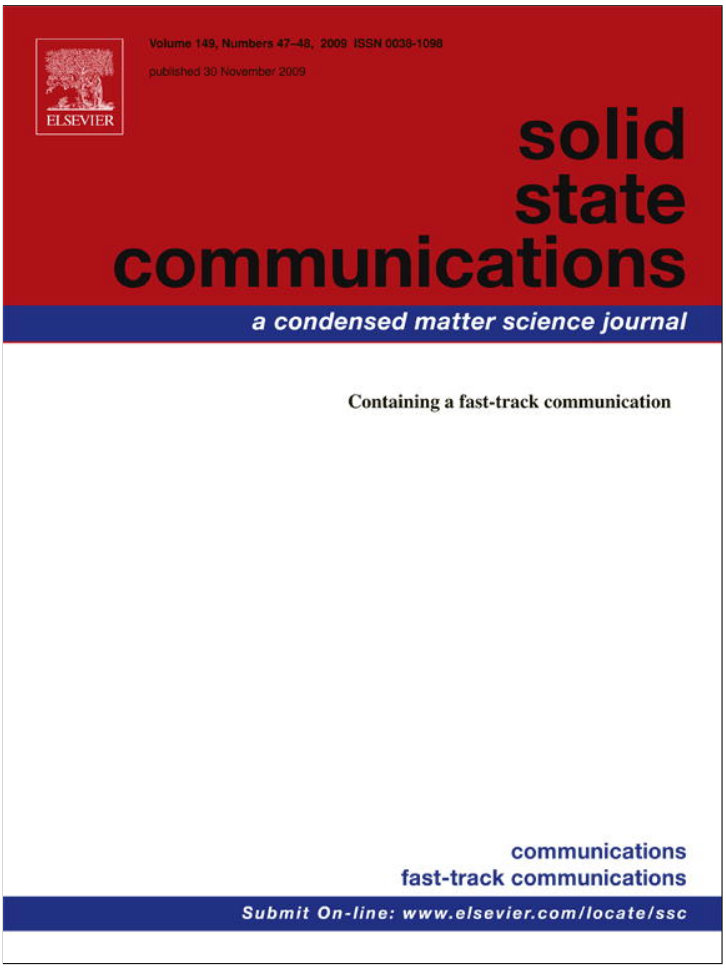

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Optical properties of metallic nanoshell composites: The effects of temperature and particle clustering

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ABSTRACT

The optical properties of a metallic nanoshell composite are studied theoretically using different effective medium theories with particular focus on the effects of variation in temperature and particle clustering on these properties. One unique result from our modeling is the persistent manifestation of the single-particle resonances of the individual nanoshells which cannot be found in a composite of *solid* particles. In addition, we observe red-shifts in the composite plasmon modes, as well as damping in the dielectric function spectrum as the temperature increases. Furthermore, a much greater red-shift will occur when these nanoshells coalesce to form fractal clusters in the composite, with the value of this shift increasing with decrease in the fractal dimension or increase in the cluster size. We further calculate the transmission at normal incidence through such composite thin films as a demonstration of how these effects can be observed experimentally.

1. Introduction

Since its first fabrication in 1998 [1], the metallic nanoshell has evolved to become one of the most versatile plasmonic systems, with significant potential applications from spectroscopic enhancements to cancer therapy [2]. Due to its high flexibility in the variations of the core and shell materials as well as in the aspect ratio, it possesses high tunability in its plasmonic resonances, covering the whole visible range and beyond. This has hence motivated a large number of studies in the past decade on the fundamental optical properties of this system, both in experiment and in theory [2]. Moreover, in applications, both individual nanoshells and composites made of these shells are of significance; and it seems that the study of the optical properties of the latter has started to receive attentions from researchers only in the last few years [3–5].

It is the purpose of our present study to report new observations from theoretical modeling on the optical behaviors of some of these composites which contain a collection of these nanoshells, dispersed randomly in the form of either isolated particles or in a clustered state throughout an insulating solid host. This mimics a kind of "nanoshell cermet", and is different from the recently studied photonic crystals composed of such shells [3,4]. The ellipsoidal shell composite studied in [5] is similar to ours, and the focus there has been on the effects from the particle shape distribution in the composite. Our focus here, however, will be on the effects from particle clustering of these shells, as well as from temperature variations on the optical properties of these composites, which previous work has not studied [5]. One motivation for the study of the temperature effects is from the recent proposition of drug-delivery applications via manipulations of these effects [6]. In addition, temperature-dependent optical bistability has been reported for composites of nanoshells made of a metallic core coated with a nonlinear dielectric [7]. We, however, study these effects over a much wider range of temperatures. Previously, we have studied these temperature effects on the optical properties of individual isolated nanoshells in their function as spectroscopic enhancers [8]. We shall employ the same temperature model for our present study of the composite; and as for the particle-clustering phenomenon, we shall assume that fractal clusters are formed in the composite and employ the previously available effective medium models from the literature. For simplicity, we shall only consider spherical nanoshells in the present study.

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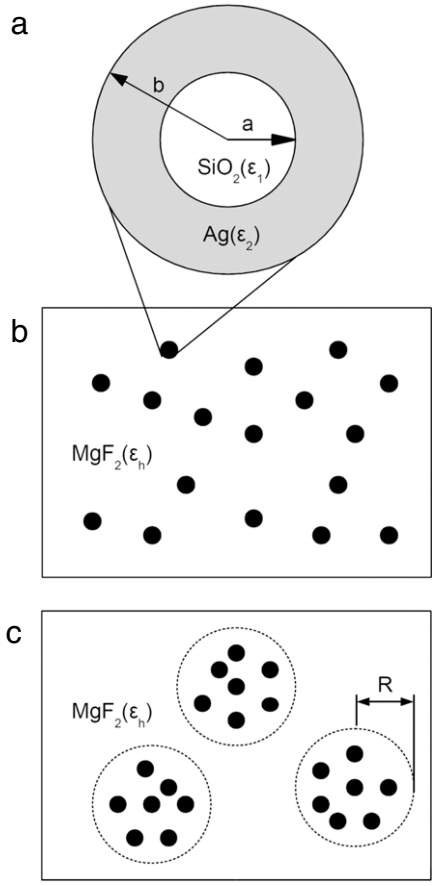

Fig. 1. Two different distributions of the nanoshell composites. (a) The geometry of the nanoshell with inner and outer radius a and b, respectively. The material of core/shell is SiO_2/Ag with dielectric functions $\varepsilon_1/\varepsilon_2$, embedding in the host medium MgF_2. (b) The three-dimensional random distribution of nanoshells; we call this the MG (Maxwell–Garnett) distribution. (c) Fractal cluster (FC) distribution of nanoshells. The averaged radius of clusters is denoted by R.

2. Theoretical model

We consider here a system of metallic nanoshells in a solid dielectric host with the shells distributed randomly, either in isolated or in clustered form, throughout the host as illustrated with various parameters specified in Fig. 1. Let us first recapitulate the essence of several models from previous literature which will be useful for our numerical studies in the present work. These include the following.

2.1. Equivalent homogeneous model for a nanoshell

To describe the optical properties of such a composite system within the context of effective medium theory (EMT), we first adopt the simple model of Li, Sun, and Chan (LSC) [3] to "replace" a single core–shell particle by an "equivalent homogeneous spherical particle". This model has been recently applied to the study of optical properties of nanoshell assembly [4] without providing many details for the justification of its validity. Here we shall take the opportunity to provide details for this model. For simplicity, we shall work in the strict electrostatic limit, ignoring the dynamic depolarization effects due to the finiteness of the optical wavelength [3,9]. This model assumes that the optical response of the shell in vacuum (with dipole polarizability α) can be replaced effectively by that of a homogeneous spherical particle of the same external size (i.e. radius b) with a dielectric function ε_S given by the standard result for the polarization of a sphere:

$$\vec{p} = \alpha\vec{E}_0 = \Omega_s\vec{P} = \Omega_s\frac{3}{4\pi}\frac{\varepsilon_S - 1}{(\varepsilon_S + 2)}\vec{E}_0, \tag{1}$$

where $\Omega_S = 4\pi b^3/3$ is the volume of the sphere and $\vec{p}, \vec{P}, \vec{E}_0$ are the induced dipole moment, polarization and external field, respectively. The result in Eq. (1) can then be rearranged to obtain the following result:

$$\frac{\varepsilon_S + 2}{\varepsilon_S - 1} = 3\Omega_s\left(\frac{1}{4\pi\alpha}\right). \tag{2}$$

Next, if we apply the same model to the following two hypothetical cases: (i) with just the core (dielectric constant ε_1 and radius a) immersed in an infinite medium of dielectric constant ε_2; and (ii) with the "effective particle" (dielectric constant ε_S and radius b) immersed in the same infinite medium as in (i), and demand the two cases to have the *same* polarizability (α') for the particle, we obtain the following results:

$$\frac{\varepsilon_1 + 2\varepsilon_2}{\varepsilon_1 - \varepsilon_2} = 3\Omega_1\left(\frac{1}{4\pi\alpha'}\right), \tag{3}$$

and

$$\frac{\varepsilon_S + 2\varepsilon_2}{\varepsilon_S - \varepsilon_2} = 3\Omega_2\left(\frac{1}{4\pi\alpha'}\right), \tag{4}$$

where $\Omega_1 = 4\pi a^3/3$ and $\Omega_2 = \Omega_S$. Eliminating the polarizability α' from Eqs. (3) and (4) leads to [3]

$$\frac{\varepsilon_s + 2\varepsilon_2}{\varepsilon_s - \varepsilon_2} = \left(\frac{b}{a}\right)^3\frac{\varepsilon_1 + 2\varepsilon_2}{\varepsilon_1 - \varepsilon_2}. \tag{5}$$

Thus, for a given nanoshell with all the dielectric functions and dimensions specified, Eq. (5) yields the dielectric function ε_S for the "effective spherical particle" of the same size (radius b), which, when put back into Eq. (2) will yield the well-known *exact* expression for the nanoshell polarizability in vacuum [see the Appendix].

2.2. EMT for randomly distributed nanoshells

Once the individual nanoshells can be replaced by an effective spherical particle of the same size as described by Eq. (5), we can apply the well-established EMT to obtain the dielectric response of the composite. For the case when the particles disperse randomly throughout the host (of dielectric constant ε_h), we have here the effective dielectric function $\bar{\varepsilon}$ given simply by the Maxwell–Garnett (MG) model in the form [10]

$$\frac{\varepsilon_s + 2\varepsilon_h}{\varepsilon_s - \varepsilon_h} = f\frac{\bar{\varepsilon} + 2\varepsilon_h}{\bar{\varepsilon} - \varepsilon_h}, \tag{6}$$

where f is the volume fraction of the particles.

2.3. EMT for clustered nanoshells

For the case when the particles coalesce to form fractal clusters (FCs) in the host, we apply the differential effective medium model available in the literature [11] and obtain the average dielectric function $\varepsilon(R)$ for a spherical FC of radius R, in the limit of low particle concentration given implicitly by the following cubic equation:

$$\frac{\varepsilon(R)}{\varepsilon_S(b)}\left[\frac{\varepsilon_h - \varepsilon_S(b)}{\varepsilon_h - \varepsilon(R)}\right]^3 = f', \tag{7}$$

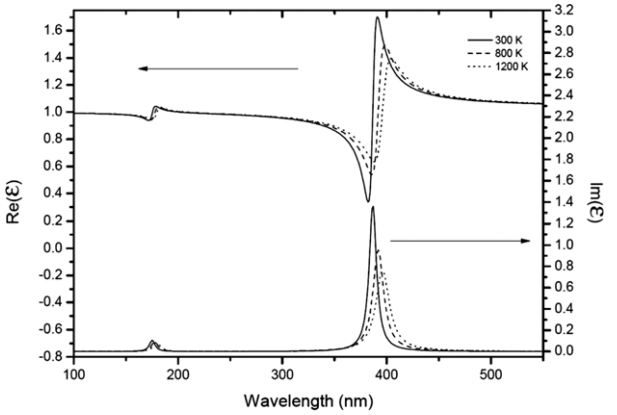

Fig. 2. Temperature dependence of dielectric function of nanoshell composites in MG distribution. The volume fraction is set at $f = 0.01$, and the aspect ratio is set at $(a/b) = (30\text{ nm}/50\text{ nm})$.

where $f' = \left[\frac{R}{b}\right]^{3(3-d_f)}$ is the volume fraction of the particles *in the cluster* with d_f the fractal dimension of the cluster. Note that we have explicitly stated the size of the effective particle (radius b) in Eq. (7). The dielectric function of the composite in this case will be obtained by applying the MG theory once more to a system with the same host but containing a randomly distributed collection of these "clustered particles" of radius R and dielectric constant $\varepsilon(R)$ obtained from solving Eq. (7). In addition, the concentration of these "clustered particles" will be given by a volume fraction $f_C = f/f'$, where f is the original given volume fraction of nanoshells in the composite. Hence, using Eq. (6) with $\varepsilon_S \to \varepsilon(R)$ and $f \to f_C$, we can finally obtain the effective dielectric function for the whole composite with the nanoshells forming fractal clusters in the host dielectric.

2.4. Model for temperature effects

To account for the temperature effects on the optical properties of these nanoshell composites, we assume that such effects are only significant for the metallic part of the shell and describe its dielectric response using the Drude model:

$$\varepsilon = 1 - \frac{\omega_P^2}{\omega\,(\omega + \mathrm{i}\omega_c)}, \tag{8}$$

where $\omega_C(T)$ is the collision frequency and $\omega_P(T)$ the plasma frequency, whose temperature dependence can be found from our previous work [9]. The collision frequency will have contributions from both phonon–electron and electron–electron scattering, as well as a surface scattering term from the two shell boundaries [9]:

$$\omega_c = \omega_{cp} + \omega_{ce} + \omega_s, \tag{9}$$

where the surface scattering term is given by

$$\omega_s = \frac{\mathrm{A}v_F}{[b(T) - a(T)]}, \tag{10}$$

with v_F being the Fermi velocity of the metal, A a geometrical factor of unity order of magnitude, and the shell radii as functions of temperature given by $b(T) = b_0\left[1 + \frac{\gamma}{3}(T - T_0)\right], \ldots$ etc., in terms of the volume expansivity of the metal. Thus Eqs. (8)–(10) provide a model for the temperature dependence of ε, which when used as ε_2 for the nanoshell together with the models in Sections 2.1–2.3 will describe the temperature variation of the optical properties for the nanoshell composite.

3. Numerical results

To illustrate the above models, we have studied numerically both the temperature and clustering effects on a composite of silver–glass core–shells in a dielectric host of magnesium fluoride: (core/shell/medium) = $(SiO_2/Ag/MgF_2)$. The reference temperature T_0 is set at 293 K, at which the dimensions and concentration of the shells are set with $a = 30$ nm, $b = 50$ nm, and $f_{shell} = 0.01$. The dielectric constants for the core and the host medium are taken as 2.25 and 1.93, respectively, and are assumed constants throughout; and that for the Drude metal can be found from our previous work [9] and references therein. Fig. 2 shows both the real and imaginary parts of the dielectric function of the nanoshell composite at three different temperatures as described by the MG theory. While the dipolar resonances of the composite plasmon modes ($\lambda = 400$ nm) are clearly seen, they are slightly red-shifted and the corresponding peak dielectric constant values are lowered with rise of temperature. This can easily be understood by referring to the lowering of the metallic plasmon frequency due to the decrease in electronic density and increase in electronic damping at high temperatures. The most unique feature of the spectra in Fig. 2 is the weak resonance that appears at $\lambda = 180$ nm, which is a manifestation of the "single-particle" nanoshell resonance. This has never been seen in a composite of *solid* particles and is unique for the nanoshell composite, as can be seen also in the subsequent figures. In the solid particle case, only resonances for the whole composite (i.e. the strong peaks) remain. To confirm this, we plot in Fig. 3 a comparison between a composite of solid spheres and shells, and this manifestation of the "single-particle resonances" can be seen only in the shell case, with a very minor dependence on the volume fraction of the particles. Fig. 4 shows how these properties vary when the nanoshells coalesce to form fractal clusters. The temperature is fixed at 300 K. Consistent with what was reported previously in the literature [11], we observe here that particle clustering among the nanoshells in the composite will lead to appreciable red-shifts in the surface plasmon resonance peak, - with these shifts being more dramatic for lower fractal dimensions (i.e. greater deviation from 3, see Fig. 4(a)) and larger cluster sizes (Fig. 4(b)). To possibly observe these changes in the optical properties of the nanoshell composite, we have plotted in Fig. 5 the transmission spectrum at normal incidence through a thin film made of such composite materials, for both non-clustering (Fig. 5(a)) and clustering (Fig. 5(b)) cases at three different temperatures. For the clustering case, we have fixed the cluster size $R = 10b$ and the fractal dimension $d_f = 2.5$, respectively. Note that in our modeling of this case, we have assumed that both the fractal dimension and cluster size stay unchanged with the rise of temperature, an assumption that should be reasonable for the present case with a *solid* host background. While the transmission dips correspond well to the plasmon resonant absorption peaks in the dielectric functions (both single-particle and composite resonances) for both cases, it is observed that the rise in temperature generally decreases the transmission slightly for both materials. From comparison between the results in Figs. 5(a) and 5(b), one observes the effect of particle clustering according to the FC model is to red-shift the composite resonance (at ∼400 nm in Fig. 5(a)) to a value of ∼1000 nm in Fig. 5(b), and to "create a new resonance" (at ∼130 nm) near the single-particle resonance wavelength, while leaving this latter resonance almost intact. This can further be confirmed by analyzing the results in Fig. 5(c) for a composite of solid particles where no single-particle resonance exists. As is clear from 5(c), one can observe again that the composite resonance (at ∼300 nm) is transformed into one at long wavelength (∼850 nm) and one at short wavelength (∼130 nm) due to fractal clustering. We have further confirmed that the short wavelength resonances (∼130 nm

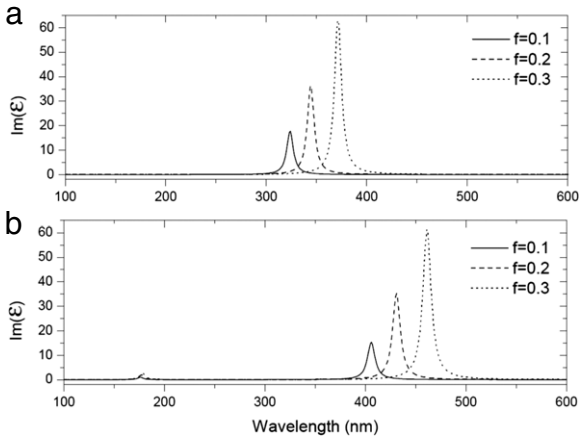

Fig. 3. The imaginary part of the dielectric functions of (a) solid sphere composites and (b) nanoshell composites in MG distribution with different volume fraction f. The temperature is fixed at 300 K for all plots.

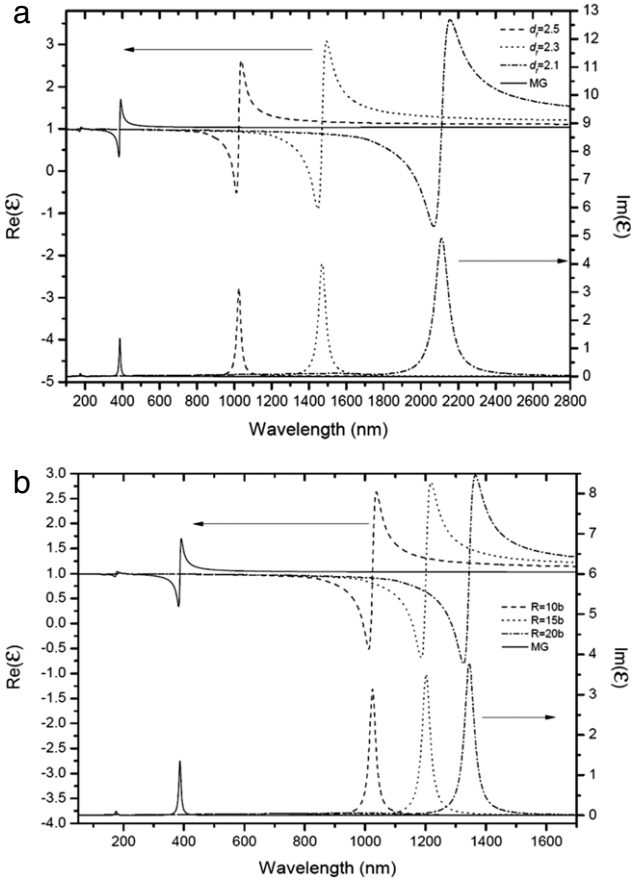

Fig. 4. (a) Fractal dimension and (b) cluster radius dependence of dielectric functions for nanoshell composites in FC distribution with the same parameters as in Fig. 2. In (a) the cluster radius is fixed at $R = 10b$, and in (b) the fractal dimension is fixed at $d_f = 2.5$. The temperature is fixed at 300 K for all plots.

in both Figs. 5(b) and 5(c)) are due to the resonance of a *single* cluster (radius R); whereas the long wavelength ones (∼1000 nm in Fig. 5(b) and 850 nm in Fig. 5(c)) arise from the characteristic absorptions of the *average* of all these clusters. All the above observations are consistent with the results reported previously in Ref. [11]. We believe that all these new signatures for particle clustering and shell particles in the composite could be checked against experiments without too much difficulty.

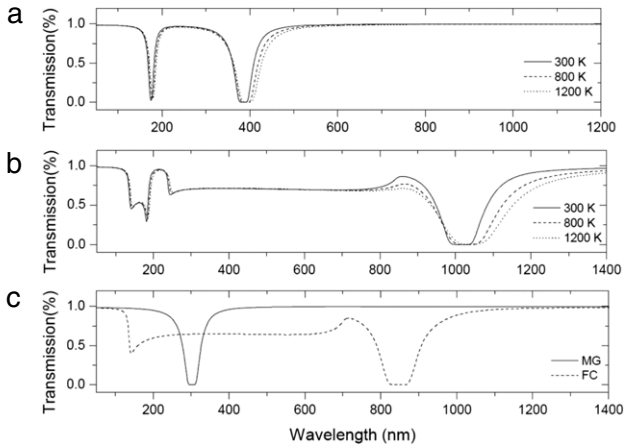

Fig. 5. The temperature dependence of the transmission spectrum for nanoshell composite films in (a) the MG case and (b)the FC case with the same parameters as in Fig. 2. (c) The transmission of solid sphere composite films in MG and FC cases. The temperature in (c) is fixed at 300 K and the thicknesses of all films are set at $d = 1\,\mu$m.

4. Conclusion

In this communication, we have provided a simple model for the description of the optical properties of metallic nanoshell composites. In particular, our model can account for both the temperature and particle-clustering effects on these properties. Among the several interesting results we obtain from our modeling such as red-shifts in plasmon resonances due to either temperature rise or fractal clustering of particles, we regard the most interesting feature revealed from our work to be the persistent manifestation of single-particle resonances of the individual nanoshells in the spectra of the dielectric functions. These resonances, while not reported in previous studies of the optical properties of similar core–shell particle composites [5,12], can provide a new signature for the optical probing of this kind of material.

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Appendix

Here we show the consistency of the LSC model, i.e. Eqs. (2)–(5), by explicitly deriving the exact dipole polarizability for the nanoshell. Thus, solving for ε_S from Eq. (5) we obtain

$$\varepsilon_S = \frac{q+2}{q-1}\varepsilon_2, \tag{A.1}$$

where $q \equiv (b/a)^3\,(\varepsilon_1 + 2\varepsilon_2)/(\varepsilon_1 - \varepsilon_2)$. Substituting (A.1) into (2) and solving for α leads to

$$\begin{aligned}\alpha &= b^3\left(\frac{\varepsilon_S - 1}{\varepsilon_S + 2}\right) = b^3\left(\frac{(q+2)\,\varepsilon_2 - (q-1)}{(q+2)\,\varepsilon_2 + 2\,(q-1)}\right)\\ &= b^3\left(\frac{q\,(\varepsilon_2 - 1) + 2\varepsilon_2 + 1}{q\,(\varepsilon_2 + 2) + 2\varepsilon_2 - 2}\right)\\ &= b^3\left(\frac{b^3\,(\varepsilon_1 + 2\varepsilon_2)\,(\varepsilon_2 - 1) + a^3\,(2\varepsilon_2 + 1)\,(\varepsilon_1 - \varepsilon_2)}{b^3\,(\varepsilon_1 + 2\varepsilon_2)\,(\varepsilon_2 + 2) + 2a^3\,(\varepsilon_2 - 1)\,(\varepsilon_1 - \varepsilon_2)}\right),\end{aligned} \tag{A.2}$$

which is the exact expression for the dipolar polarizability of the nanoshell [13].

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