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Strain effects on the SERS enhancements for spherical silver nanoparticles

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Abstract

We demonstrate in the present work through the utilization of classical Mie scattering theory in conjunction with a radiation damping and dynamic depolarization-corrected electrostatic approximation the significant effect that mechanical strain has on the optical properties of spherical silver nanoparticles. Through appropriate modifications of the bulk dielectric functions, we find that the application of tensile strain generates significant enhancements in the local electric field for the silver nanoparticles, leading to large SERS enhancements of more than 300% compared to bulk, unstrained nanoparticles when a 5% tensile strain is applied. While the strain-induced SERS enhancements are found to be strongest for nanoparticle diameters where radiation damping effects are minimized, we find that the surface plasmon resonance wavelengths are relatively unchanged by mechanical strain, and that the various measures of the far field optical efficiencies (absorption, scattering, extinction) can be enhanced by up to 150% through the application of tensile strain. The present findings indicate the opportunity to actively engineer and enhance the optical properties of silver nanoparticles through the application of mechanical deformation.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Due to the coherent oscillation (resonance) of the conduction electrons with an interacting electromagnetic field, noble metal nanostructures such as gold and silver exhibit a unique optical response known as localized surface plasmon resonance (LSPR) [1], which has proven to be exceptionally useful for a variety of applications involving optical sensing, detection and imaging [2–4]. Other applications, as well as detailed summaries of the LSPR phenomena can be found in one of the many excellent reviews on this subject that have been written in the past decade [5, 6].

The interactions between the metallic nanostructures and the incident electromagnetic field can also lead to significant enhancements in the local electric field at the surfaces of the nanoparticles. These enhancements in the electric field have significant ramifications for surface enhanced Raman scattering (SERS) applications, with the majority of the interest being in using the significant SERS enhancement for the detection of single molecules [7, 8].

The various features that are known to lead to SERS enhancements have been studied extensively in recent years. Through these efforts, researchers have determined that the majority of the SERS enhancement is electromagnetic in nature [9], that sharp points and corners can significantly improve the local SERS enhancement [10, 11], and that the SERS enhancement can be substantially improved by considering the interactions of dimers of nanoparticles [11–13].

While the previously discussed approaches are representative examples of the extensive literature with regards to tuning the optical properties through the geometric properties of the as-synthesized or fabricated nanostructure, comparatively little research exists as to the possibility of actively tuning the nanostructure optical properties. We note that recent research has examined various methods of active optical tuning, i.e. through thermal [14], electronic [15], ferroelectric [16], optical [17], and mechanical [18–24] means.

The previous studies of mechanically tuning the optical properties have focused upon metal–elastomer substrates with voided structures [18–21], in using pressure to

control the SERS activity of metal substrates [24], or in using metal nanostructures as optical strain sensors for biological applications [22, 23]. However, these works did not consider how strain impacts the dielectric properties, and thus the optical properties of individual metal nanoparticles. Therefore, we focus in the present work on understanding how mechanical strain impacts both the far field (extinction, scattering and absorption efficiencies) and near field (SERS enhancements) optical properties of individual silver nanoparticles.

Mechanical strain can be generated in nanomaterials by many different means. For example, thermal stresses resulting from changes in temperature can cause expansion or contraction of nanoparticles [25, 26]. Similarly, strain can be induced in nanoparticles due to lattice mismatch with the surrounding or underlying substrate [25]. We note that surface stresses, which have a significant effect on nanostructures, can cause both expansion [27, 28] and contraction [29–31] of nanoparticles. Finally, nanoparticles can be deformed by first embedding them in a soft matrix, and then mechanically straining the matrix [18–21]; we note that strains exceeding 20% have been achieved in this fashion [18, 19, 22].

In this sense, the present work is analogous to the successful and long-standing tradition of strain-driven bandstructure engineering in both bulk and nanostructured semiconductors [32–34]. In contrast, with the exception of some recent work discussing the effects of surface-stress-induced lattice contraction effects on the plasmon resonance wavelength of ultrasmall (diameter smaller than 2 nm) metal nanoparticles [25, 35–37], and recent work studying strain effects on the optical properties of individual gold nanoparticles [38], we are unaware of any general studies quantifying the effects of mechanical strain on the optical properties of individual silver nanoparticles.

Because we have previously studied strain effects on the optical properties of spherical gold nanoparticles [38], the objective of the present work is to apply similar techniques to develop a fundamental understanding of how strain impacts the optical properties of a different metallic nanostructure of interest. We focus upon silver nanoparticles which, as we demonstrate, exhibit a significantly different optical response to applied strain because silver is a free electron dominated optical material compared to gold because its plasmon resonance wavelength does not coincide with its interband transition wavelength, as it does for gold. Furthermore, the optical properties of silver nanoparticles are negatively impacted by radiation damping at sizes that are considerably smaller than for gold nanoparticles [39].

We therefore in this work utilize classical Mie theory in conjunction with dielectric functions that account for the effects of mechanical strain to analyze the effects of both tensile and compressive mechanical strain on the optical properties of spherical silver nanoparticles. We detail strain effects on the far field optical efficiencies of interest (scattering and extinction), shifts in the plasmon resonance wavelength, and finally on the local electric fields with a specific interest in the potential SERS enhancements.

2. Strain-induced modifications of the bulk dielectric functions

The effects of mechanical strain are accounted for in the present work through appropriate modifications of the bulk dielectric functions for silver, which are obtained from the experimental work of Johnson and Christy [40]. We note that the strain, both tensile and compressive, was applied isotropically to the spherical nanoparticles. Because the approaches we utilized to modify the dielectric functions are described in detail in our previous work [38], we will discuss them only briefly here.

Specifically, the final dielectric functions for silver are obtained by modifying the bulk dielectric functions of Johnson and Christy [40] by accounting for strain effects on the free electron density [25], the ionic core (bound electrons) [35], as well as accounting for size-dependent surface damping effects through the methodology proposed by Coronado and Schatz [41]. Further details on the methodology for including strain effects on the dielectric functions can be found in the work of Qian and Park [38].

3. Numerical methodology

To calculate the optical spectra of the spherical silver nanoparticles, we utilize Mie scattering theory [42], which provides analytic solutions to Maxwell's equations [43, 44] for a restricted number of geometries, most typically spheres, in conjunction with the strain-modified dielectric functions for silver.

The local electric field outside the surface of a sphere (nanoparticle), which is important for the SERS enhancement, can be written as [44]

$$\mathbf{E}_{\text{out}}(r) = \mathbf{E}_0 \sum_{n,m} \{A_{nm}\mathbf{M}^{(1)}_{nm}(k_{\text{M}}, \mathbf{r}) + B_{nm}\mathbf{N}^{(1)}_{nm}(k_{\text{M}}, \mathbf{r}) + C_{nm}\mathbf{M}^{(3)}_{nm}(k_{\text{M}}, \mathbf{r}) + D_{nm}\mathbf{N}^{(3)}_{nm}(k_{\text{M}}, \mathbf{r})\}, \quad (1)$$

where the detailed expressions for A, B, C, D, M and N can be found in appendix H of Le Ru and Etchegoin [44], and where the effects of strain on the local electric field occur through the strain-modified dielectric functions. In the following numerical simulations, we calculate the extinction (Q_{ext}) and scattering (Q_{sca}) efficiencies as well as the local electric field enhancement factors using the SPlaC code of Le Ru and Etchegoin [44].

4. Electrostatic approximation and radiation damping

Before presenting our results describing the effects of strain on the optical properties of silver nanospheres, we briefly discuss some well-established theoretical concepts that will help in understanding our results. Specifically, we discuss theoretical approximations within the framework of the electrostatic approximation (ESA), which is valid for nanosphere diameters that are considerably smaller than the incident wavelength of light [5, 44]. We also discuss size-dependent corrections to the ESA that become important

for larger diameter nanospheres, i.e. radiation damping and dynamic depolarization [5, 39, 44, 45]. The predictions of both of these approximations will be compared to the Mie theory results accounting for strain effects in the upcoming sections, where the relevance of the radiation damping and dynamic depolarization-corrected ESA will be made evident.

4.1. Electrostatic approximation of dipole plasmon resonance

For a spherical particle with strain-corrected dielectric constants, the solution to the Laplace equation shows that the dipolar polarizability of a spherical particle is written as [5]

$$\alpha = \beta_S r^3, \tag{2}$$

where β_S is the non-dimensional dipolar polarizability of the spherical particle and is given by

$$\beta_S(\omega) = \frac{\epsilon(\omega) - \epsilon_M}{\epsilon(\omega) + 2\epsilon_M}, \tag{3}$$

where ϵ_M is the dielectric constant of the surrounding medium. Furthermore, within the ESA [5, 44], the extinction and scattering efficiencies can be written as [5, 44]

$$Q_{ext} = 4x\mathrm{Im}(\beta_S), \tag{4}$$

and

$$Q_{sca} = \tfrac{8}{3}x^4|\beta_S|^2, \tag{5}$$

where $x = k_M r = 2\pi(\epsilon_M)^{0.5} r\lambda^{-1}$, k_M is the wavevector of incident light in the surrounding medium, r is the radius of the sphere and λ is the wavelength of the incident beam of light. According to Le Ru and Etchegoin [44], the SERS enhancement factor for a spherical particle within the ESA can be written as

$$\rho(\mathbf{r}_m, \omega) = 16|\beta_S(\omega)|^4. \tag{6}$$

4.2. The influence of dynamic depolarization and radiation damping on the plasmon resonance

For sufficiently large spherical silver nanoparticles as discussed by Meier and Wokaun [39], the plasmon resonance and the local electric field surrounding the nanosphere can be strongly affected by both dynamic depolarization and radiation damping [39, 44]. Accounting for both dynamic depolarization and radiation damping (DD–RD), the non-dimensional polarizability in equation (3) of a sphere can be rewritten as [39, 44]:

$$\beta_S(\omega)^{DD-RD} = \frac{\beta_S}{1 - x^2\beta_S - 2/3\mathrm{i}x^3\beta_S}. \tag{7}$$

We note that in the denominator of equation (7), the $x^2\beta_S$ term represents the effects of dynamic depolarization, while the $x^3\beta_S$ term represents the effects of radiation damping. According to Meier and Wokaun [39], as the diameter of the silver nanosphere increases, dynamic depolarization will lead to a redshift of the plasmon resonance wavelength. When both radiation damping and dynamic depolarization are accounted for, the modified radiation condition states that the real part of the denominator of equation (7) approaches zero, which implies that [39]

$$\epsilon_1(\omega)(1 - x^2) + (2 + x^2) + \tfrac{2}{3}\epsilon_2(\omega)x^3 = 0, \tag{8}$$

where $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ are the real part and imaginary part of $\epsilon_M(\omega)$, respectively; the solution of equation (8) will provide the plasmon resonance wavelength of the silver nanospheres. We utilize the non-dimensional dipolar polarizability β_S^{DD-RD} in equation (7) to calculate the extinction and scattering efficiencies for silver nanoparticles as it naturally accounts for the size-dependent radiation damping and dynamic depolarization effects we have discussed.

5. Numerical results

For the upcoming numerical studies, we considered three cases, that of 5% tensile strain, 5% compressive strain, and 0% strain, or the standard bulk material; the strain was applied isotropically to the spherical nanoparticles. We note that for previous work involving gold nanoparticles [38], we did not consider situations in which the strain along the k-vector of the incident light is different from that perpendicular to the k-vector, though we have considered the effects of surface stress-driven uniaxial lattice contraction on the optical properties of ultrasmall silver nanowires [37]. However, we have not considered applied uniaxial strain on larger FCC metal nanowires, which may be important due to the uniaxial state of strain that is likely to be achieved experimentally [18]. These effects will be considered in future studies by relating changes in the unit cell volume to the generalized strain or deformation tensor.

For the cases where tensile or compressive strain was applied, the SPlaC calculations were performed modifying both the bulk dielectric functions to account for strain and size effects, as previously discussed, and also changing the geometries of the spheres to account for strain while using the bulk dielectric functions of Johnson and Christy [40] to isolate strain-driven geometric effects on the optical response. The 5% strain limits were chosen to represent upper and lower bounds for reasonable states of strain in nanoparticles before significant amounts of inelastic deformation could be expected [46], though we note that strains in excess of 20% have been reported in recent optomechanical coupling experiments [18, 19, 22].

5.1. Strain effects on the optical efficiencies and plasmon resonance wavelength shifts

We first discuss the shift in the plasmon resonance wavelength that occurs due to strain for extinction and scattering. As can be seen in figure 1, there is a slight redshift that occurs due to tensile strain, with a very slight blue-shift that occurs due to compressive strain. We note that figure 1 shows results for scattering only; similarly small red and blue-shifts due to strain are also found for absorption and extinction. Both of these trends may be expected from the observed fact that the plasmon resonance wavelength is known to very slightly redshift with increasing nanoparticle diameter [4].

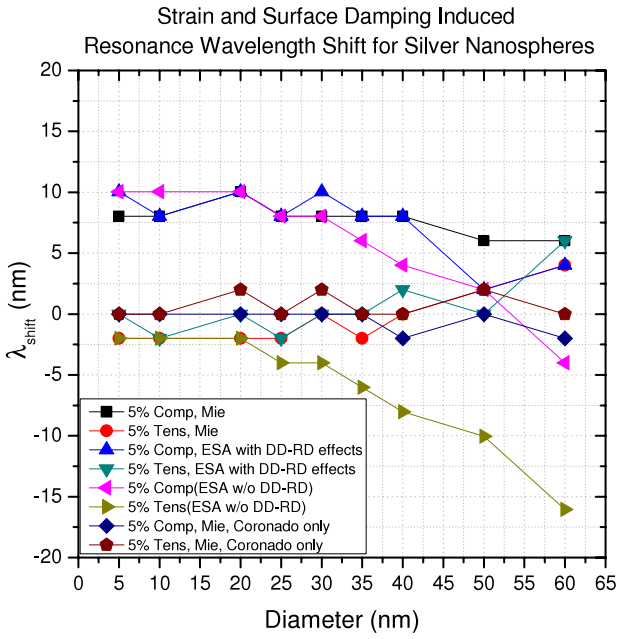

Figure 1. Strain-induced shift in the plasmon resonance wavelength for scattering.

The finding that the plasmon resonance wavelength is essentially unshifted for silver nanoparticles due to compressive strain when strain affects both the core and free electrons is in agreement with previous studies by Lerme *et al* [35]. Specifically, Lerme *et al* [35] found that the blue-shift that results from the increase in the free electron density is essentially balanced by the redshift that occurs due to the enlargement of the bound electron dielectric function, a result that is also found in the present work.

We now compare in figure 1 the resonance wavelength shift that occurs as calculated using Mie theory under 5% tensile and compressive strain as compared to that predicted by solving equation (8). Figure 1 clearly demonstrates that the resonance wavelength shift decreases with increasing nanoparticle size simply due to the effects of dynamic depolarization and radiation damping [39]; we note that strain-corrected dielectric functions were utilized in equation (8) to generate the results in figure 1.

We have also quantified in figure 1 the effect of neglecting the DD–RD effects. As can be seen in figure 1, for nanosphere diameters smaller than about 25 nm, little change is observed by neglecting the DD–RD effects. However, for both tensile and compressively strained nanospheres, for diameters larger than about 25 nm, a significant blue-shift is predicted if DD–RD effects are not accounted for. We also note that figure 1 demonstrates that if strain effects on the dielectric functions are neglected, as in the Coronado only cases, then essentially no wavelength shift is observed, which indicates that geometric changes due to strain have little effect on the plasmon resonance wavelength.

The strain-induced shifts in the plasmon resonance wavelength that are observed in figure 1 are considerably smaller than strain-induced shifts in the plasmon resonance wavelength for spherical gold nanoparticles previously studied by Qian and Park [38], where wavelength shifts exceeding 100 nm were observed for both 5% tensile and compressive strain. The reason for this is because for silver, the plasmon resonance wavelength, which occurs around 360 nm, is not coincident with the interband transition wavelength, which occurs around 330 nm for silver [40]. In contrast, the plasmon resonance wavelength for gold nanoparticles of about 525 nm is nearly coincident with the interband transition wavelength of about 515 nm. Because of this, strain has a significant effect on the bound electron contribution to the dielectric function for gold, which causes a dramatic change in the real part of the dielectric constant ϵ_1 at the interband transition wavelength. Because variations in ϵ_1 are known to be the cause of plasmon resonance wavelength shifts [47], the strain effects lead to substantial shifts in the plasmon resonance wavelength with strain for gold. Because silver does not have the same overlap between the interband transition wavelength and the plasmon resonance wavelength, the wavelength shift that is observed due to strain is found to be significantly smaller than in gold [38].

While the plasmon resonance wavelength shift due to strain as seen in figure 1 was found to be relatively small, we find that there are substantial gains in the scattering and extinction efficiencies due to strain as seen in figure 2, where figure 2 was obtained by using equations (4) and (5) in conjunction with the radiation damping and dynamic depolarization-corrected β_S^{DD-RD} in equation (7). Here and in later figures, the strain-induced gain in the far field optical efficiencies and the SERS enhancement are in units of percentage and defined as

$$\eta = 100\left(\frac{Q^{\text{strain}}}{Q^{\text{bulk}}} - 1\right). \tag{9}$$

There are a variety of interesting details in figure 2, which we now discuss. First, we find for both extinction and scattering that the efficiencies increase with applied tensile strain, and decrease with applied compressive strain. Specifically, with the application of 5% tensile strain, the increase in the scattering efficiency is found to reach 150% for nanoparticle diameters smaller than 25 nm, while the corresponding increase in extinction efficiency is found to be nearly 50%. In contrast, when 5% compressive strain is applied, there is a greater than 50% reduction in scattering efficiency, while a similar reduction in extinction efficiency is observed. The increase in far field optical properties due to tensile strain indicates that the tensile strain can be utilized to actively tailor and enhance the far field efficiencies as required by varying the level of tensile strain applied, particularly when the nanosphere diameter is in the range between 5 and 30 nm.

Second, we find that the strain-induced gain or reduction η_{ext} and η_{sca} in the extinction and scattering efficiencies match very well between the Mie theory results, and those obtained using the RD–DD-corrected ESA. Furthermore, for both extinction and scattering, we find that the gain in the optical efficiencies due to tensile strain reaches a maximum for nanosphere diameters between 10 and 25 nm; for larger nanosphere diameters, this demonstrates that the reduction in optical efficiency due to radiation damping overcomes

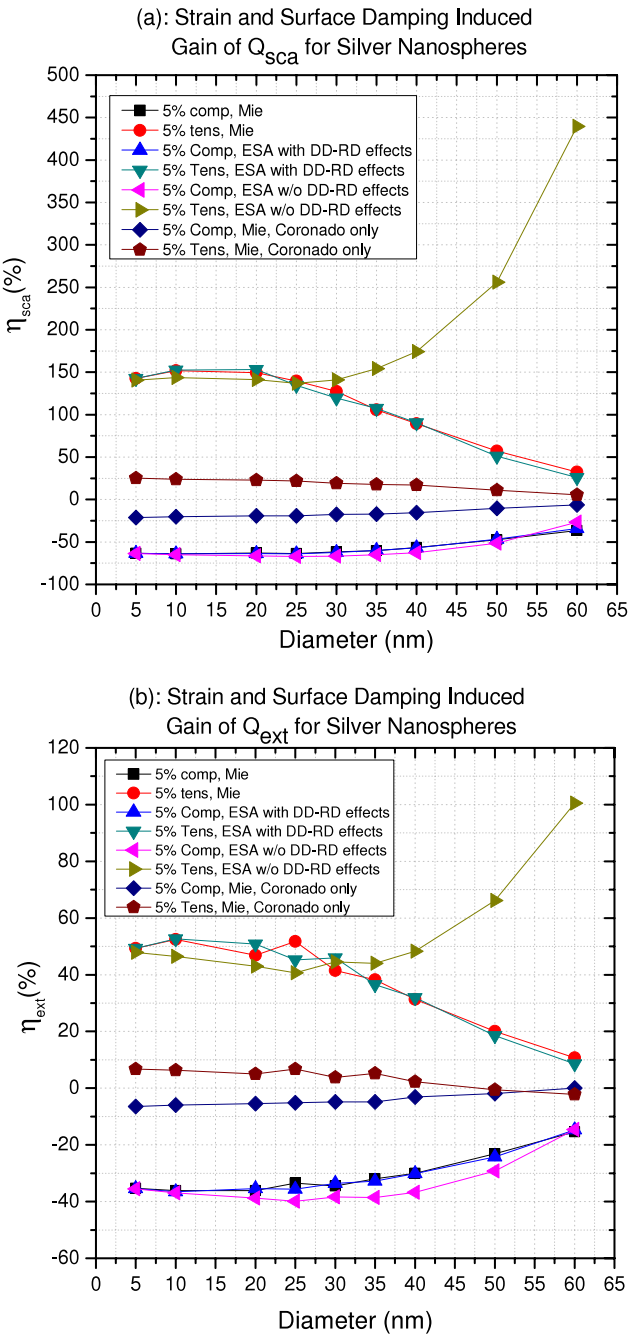

Figure 2. Per cent enhancement in (a) scattering and (b) extinction efficiencies due to strain for a range of silver nanoparticle diameters.

the tensile-strain-induced gain, thus leading to a decline in the effectiveness of strain-induced optical engineering for the silver nanospheres as the diameter increases.

We have also calculated the enhancement in scattering and extinction efficiencies that would occur for two other cases, the first where strain effects on the dielectric function are neglected (Coronado only in figure 2), and the second where the DD–RD effects are neglected. If strain effects on the dielectric function are neglected, figure 2 shows that a small enhancement in scattering and extinction efficiencies is obtained; however, this geometric enhancement accounts for only about 20% of the total enhancement that is observed, which strongly suggests that tensile strain effects on the dielectric function are the main cause for the observed enhancement in the optical efficiencies. Furthermore, it can be seen in figure 2 that if DD–RD effects are neglected, an erroneous prediction of even larger enhancements of the efficiencies with an increase in nanoparticle diameter is obtained, which illustrates the importance of accounting for the DD–RD effects.

Third, we note that the strain-induced enhancement for the scattering efficiency far exceeds the strain-induced enhancement for the extinction efficiency. This is because, as seen in equations (4) and (5), the scattering efficiency is proportional $|\beta_S|^2$, while the extinction efficiency is proportional to $\mathrm{Im}(\beta_S)$. Therefore, it is clear that the scattering efficiency will change more rapidly in response to changes in β_S than the extinction efficiency, thus leading to the larger gain in scattering efficiency due to tensile strain.

5.2. Strain effects on the local electric field (SERS) enhancements

One of the main motivations for the present work is to analyze the effects of strain on the local electric field, due to its importance in the resulting SERS enhancements that are possible for small metallic nanoparticles. In the present work, the SERS enhancement is defined as the fourth order power enhancement of the local electric (E)-field at the corresponding plasmon resonance wavelength for scattering, i.e. [48]

$$\rho(\mathbf{r}_m, \omega) = \left| \frac{\mathbf{E}(\mathbf{r}_m, \omega)}{E_{\mathrm{inc}}(\omega)} \right|^4, \tag{10}$$

where ρ is the SERS enhancement factor, $E_{\mathrm{inc}}(\omega)$ is the electric field due to the incident plane wave, and $\mathbf{E}(\mathbf{r}_m, \omega)$ is the total electric field at position $\mathbf{r}_m$. We emphasize that ρ is the quantity of interest for Raman-based single molecule detection within the chemistry community [6, 11].

Before discussing the results we have obtained regarding strain effects on the SERS enhancements, we discuss the approximations we have made in calculating the SERS enhancements. First, we note that we follow Kneipp *et al* [49] in calculating equation (10) in that we do not consider chemical contributions to the SERS enhancement due to the formation of chemical bonds and the hybridization of electrons between the molecular orbitals and the Bloch functions of silver; only electromagnetic enhancements are considered in the present work.

Second, we neglect E-field enhancements that may occur due to topological changes at the nanostructure surface brought about by the large mechanical strains that we have considered. For example, surface steps, and other discontinuities would likely result in a spherical nanostructure due to dislocations caused by the large mechanical strains. Furthermore, such surface topological changes have previously been found by Hao and Schatz [11] to result in significant enhancements to the local E-field. Finally, it is likely that the presence of defects would change the plasma frequency, and thus the free electron portion of the dielectric function, as well as the core contribution to the dielectric function. However, in the present work, we have considered only the changes in E-field due to

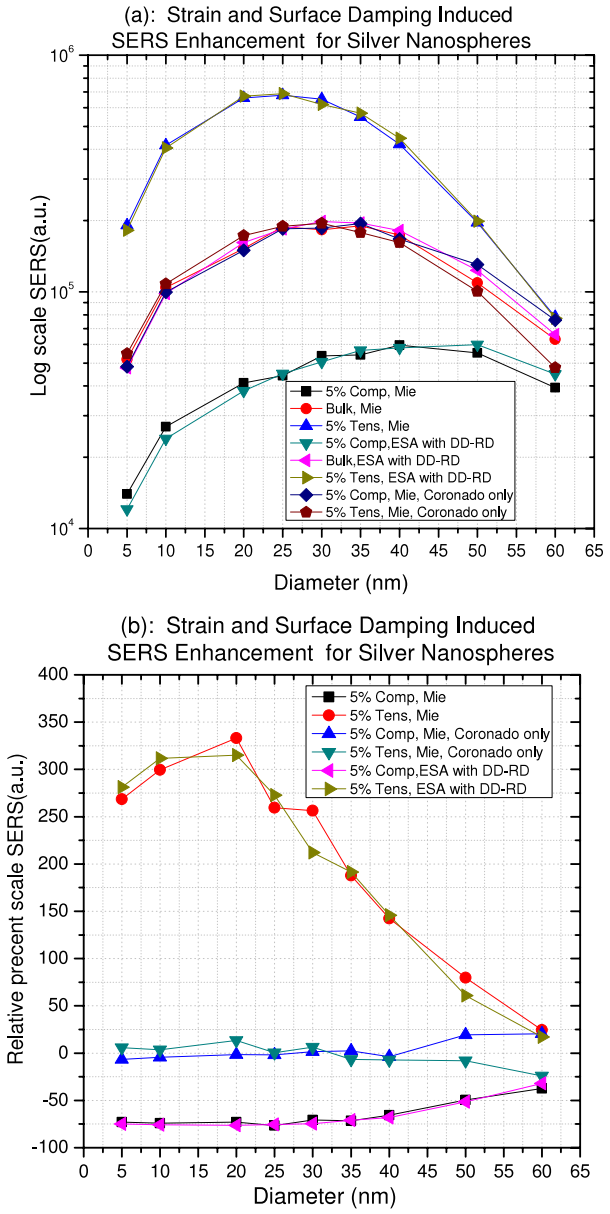

Figure 3. Strain effects on SERS enhancements of spherical silver nanoparticles for a range of nanoparticle diameters.

strain, and not due to surface topological changes or defect-generated variations in the dielectric functions.

Figure 3 summarizes the effects of mechanical strain on the SERS enhancement factor for silver nanospheres with diameters ranging from 5 to 60 nm; figure 3 was generated by using equation (6) in conjunction with the radiation damping and dynamic depolarization-corrected polarizability $\beta_S^{\mathrm{DD-RD}}$ in equation (7). Again, we note the excellent agreement between the Mie theory results and the DD–RD-corrected ESA results.

The first trend of interest is that 5% compressive strain significantly reduces the SERS enhancement, with the reduction being more than 50% across the range of nanoparticle diameters that were considered. In contrast, 5% tensile strain is observed to significantly increase the SERS enhancements, particularly for nanoparticle diameters smaller than about 25 nm, where the SERS enhancement in figure 3(b) is found to be more than 300%.

The other major trend we discuss are the nanoparticle sizes for which the tensile mechanical strain is observed to lead to significant improvements in SERS enhancement, i.e. for nanoparticle diameters that are smaller than about 25 nm. Again, this suggests that the SERS enhancements due to tensile strain do not fundamentally change any physics associated with radiation damping effects, which as previously discussed decreases the magnitude of SERS as the silver nanosphere diameter increases [39, 44, 45]. We note that for unstrained silver nanoparticles, Meier and Wokaun [39] observed that radiation damping effects become significant for nanosphere diameters larger than 25 nm, which is in good agreement with the results in figure 3.

We also delineate the relative effect of geometric changes due to strain and the strain effects on the dielectric function on the SERS enhancements that are shown in figure 3. Specifically, if purely geometric changes due to strain (i.e. neglecting strain effects on the dielectric function) are considered in figure 3 through the Coronado only cases, an extremely small SERS enhancement is obtained. Thus, similar to the optical efficiencies in figure 2, the SERS enhancement in figure 3 appears to be nearly entirely due to the tensile strain effects on the dielectric function.

Interestingly, the nanosphere diameter at which the radiation damping effects begin to dominate (≈25 nm), is considerably smaller than the diameter at which radiation damping effects were found to degrade the strain-induced SERS enhancement for gold nanospheres studied in our previous work (110 nm) [38]. This is likely due to the fact that such radiation damping and retardation effects become significant only when the diameter is a non-trivial fraction of the plasmon resonance wavelength λ_M in the surrounding medium [50]. Because the λ_M is about 530 nm for spherical gold nanoparticles and 360 nm for spherical silver nanoparticles, this explains why silver nanoparticles experience radiation damping effects at much smaller diameters than do gold nanoparticles.

We continue our discussion by plotting in figure 4(a) the core and free electron contributions to the strain-induced SERS gain. As can be seen, for the smallest nanoparticle diameters (5 nm), the strain-induced gain in SERS due to the free electron contribution is about 65%. However, as the nanoparticle diameter increases, the free electron contribution gradually accounts for an increasing percentage of the overall strain-induced gain in SERS.

This finding mirrors the trend observed for the tensile-strain-induced $Q_{\mathrm{sca}}/Q_{\mathrm{ext}}$ ratio that is also plotted in figure 4(b), where the well-known trend that scattering becomes the dominant contribution to the extinction with increasing nanoparticle size is observed due to the increasing importance of the free electron contribution with increasing nanoparticle size. We note that figure 4(b) shows that the $Q_{\mathrm{sca}}/Q_{\mathrm{ext}}$ ratio increases faster with increasing nanoparticle diameter than does the $\rho_{\mathrm{free}}/\rho_{\mathrm{free+core}}$ ratio; this is because the resonance wavelength λ for silver is insensitive to strain as previously discussed and is about 360 nm for all values of strain, and thus via equations (4) and (5), the $Q_{\mathrm{sca}}/Q_{\mathrm{ext}}$ ratio can be converted into an expression that is proportional to x^3, where

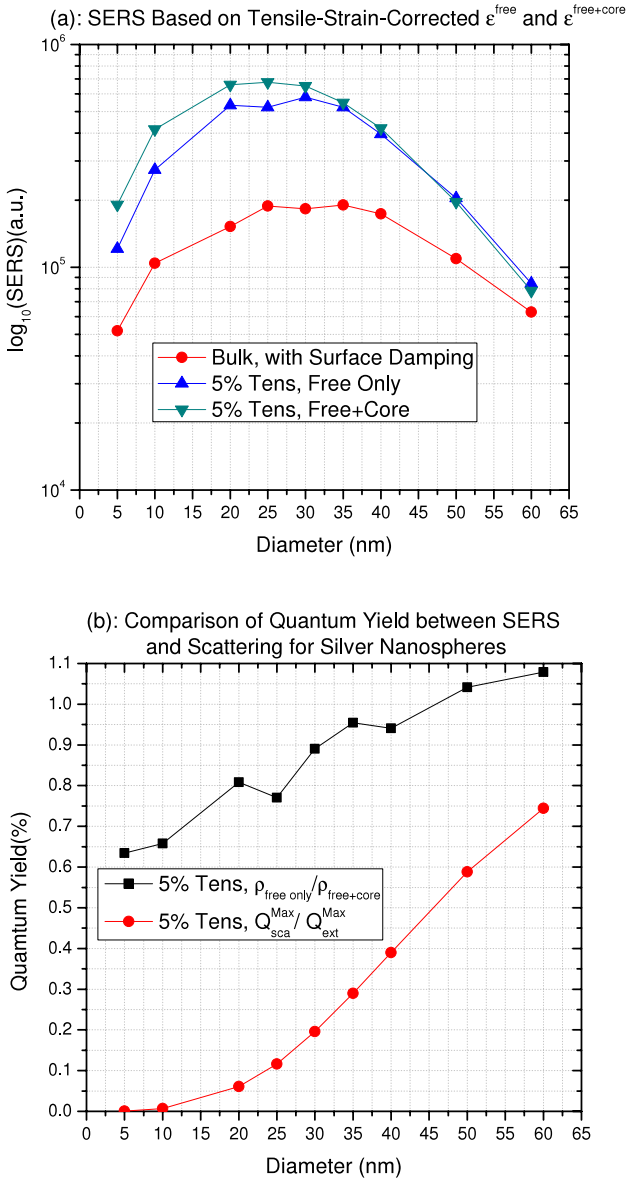

Figure 4. (a) Tensile-strain-induced SERS enhancements accounting for free electrons only and both free and core electrons of spherical silver nanoparticles for a range of nanoparticle diameters. (b) Delineation of free electron contribution to the strain-induced enhancement in scattering efficiency and SERS enhancement.

x is proportional to (r/λ), with r being the radius of the sphere. This highly size-dependent x^3 thus reflects the size-dependence of this ratio as described in figure 4(b).

We close this discussion of strain effects on the optical properties of silver nanospheres by noting the SERS enhancements that are possible for individual silver nanoparticles of different shapes and geometries. Such a study was performed by [11], who used numerical simulations based upon the discrete dipole approximation to study the SERS enhancements for spherical nanoparticles, along with triangular prisms, nanorods and spheroids. The SERS enhancements for those shapes ranged from about 1.2×10^7 to 2.5×10^7, which is slightly more than ten times the largest tensile strain-driven SERS enhancements for silver nanospheres predicted in the present work. While this demonstrates that silver nanospheres will not compete with the SERS enhancements seen using other nanostructure shapes even with the added strain-driven enhancements, it does suggest that strain may be a very useful tool for actively enhancing both the near and far field optical properties for other nanostructure geometries, which may exhibit a superior strain sensitivity to that of nanospheres; this will be studied in future work.

6. Conclusions

In conclusion, we have demonstrated by using analytic Mie scattering theory in conjunction with strain-corrected dielectric functions for silver that mechanical strain, and in particular tensile mechanical strain, can significantly enhance the local electric fields at the surfaces of silver nanoparticles, thus significantly increasing their SERS enhancement factors. For nanoparticle diameters smaller than about 25 nm, i.e. before radiation damping effects begin to reduce the strain-induced enhancements for both the far and near field optical properties, tensile strain was shown to enhance both the far field optical efficiencies between 50 and 150%, while simultaneously leading to near field SERS enhancements exceeding 330% as compared to unstrained silver nanospheres. For the tensile strain-driven SERS enhancement, the majority of the enhancement regardless of nanoparticle diameter was found to occur due to strain effects on the free electron dielectric function, and not due to strain-driven geometric changes of the nanoparticle shape or diameter. The present findings indicate the opportunity to actively engineer and enhance the optical particles of silver nanoparticles through the application of mechanical deformation.

Acknowledgments

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