Second harmonic generation by metal core - dielectric shell spherical nanoparticles: spatial vs. plasmon resonances

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Abstract. An analytical study of the second harmonic generation by metal core - dielectric shell spherical nanoparticles was performed. Dependences of the second harmonic intensity on the dielectric shell thickness were calculated. We demonstrated that the thin coating allows tuning surface plasmon resonance wavelength, whereas in presence of the thick shell spatial Mie resonances occur. Estimated efficiency of these resonances surpasses the impact of the plasmon enhancement in the second harmonic generation. Possibility to combine plasmon (metal) and spatial (dielectric) resonances to achieve even more advantage in the second harmonic generation was shown.

1. Introduction
The second harmonic generation (SHG) by nanoparticles (NPs) is under extensive study due to its applicability in sensing [1]. Metal NPs in which the nonlinear response can be greatly enhanced by the surface plasmon resonance (SPR) phenomenon [2, 3] are of particular interest. Their plasmonic properties are very sensitive to the NPs composition/structure, environment, size and shape [4-7] that allows spectral positioning of the SPR. Particularly, a thin dielectric covering of a metal NP offers a possibility to tune the SPR wavelength that was multiply demonstrated [8, 9]. At the same time, a thick coating does not affect NPs plasmonic properties more than the thin one, but supports spatial Mie resonances. Using these effects, significant advantage in the SHG can be achieved. In this study, we theoretically analyze the influence of the dielectric cover on the efficiency of the SHG by spherical metal NPs focusing on the potential of combining the plasmon (metal) resonances with the spatial (dielectric) ones. To follow general features of the process we limit our consideration by a model with a Drude-metal core and a non-dispersive isotropic dielectric shell.

2. Theory
Solution of the problem of nonlinear scattering by NPs is based on the nonlinear Mie theory [10-12] and includes three steps: 1) solution of the classical Mie problem to calculate fundamental electromagnetic fields, 2) definition of nonlinear sources using these fields, and 3) calculation of...
the second harmonic (SH) fields. A similar problem for the inverted structure (dielectric core -
metal shell) has recently been considered [10]. We partly follow their methodology and all the
details can be found in Ref. 10, despite that solution cannot satisfy the present problem since
different fields expansions should be used.

We consider a spherical metal particle (core) of radius \(a\) coated with a spherical layer (shell)
of outer radius \(b\) and thickness \(h = b - a\) illuminated by the X-polarized and Z-directed plane
light-wave of frequency \(\omega\) (wavelength \(\lambda\)). Using the solution of the linear Mie problem for
core-shell spherical NPs (expansions of the electromagnetic fields via vector spherical harmonics
and expressions for the expansion coefficients can be found elsewhere [13, 14]) we define spatial
distribution of nonlinear sources. Only surface second order susceptibility, \(\chi_s\), is considered
because the materials are centrosymmetric. We also presume that the core-shell interface is the
only nonlinear surface and that the tensor component \(\chi_{s\perp\perp}\) dominates. In this case, the surface
second order polarization is [10]:

\[
P_{s\perp}^{2\omega}(2\omega) = \chi_{s\perp\perp}^2 E_{\perp}(\omega)E_{\perp}(\omega),
\]

where \(E_{\perp}(\omega)\) is the normal-to-the-surface component of the fundamental (at frequency \(\omega\))
field at the core-shell interface. The expression for the nonlinear polarization given by equation
(1) needs to be expanded via certain components of the vector spherical harmonics. Here we
omit this technical step, details of which can be found elsewhere [10, 11].

Next, we derive the SH electromagnetic fields generated by the calculated nonlinear sources.
The following boundary conditions for transversal components of the SH electric, \(E(2\omega)\), and
magnetic, \(H(2\omega)\), fields at the core-shell interface are used:

\[
\begin{align*}
\mathbf{E}_{\text{shell}}^{\phi}(2\omega) - \mathbf{E}_{\text{core}}^{\phi}(2\omega) &= -\frac{4\pi}{\varepsilon_{\text{shell}}(2\omega)} \nabla_{\phi} P_{s\perp}^{1}(2\omega), \\
\mathbf{H}_{\text{shell}}^{\phi}(2\omega) - \mathbf{H}_{\text{core}}^{\phi}(2\omega) &= \frac{4\pi}{c} 2i\omega [\hat{e}_r \times \mathbf{P}_{s\perp}^{1}]_{\phi},
\end{align*}
\]

where \(r, \phi\) denote the orts of the spherical coordinate system, \(\hat{e}_r\) is a corresponding unit
basis vector, \(\varepsilon_{\text{shell}}(2\omega)\) is the dielectric permittivity of the shell. Boundary conditions at the outer
interface are trivial. Using these equations, we determine the SH fields distribution throughout
the space. Finally, we present the derived equation to calculate the total SH intensity:

\[
W_{2\omega} = \frac{c}{8\pi^2 K_{\text{out}}} \sum_{n=1}^{\infty} \left[ \frac{2n(n+1)}{2n+1} |C_{0n} a_n^{2\omega}|^2 + \frac{2(n-1)n^2(n+1)^2(n+2)}{2n+1} |C_{2n} a_n^{2\omega}|^2 \right],
\]

where

\[
a_n^{2\omega} = \psi_n(m_1x) \frac{im_1[\psi_n'(m_2x) - A_n \chi_n'(m_2x)]}{\psi_n(m_1x) m_2 \xi_n'(y)|\psi_n(m_2y) - A_n \chi_n(m_2y)| - \xi_n(y)|\psi_n'(m_2y) - A_n \chi_n'(m_2y)|},
\]

\[
C_{mn} = -\frac{1}{2} \left\{ \int_{-1}^{1} P_{n1}(t) P_{m1}(t) dt \right\}^{-1} \chi_{s\perp\perp}^{2n+1}
\cdot \sum_{n_1,n_2=1}^{\infty} n_1(n_1+1)n_2(n_2+1) E_{n_1} E_{n_2} d_{n_1}^{n_2}(m_1x) j_{n_1}(m_1x) j_{n_2}(m_2x) (m_1x)^2 \int_{-1}^{1} P_{n1}(t) P_{m1}(t) dt, \]

\[
d_{n}^{n^2} = \frac{1}{\psi_n'(m_1x) m_2 \xi_n'(y)|\psi_n(m_2y) - A_n \chi_n(m_2y)| - \xi_n(y)|\psi_n'(m_2y) - A_n \chi_n'(m_2y)|},
\]

\[
A_n = \frac{m_2 \psi_n'(m_1x) \psi_n(m_2x) - m_1 \psi_n(m_1x) \psi_n'(m_2x)}{m_2 \psi_n'(m_1x) \xi_n(m_2x) - m_1 \psi_n(m_1x) \xi_n'(m_2x)},
\]
\( x = \frac{2\pi n_{\text{core}}}{\lambda}, \quad y = \frac{2\pi n_{\text{shell}}}{\lambda} \) are dimensionless size parameters; \( m_1 = \frac{n_{\text{core}}}{n_{\text{out}}} \), \( m_2 = \frac{n_{\text{shell}}}{n_{\text{out}}} \) are relative refractive indices; \( \psi_n, \xi_n, \chi_n \) are, respectively, Riccati-Bessel spherical functions of the first kind, Riccati-Bessel spherical functions of the second kind and Riccati-Hankel spherical functions of the first kind (sometimes called Riccati-Bessel spherical functions of the third kind); \( K_{\text{out}} \) is the SH wavenumber in the surrounding medium; \( j_n \) - a spherical Bessel function of the first kind; \( P_{m,n} \) - associated Legendre polynomial; \( E_n = E_0 i^{n} \frac{2n+1}{n(n+1)} \), \( E_0 \) is the incident field magnitude further taken as unit; \( n_1, n_2, n \) are multipole orders of two fundamental and one SH modes, respectively. Note that all the frequency-dependent factors in equation (5) should be taken at frequency \( 2\omega \).

3. Results

We calculate the spectra of the SHG by a spherical NP of Drude metal covered with a differently thick non-dispersive dielectric shell with permittivity \( \varepsilon_{\text{shell}}=4.0 \) using the analytical solution given by equation (4). The plasma wavelength of the metal was chosen \( \lambda_p=200 \text{ nm} \) and relaxation rate \( \gamma=3 \cdot 10^{13} \text{ sec}^{-1} \) to consider the behaviour of SPRs in the visible range.

3.1. Thin shell case

We fix the radius of the NP, 5 nm, while the thickness of the shell is varied up to 20 nm. Dependences of the SH intensity on the fundamental wavelength are presented in figure 1a.

![Figure 1](image-link)

Figure 1. a) SH intensity spectra of 5 nm in radius spherical NP of Drude-metal covered with a differently thick dielectric shell (\( \varepsilon_{\text{shell}}=4.0 \); the shell thickness is labelled near each spectrum; the curves are separated along y-axis with the offset of \( 10^4 \)). b) SH intensity, fundamental wavelength \( \lambda=1000 \text{ nm} \), vs. shell thickness. These spectra demonstrate four resonance peaks, which origin in a non-coated NP was discussed elsewhere [12]. Briefly, short-wavelength peaks are quadrupole and dipole SPRs of the fundamental wave, whereas long-wavelength ones are resonances of the SH wave. The quadrupole peaks appear in the nonlinear spectra of the small NP because the pure dipole mechanism of the nonlinear interaction (two dipole fundamental modes beget a dipole SH mode) is forbidden by the spherical symmetry [11, 12] and the quadrupole impact is essential. The SPRs red-shift with the shell thickness increasing that, albeit being a well-known phenomenon, offers a way to tune SPR wavelength - see figure 1b where the dependence of the SH intensity on the shell thickness at the fundamental wavelength \( \lambda=1000 \text{ nm} \) is shown. The peaks marked with the arrows in figure 1b correspond to the shell thicknesses at which the fundamental wavelength coincides with doubled dipole and quadrupole SPR wavelengths. Essentially, in figure 1b it can be seen that the SH signal for thicker coatings stays three orders higher than one from the
non-coated NP in spite of detuning the resonance. This originates not only from the proximity of the resonance but also from the monotonic increase of both resonant and non-resonant local fields when the particle is embedded in an optically denser medium. This effect arises from a plain fact that the local electric field of a spherical inclusion grows with increasing permittivity of the outer medium in accordance with formula:

\[ E_{\text{loc}} \sim \frac{3\varepsilon_{\text{out}}}{\varepsilon_{\text{Me}} + 2\varepsilon_{\text{out}}} E_0, \]  

where \( \varepsilon_{\text{Me}} \) and \( \varepsilon_{\text{out}} \) are permittivities of the inclusion and the outer medium, respectively. \( \varepsilon_{\text{out}} \) in the numerator of equation (9) acts as a general scale factor for both resonant and non-resonant fields. In the case of a core-shell NP, the shell can be treated as an effective outer medium, which permittivity monotonically grows up to \( \varepsilon_{\text{shell}} \) with coating thickness. Note that this effect does not depend on the SPR position and, therefore, it is of general nature. Moreover, in a more lossy metal, like gold, it dominates the resonant enhancement. We discussed this effect in details in our previous paper [15].

### 3.2. Thick shell case

Above we considered thin, up to a few particles radii, shells. Such shells affect NPs plasmonic properties while the electromagnetic fields are not fully localized in the coating layer and the NP feels the surrounding depending on the shell thickness. A different kind of influence takes place in a thick, about an order of optical wavelengths, shells because of spatial Mie resonances. In figure 2 we present the dependence of the SH intensity on shell thickness at fundamental wavelength \( \lambda=1000 \text{ nm} \) of a covered (\( \varepsilon_{\text{shell}}=4.0 \)) spherical, 5 nm in radius, NP of Drude-metal (\( \lambda_p=200 \text{ nm}, \gamma=3 \cdot 10^{13} \text{sec}^{-1} \)). In all the further calculations the metal core is the same. Essentially, figure 2 represents an extension of figure 1b.

![Figure 2. SH intensity vs. shell thickness, fundamental wavelength \( \lambda=1000 \text{ nm} \).](image)

Two thick-shell peaks in figure 2, marked with I and II, are the spatial Mie resonances. Peak I corresponds to the spatial resonance of the SH wave, whereas peak II corresponds to the spatial resonances of both SH and fundamental waves (the SH wave resonates in the next order). Important to note that the efficiency of these Mie resonances surpasses the plasmonic enhancement (the thin-shell peaks) by 1.5-2 orders. This follows from the well-known general dependence of the SHG intensity: \( W_2 \sim |E_{2\omega}|^2|E_\omega|^4 \) [3]. The SPR enhancement relates only to one factor (the SH field \( E_{2\omega} \) in this case) if the NP is not specifically tailored [16], whereas spatial resonance II affects both fields at once; basically, the 6th power beats the 2nd. Thus, thicker coating is more efficient for the SHG regardless the SPR position, and about 5-6 orders total increase compared to non-covered NPs can be provided.
The shell which thickness is above a few NPs radii barely affects NPs plasmonic properties and the SPR position in particular. This offers an appealing possibility to combine the plasmonic (metal) enhancement with the spatial (dielectric) one by specific choice of the excitation wavelength. In figure 3 we demonstrate dependences of the SH intensity on the shell thickness at fundamental wavelengths $\lambda=603$ nm (dipole SPR wavelength of the NP covered with the thick shell with $\varepsilon_{\text{shell}}=4.0$) and $\lambda=1206$ nm (doubled dipole SPR wavelength).

![Figure 3](image-url)  
**Figure 3.** The SH intensity vs. shell thickness, fundamental wavelengths $\lambda=1206$ nm (a) and $\lambda=603$ nm (b). The dependences are normalized by the SHG by the non-covered NP.

The marks, I and II, of the peaks refer to ones introduced in figure 2 (marks I* and II* in figure 3b indicates the next orders of the corresponding resonances). Note that in figure 3 we normalize the dependences by the SH signal from the non-covered NP. In the case of combining the resonances the advantage in the SHG is more significant: almost 8 orders when the SH wave is SPR-enhanced and 10 orders when the fundamental wave is SPR-enhanced. However, one should note that adjusting the fundamental wavelength to the SPR results in the SH wave being ultraviolet (UV), and many dielectric materials typically have substantial losses in the UV region. We consider this effect introducing an imaginary part to the dielectric permittivity of the shell at the SH frequency: $\varepsilon_{\text{shell}}(2\omega)=4.0+3.0i$, the dielectric permittivity at fundamental frequency being the same: $\varepsilon_{\text{shell}}(\omega)=4.0$. In this case, the dependence of the SH intensity on the shell thickness at fundamental wavelengths $\lambda=603$ nm is presented in figure 4.

![Figure 4](image-url)  
**Figure 4.** The SH intensity vs. shell thickness, fundamental wavelength $\lambda=603$ nm. The losses in the shell at the SH frequency are introduced: $\varepsilon_{\text{shell}}(2\omega)=4.0+3.0i$; $\varepsilon_{\text{shell}}(\omega)=4.0$.

The SH intensity drastically drops for thicker coatings if the absorption in the shell is taken into account. Therefore, despite the fact that the SPR enhancement of the fundamental wave provides more intense SHG, the UV losses of the shell can suppress this effect.
4. Conclusion
We theoretically analyzed the influence of the dielectric cover on the efficiency of the SH scattering by spherical metal NPs. The possibility to adjust SPR to a certain wavelength by covering a NP with a thin shell was demonstrated. A few orders non-resonant growth of the SHG resulted from the increase of the NPs local fields under the thin coating was shown. We considered thicker, up to an order of optical wavelengths, shells supporting spatial Mie resonances, which efficiency surpasses the SPR impact in the SHG. Moreover, since the thicker shell does not affect the NPs SPR position, the SPR can be easily combined with the spatial Mie resonances. Advantage in the SHG in this case relatively to non-coated NPs was evaluated: up to 8 orders when the SH wave is SPR-enhanced and about 10 orders when the fundamental wave is SPR-enhanced. However, we demonstrated that in the latter case the SHG efficiency can be supressed by UV losses which are typical for many dielectrics.

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