = 10 nm.

presence of spherical anisotropy is really helpful to achieve large SERS enhancement at the resonant frequency. However, for the antisymmetric high-frequency mode  $\omega_{1+}$ , we observe the inverse dependence; i.e., the introduction of spherical anisotropy leads to the decrease of  $R_{\text{max}}$  at  $\omega_{1+}$ ) (Figure 4b). To one's interest, we further show that both the antisymmetric and symmetric modes are blue-shifted once  $\varepsilon_{\text{ct}}/\varepsilon_{\text{cr}}$  diverges from 1, in accordance with the observation from Figure 2. The resonant frequencies obtained from the numerical calculations by searching the peak positions of R (solid circles) for case A (anisotropic core and metallic shell) agree well with those ideal results (red dotted lines) predicted by eq 16 analytically.

In Figure 5, we study the size effects of SERS enhancement against  $\omega/\omega_{\rm p}$  at various inner radii *a* with the same anisotropy  $\varepsilon_{\rm ct}/\varepsilon_{\rm cr} = 1/4$ . It is obvious that with the decrease of the inner radius a (i.e., the metallic component occupies more volume), the SERS enhancement peak  $R_{\rm max}$  in the symmetric lowfrequency mode becomes stronger, accompanied by the blue shift in the resonant frequency. It is interesting to note that, when the size of the core keeps shrinking, the SERS enhancement in both symmetric and antisymmetric modes will be further enlarged first, and then the SERS enhancement of antisymmetric modes will be gradually suppressed. Actually, in the limit of  $a \rightarrow a$ 0, the anisotropic coated nanoparticle degenerates to a purely metallic sphere at the radius *b*. Moreover, we find that shells may indeed act as better enhancers at lower frequencies and the frequency exhibits a blue shift with the decrease of the core size, which are in agreement with the findings of Halas et al.  $^{14-17}$ 

**SERS Enhancement Ratio** *R* **for Case B.** Here, the coated nanoparticle is composed of the metallic core and a spherically anisotropic shell. Thus, we let

$$\varepsilon_{\rm cr} = \varepsilon_{\rm ct} = \varepsilon_{\rm c} = 1 - \frac{\omega_{\rm p}^2}{\omega^2 + i\omega\gamma}$$
 (17)

where  $\gamma = \gamma_f + Av_f/a$ . In this situation, one expects the surface plasmon resonance near the interface between the metallic core and anisotropic shell. As a consequence, there exists only one plasmonic resonant frequency of *l*th order instead of two resonant frequencies in case A. Again, by using the undamped Drude model for  $\varepsilon_c(\omega)$ , the resonant frequency for the *l*th multipole can be solved from

$$y^{2}[IX(1-\varepsilon_{\rm sr}\nu_{\rm sl})-J(1+\varepsilon_{\rm sr}+\varepsilon_{\rm sr}\nu_{\rm sl})]+y[J-IX]=0 \quad (18)$$



**Figure 6.** SERS enhancement ratio *R* in case B (metallic core and radially anisotropic nanoshell) as a function of  $\omega/\omega_{\rm p}$  for various spherical anisotropy ratios in the shell  $\varepsilon_{\rm st}/\varepsilon_{\rm sr}$  when (a) a = 2.5 nm, (b) a = 5.0 nm, and (c) a = 9.5 nm.

where X is the same as that in eq 16,  $I = 2\varepsilon_m - \varepsilon_{sr} - \varepsilon_{sr}\nu_{sb}$  and  $J = 2\varepsilon_m + \varepsilon_{sr}\nu_{sl}$ .

In Figure 6, the SERS enhancement ratio R is demonstrated for case B (metallic core and anisotropic nanoshell) against the normalized frequency  $\omega/\omega_{\rm p}$  for different anisotropies in the shell. The following features are clearly noted: (1) there exists only one resonant frequency for each curve, as observed from experimental results of Au–SiO<sub>2</sub> (core–shell) nanoparticles;<sup>39</sup> (2) when spherical anisotropy in the shell is taken into account, the resonant frequency may exist as a blue shift or red shift depending on both the anisotropy ratio  $\varepsilon_{st}/\varepsilon_{sr}$  and the core size *a*, and such behavior is quite different from that of case A; (3) the enhancement ratio R at the resonant frequency is always enhanced when  $\varepsilon_{st}$  is decreased, and such a feature is independent of the core radii; (4) for a given finite  $\varepsilon_{st}/\varepsilon_{sr}$ , the increase of the core size leads to the increase in the resonant peak of R and the red-shift of the resonant frequency compared to the resonance for smaller radii a.

In the end, we study the significance of anisotropy ratio  $\varepsilon_{\rm st}/\varepsilon_{\rm sr}$ on the surface plasmon resonant frequency  $\omega_{\rm r}$  and the corresponding resonant peak  $R_{\rm max}$  as shown in Figure 7. It can be seen that, by decreasing the anisotropy ratio  $\varepsilon_{\rm st}/\varepsilon_{\rm sr}$ ,  $R_{\rm max}$  is increased monotonically. It reveals that, the smaller the anisotropy ratio, the larger enhancement of SERS signal is. On the other hand, the resonant frequency  $\omega_{\rm r}$  takes nonmonotonic behavior versus  $\varepsilon_{\rm st}/\varepsilon_{\rm sr}$ . As a consequence, increasing  $\varepsilon_{\rm st}/\varepsilon_{\rm sr}$  results in either a blue shift or red shift in the resonant frequency. Such complicated behavior can be qualitatively understood as follows: the



**Figure 7.** Surface resonant frequency and the corresponding maximal value of SERS enhancement  $R_{\text{max}}$  computed for case B, as a function of  $\varepsilon_{\text{st}}/\varepsilon_{\text{sr}}$  for (a) a = 2.5 nm, (b) a = 5.0 nm, and (c) a = 9.5 nm. The notations of line symbols are the same as those for case A in Figure 4.

introduction of spherical anisotropy ( $\varepsilon_{\rm st}/\varepsilon_{\rm sr} \neq 1$ ) leads to the blue shift of the resonant frequency, while the increasing of size *a* results in the red shift. For a given anisotropy ratio and the core size, the final shift is dominated by the one that prevails.

#### 4. CONCLUSION

In this paper, we have investigated the SERS enhancement spectra from coated nanoparticles involving spherical anisotropy. Two types of core-shell structured nanospheres are studied. The interconnections between SERS enhancement ratio, anisotropy ratio, core-shell structure, resonant shifts, and the size dependence are systematically studied. To this end, we derive the multipole polarizability from the coated nanosphere with spherical anisotropy by the first-principles approach and present the formula for the SERS enhancement ratio with the aid of the Gersten-Nitzan model. Numerical results show that the introduction of spherical anisotropy will provide an alternative promising way to achieve significant enhancement of SERS signal and to adjust the surface plasmon resonant frequencies in a wide frequency region, exhibiting a tunable Raman scattering. Our study should be useful to the prospective SERS schemes in modern nano-optics and plasmonics.

Here some comments are in order. The SERS enhancement in our paper is still due to surface plasmon resonance, though the anisotropy in the core or the shell is taken into account. To

observe much higher Raman gain, one may combine the resonant excitation of whispering-gallery modes and the surface plasmon modes. In this connection, one can assume the core or the shell to be composed of metamaterial with near-zero permittivity.<sup>18</sup> In addition, the hot spots give rise to increased SERS signal, because they facilitate enhanced optical fields, which in turn contribute to the electromagnetic enhancement when a molecule is in the vicinity of these spots. The hot spots in coated nanoparticles with pinholes were investigated by means of experimental method<sup>40</sup> and finite element numerical simulation.<sup>41</sup> It is of great interest to study the hot spots in coated nanoparticles with spherical anisotropy. Our work is only valid in the quasistatic limit. For relatively large coated nanoparticles, one should resort to fullwave electromagnetic theory.<sup>26</sup> On the contrary, when the nanoparticles are smaller than  $b \leq 5$  nm, the liftetime of surface plasmon is reduced due to Landau damping. For instance, for small clusters with a few hundreds of electrons, the surface plasmon's lifetime is about several femtoseconds. Therefore, the quantum size effect may be taken into account.<sup>9</sup>

# AUTHOR INFORMATION

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