Size dependent local field enhancement factor of CdSe based core@shell spherical nanoparticles

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Abstract
We investigated the size dependent local field enhancement factor (LFEF) of CdSe@Ag and CdSe@ZnSe@Ag core/shell spherical nanoparticles theoretically and numerically within the framework of quasi-static approximation. From the potential distributions in the core, shell(s), and host medium, and using the modified Drude-Sommerfeld model, we separately obtained the expressions for LFEF of core/shell and core/spacer/shell nanocomposites. By changing the sizes of each of the components of the nanocomposites in these expressions, we found that the LFEF of CdSe@Ag increases with a decrease in the size of the core. At the same time, the resonance peaks are red shifted in the inner interface and blue shifted in the outer interface of the shell. The result also reveals that whether the shell radius is kept constant or decreased, increasing the core size produces a lower field enhancement factor showing that the core size is a crucial parameter to change the field enhancement factor of the dielectric core and metal shell nanoparticle (NP). When the spacer (ZnSe) is placed between the core (CdSe) and the shell (Ag), the resonance peaks increased with increase in the size of the core which was not observed in the case of the two layered core/shell nanocomposites having the same core and shell sizes. We also found that placing the spacer and varying the sizes of the core, the spacer, and the shell show different effects on the LFEF of the nanocomposite. The possibility of obtaining size dependent LFEF by adjusting the sizes of nanoparticles makes these nanocomposites attractive for applications in nonlinear optics, photocatalysis, and optoelectronics.

1. Introduction
Recent studies show that core/shell nanocomposites have attracted increasing research interest due to their outstanding properties such as versatility, tunability, and stability [1,2]. A core/shell nanocomposite consists an inner core and outer shell(s) that is composed of different materials. The combination of different material properties in a single core–shell system leads to several novel properties for potential applications in various fields such as electronics, optics, biomedicine, environmental science, materials, energy, magnetism, and catalysis [3,4]. Moreover, the properties of these core/shell materials can be easily tuned by varying the size, shape, morphology as well as the type of the core, shell, and embedding medium [5–7].

Among the widely studied core–shell nanocomposites is the CdSe-based quantum dots (QDs). In particular, the emission intensity of CdSe QDs can be increased several times when it is capped with a ZnS shell to form a CdSe/ZnS core–shell structure [8]. In addition, CdSe nanocrystals are considered as the most promising emitting materials in the visible spectral region because their emission color can dramatically be adjusted from blue to red. Wide band gap semiconductors such as ZnS, CdS, and ZnSe can be used as the shell material [9] to cap a CdSe core. But, among these semiconductors, ZnSe over coated CdSe nanoparticles have shown advantages that not only the bandgap of ZnSe (2.72 eV) is larger than that of CdSe (1.76 eV), but also it has shown low toxicity as compared to CdS and ZnS [10]. Moreover, its lattice parameter and binding energy are 5.67 Å and 20 meV, respectively, while the band gap alignment is of type I, where both electrons and holes are...
confinned in the CdSe core [11–13]. The lattice parameter mismatch of ZnSe relative to the CdSe core (6.3%) is significantly smaller when compared with the most commonly used ZnS shell (10.6%) material [14, 15]. All these material parameters makes ZnSe an excellent shell material to cap a CdSe core in a core–shell nanocomposite.

In support of this, experimental studies show that when CdSe is covered with ZnSe, the optical properties of the combination is enhanced [16]. It was also reported that CdSe@ZnSe core/shell quantum dot are novel materials incorporating CdSe core in a ZnSe shell [17]. For instance, the photoluminescence intensity of a CdSe@ZnSe core–shell nanocomposites can be significantly enhanced by coating (capping) the CdSe core with a few layers of ZnSe shell [18]. But, to the best of our knowledge, few or no theoretical and numerical studies were carried out to support those many experimental works. Moreover, as the heterostructures formed with metal and semiconductor composite nanostructures provide another efficient opportunity for tuning the unique optical properties of nanoparticles [19], the plasmonic effects are also found to be interesting. For CdSe based core/shell nanostructures, the effect of the sizes of the core, the shell (metal), and the spacer (semiconductor) on the local field enhancement factor (LFEF) were not further studied yet. Hence, this study focuses on the theoretical and numerical investigations of the size dependent LFEF of CdSe@Ag and CdSe@ZnSe@Ag core/shell spherical nanoparticle embedded in the host matrix, SiO<sub>2</sub>.

2. Theoretical models and calculations

2.1. Core and single shell spherical nanoparticles

When the size of a particle is much smaller than the wavelength of the incident electromagnetic radiation [20], the electric field may be considered to be spatially uniform over the whole range of the particle [21]. Consequently, the particle may be represented by an oscillating dipole and this is known as the quasi-static approximation [22, 23]. This approximation is important for a qualitative understanding of the interaction of light with nanoparticles as it considerably simplifies the mathematical analysis.

In this paper, we considered a model of spherical core@shell nanoparticle in the quasi-static limit. In this approach, the electrostatic solution can easily be calculated by solving the Laplace’s equation. In our model, we separately considered CdSe@Ag and CdSe@ZnSe@Ag both embedded in a dielectric material. As shown in figure 1, the radius of the core is \( r_1 \) and its dielectric permittivity is \( \varepsilon_1 \). The shell is characterized by the radius \( r_2 \) and dielectric permittivity \( \varepsilon_2 \) (where \( r_1 < r_2 \)). The embedding material (SiO<sub>2</sub>) has an electric permittivity \( \varepsilon_3 \). The expressions needed to calculate the electric potential in the system under the quasi-static approach is given by [24, 25]. Accordingly, the electric potential in the dielectric core, the shell, and the surrounding medium can be written as

\[
\varphi_1(r, \theta) = -E_0 A r \cos \theta, \quad (r \leq r_1)
\]
\[
\varphi_2(r, \theta) = -E_0 \left( A_2 r - \frac{B_2}{r^2} \right) \cos \theta, \quad (r_1 \leq r \leq r_2)
\]

\[
\varphi_3(r, \theta) = -E_0 \left( r - \frac{B_3}{r^2} \right) \cos \theta, \quad (r \geq r_2)
\]

where, \(\varphi_1(r, \theta)\), \(\varphi_2(r, \theta)\), and \(\varphi_3(r, \theta)\) are the electric potentials in the dielectric core, metallic shell, and embedding medium, respectively. \(E_0\) is the incident electric field (chosen along the z-axis), \(r\) and \(\theta\) are the spherical coordinates of the observation point. The unknown coefficients \(A_1\), \(A_2\), \(B_2\), and \(B_3\) are to be calculated from the continuity conditions of the potential and the displacement vector at the interfaces of the dielectric core/metal and metal/embedding medium.

The local electric field \(E_1\) induced in the dielectric core of the nanocomposite is related to the incident electric field, \(E_0\), by the following equation [26]:

\[
E_1 = A_1 E_0.
\]

In this equation \((E_1 = A_1 E_0)\), the coefficient \(A_1\) can be shown to be given by

\[
A_1 = \frac{Q \varepsilon_2 \varepsilon_3}{p \Delta},
\]

where \(Q = n^2/(n - 1)\) and \(p = 1 - (\eta_1/\eta_2)^3\) is the volume fraction of the metal coated particle. Also, \(n\) represents the dimension of the problem, which for a spherical nano inclusion is 3. In equation (4), \(\Delta\) is given by

\[
\Delta = \varepsilon_2^2 + q \varepsilon_2 + \varepsilon_3,
\]

where

\[
q = \left( \frac{3}{2p} - 1 \right) \varepsilon_1 + \left( \frac{3}{p} - 1 \right) \varepsilon_3.
\]

In this study, we used silver metal as a shell material. From the Drude-Sommerfeld model, the electric permittivity of metals is given by [27]:

\[
\varepsilon_2 = \varepsilon_\infty - \frac{\omega_p^2}{\omega(\omega + i\gamma)},
\]

where \(\varepsilon_\infty\) is the phenomenological parameter that represents the contribution of bound electrons to polarizability, \(\omega_p\) is the bulk electron plasma frequency, and \(\gamma\) is a parameter associated with damping in the bulk material. Clearly, equation (6) has real and imaginary parts which can be rewritten as

\[
\varepsilon_2 = \varepsilon_2' + i\varepsilon_2'',
\]

where

\[
\varepsilon_2' = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + \gamma^2}, \quad \varepsilon_2'' = \frac{\omega_p^3 \gamma}{\omega^2 + \gamma^2}.
\]

Now, substituting equations (5) and (7) into equation (4), we find that \(A_1\) becomes a complex function. Rather, it would be convenient to deal with the real quantity \(|A_1|\), which is called the enhancement factor. It can be presented as [28]:

\[
|A_1|^2 = \frac{81 \varepsilon_3^2}{4p^2} \left( \varepsilon_2'^2 + \varepsilon_2''^2 + q \varepsilon_2'^2 + \varepsilon_3 \right)^2 + \varepsilon_2''^2 \left( q + 2 \varepsilon_2'' \right)^2.
\]

### 2.2. Triple layer spherical nanoparticles

Here, let’s first consider a concentric n-layer nanocomposite that consists of multiple nanoscale layers of controllable thickness. The electrostatic potential for each of the regions (layers) satisfy the Laplace’s equation which is given by \(\nabla^2 \varphi = 0\), where \(\varphi\) is the electric potential associated with the electric field induced inside and outside the nanocomposite, \(\varphi_2\) is the region where electric potential is to be determined. Let, the dielectric function of the \(i\)th region be represented by \(\varepsilon_i\).

The potential distribution in the different regions of the n-layered nanocomposite is obtained by solving the Laplace’s equation. Accordingly, the potential \(\varphi_i\) in each region is given by [29]:

\[
\varphi_i(r, \theta) = \left( A_i r + \frac{B_i}{r^2} \right) \cos \theta,
\]

where \(A_i\) and \(B_i\) are the coefficients that corresponds to the electric monopole and dipole terms, respectively. These coefficients, \(A_i\) and \(B_i\) are to be determined by employing the appropriate boundary conditions for the
continuities of the tangential and normal components of the electric field and the displacement vector, respectively [30]. In our case, the spherical coordinates \( (r, \theta) \) are used, where \( r \) is the radial distance and \( \theta \) is the polar angle, while the direction of the applied field \( E_0 \) is chosen along the \( z \)-axis. Then, the electric field \( \mathbf{E} \) in the \( i^{th} \) region for the concentric spherical \( n \)-layered nanocomposite is obtained using the equation

\[
\mathbf{E}_i = -\nabla \Phi_i(r, \theta) \tag{10}
\]

where \( \Phi_i(r, \theta) \) is given by equation (9) [31]. Hence, the field takes the following form:

\[
\mathbf{E}_i = A_i (\cos \theta \mathbf{e}_r + \sin \theta \mathbf{e}_\theta) + B_i r^{-3} (2 \cos \theta \mathbf{e}_r + \sin \theta \mathbf{e}_\theta),
\]

Next, we consider a triple layered \((n = 3)\) core/shell nanostructure shown in figure 2, in which region one with \( i = 1 \) is a semiconductor core (CdSe) of dielectric function \( \varepsilon_1 \), while the outer region is the embedding medium (SiO\(_2\)) with real dielectric constant \( \varepsilon_{n+1} = \varepsilon_4 \). The dielectric functions of the spacer (ZnSe) and metallic shell (Ag) are \( \varepsilon_2 \) and \( \varepsilon_3 \), respectively. Similarly, the radii of the dielectric core, spacer, and metallic shell are denoted by \( r_1 \), \( r_2 \), and \( r_3 \), respectively.

For triple layered nanocomposite, there are four regions [32]. Thus, by extending equation (10) to the spherical nanocomposite, we find the electric fields in each of the four regions to be:

\[
\mathbf{E}_1 = A_1 (\cos \theta \mathbf{e}_r + \sin \theta \mathbf{e}_\theta) + B_1 r^{-3} (2 \cos \theta \mathbf{e}_r + \sin \theta \mathbf{e}_\theta), \tag{11}
\]
\[
\mathbf{E}_2 = A_2 (\cos \theta \mathbf{e}_r + \sin \theta \mathbf{e}_\theta) + B_2 r^{-3} (2 \cos \theta \mathbf{e}_r + \sin \theta \mathbf{e}_\theta), \tag{12}
\]
\[
\mathbf{E}_3 = A_3 (\cos \theta \mathbf{e}_r + \sin \theta \mathbf{e}_\theta) + B_3 r^{-3} (2 \cos \theta \mathbf{e}_r + \sin \theta \mathbf{e}_\theta), \tag{13}
\]
\[
\mathbf{E}_4 = A_4 (\cos \theta \mathbf{e}_r + \sin \theta \mathbf{e}_\theta) + B_4 r^{-3} (2 \cos \theta \mathbf{e}_r + \sin \theta \mathbf{e}_\theta), \tag{14}
\]

where \( A_4 = -E_0 \) and \( A_1, A_2, A_3, B_2, B_3, \) and \( B_4 \) are unknowns to be determined by imposing the appropriate boundary conditions. In particular, the coefficient \( B_1 = 0 \), since the magnitude of the electric field in the dielectric core is constant.

To investigate the LFEF inside the concentric sphere, it is suffice to determine the electric field induced inside the dielectric core. This means that (since \( B_1 = 0 \)), we only need to determine the coefficient \( A_4 \) found in equation (11). Hence, employing the relevant boundary condition at the interfaces, this coefficient can be shown to have the following form:

Figure 2. Triple layer spherical nanostructure embedded in host matrix.
\[ A_4 = \frac{27 \varepsilon_2 \varepsilon_3 \varepsilon_4}{2 \varepsilon_f M} E_0, \]  
(15)

where

\[ M = \gamma_1 \varepsilon_3^2 + \gamma_2 \varepsilon_3 + \gamma_3, \]

\[ f_1 = 1 - \left( \frac{n}{n_0} \right)^3 \]

\[ \gamma_1 = f_1 (\varepsilon_1 - \varepsilon_2) + 3 \varepsilon_3, \]

\[ \gamma_2 = \left( \frac{3}{f_2} - 1 \right) \left[ \frac{3}{2} \left( \frac{\varepsilon_1}{2} + \frac{2 \varepsilon_3}{3} \right) \varepsilon_2 + f_1 (\varepsilon_1 - \varepsilon_2)(\varepsilon_3 - \varepsilon_2) \right] \]

\[ + \varepsilon_2 \left[ f_1 (\varepsilon_1 - \varepsilon_2) - \varepsilon_2 - \frac{3}{2} \varepsilon_2 \right], \]

\[ \gamma_3 = \varepsilon_2 \varepsilon_4 (3 \varepsilon_1 + 2f_1 (\varepsilon_2 - \varepsilon_4)), \]

Substituting equation (15) into equation (11), the magnitude of induced field inside the dielectric core is found to be

\[ E_i = \frac{27 \varepsilon_2 \varepsilon_3 \varepsilon_4}{2 \varepsilon_f M} E_0. \]  
(16)

The coefficient of \( E_0 \) in equation (15) is the local field enhancement factor (F). That is,

\[ F = \frac{E}{E_0} = \frac{27 \varepsilon_2 \varepsilon_3 \varepsilon_4}{2 \varepsilon_f M}, \]  
(17)

and the modulus square of the LFEF becomes:

\[ |F|^2 = \left| \frac{27 \varepsilon_2 \varepsilon_3 \varepsilon_4}{2 \varepsilon_f M} \right|^2. \]  
(18)

The optical properties of metals can be described by the Drude-Sommerfeld model of the frequency-dependent dielectric function, \( \varepsilon(\omega) \) [33]. In our case (i.e., equation (18)), \( \varepsilon_3 \) represents the dielectric permittivity of the metallic shell (silver) and can be written as

\[ \varepsilon_3 = \varepsilon_\infty - \frac{\omega_p^2}{\omega (\omega + i\gamma)}. \]  
(19)

For silver, \( \omega_p = 1.37 \times 10^{16} \text{ Hz} \), \( \varepsilon_\infty = 9.01 \text{eV} \), and \( \omega = 2\pi c/\lambda \) is the angular frequency of the applied electromagnetic field, \( \varepsilon \) is the speed of electromagnetic wave [34] and \( \gamma \) is a parameter associated with damping [35]. If the mean free path of electron in the nanostructure depends on size of the nanocomposites, then its damping parameter differs from its bulk counterpart, and hence \( \gamma \) in equation (19) can be modified to [36]:

\[ \gamma = \gamma_\text{bulk} + A \frac{v_F}{r_{eff}}, \]  
(20)

where \( \gamma_\text{bulk} \) is the damping constant of the bulk material (for Ag: \( \gamma_\text{bulk} = 3.23 \times 10^{13} \text{ Hz} \)), \( v_F \) is the velocity of an electron at the Fermi surface \( (v_F = 1.4 \times 10^6 \text{ m/s for silver}) \), \( A \) is an empirical parameter, usually set to be unity, \( r_{eff} \) is the effective mean free path of electrons and is calculated using the following equation [37]:

\[ r_{eff} = \frac{(r_1 - r_2)(r_1^2 - r_2^2)^{1/2}}{2}. \]  
(21)

3. Results and discussions

3.1. Core and single shell nanoparticles

In this section, we investigated the local field enhancement factor for the core and single shell GdSe@Ag nanoparticles. Figures 3 and 4 depict the graphs of the enhancement factor for different core, shell, and QD sizes as a function of wavelength plotted using equation (8).
From figure 3(a), it is observed that as the size \( r_1 \) of the core (CdSe) of the nanocomposite is reduced from 10 nm to 2 nm for a fixed radius \( r_2 = 20 \) nm of the silver (Ag) metal, the peaks of the resonances are increased by 18.2 folds (increased from about 1, 743 at 452 nm to 31, 760 at 478 nm) at the interface between CdSe@Ag. This is observed when the core radius is relatively the smallest (2 nm) and the metal shell thickness is the largest (18 nm), where 18 nm is the difference of the two radii \( 20 \) nm \(- \) \( 2 \) nm \( = 18 \) nm). From this, one can see that when the core radius decreases and the shell thickness increases simultaneously at constant shell radius \( 20 \) nm, the local field is enhanced and the surface plasmon peaks shift to the higher energy. This result agrees with other research findings that when the core size is made smaller, the resonance peaks are enhanced \([28, 37]\). This may be explained with the fact that as the shell thickness increases, the hybridization between the two plasmon frequencies of the inner and outer surfaces decrease, leading to the blue shift. Moreover, the metal content of the particle increases with decrease in the core radius so that there are more electrons to participate in the oscillation. As a result, the coupling of localized surface plasmon resonance becomes stronger and leads to the enhancement of the local field. Our findings are in good agreement with the previous findings \([36, 38, 39]\). For the same core/shell nanoparticle parameters, the field enhancement factor has increased by about 6.3 times (nearly increased from 8, 434 to 12, 270) at the interface between the shell (Ag) and the host matrix (SiO\(_2\)). From figure 3(a), it is observed that the resonance peaks shift towards the longer wavelength (red shift) of the visible region of electromagnetic spectrum at the inner interface of CdSe@Ag, and towards the shorter wavelength at its outer interface. Taking the ratio of the magnitudes of the resonance peaks of the outer interface to the inner interface of CdSe@Ag, the local electric field is enhanced by about 1.7 factor (from 53, 960 to 31, 760). Moreover, the result also reveal that the local field enhancement factor of the CdSe@Ag has been increased with the decrease in the core size.

Furthermore, figure 3(b) shows that keeping the core size constant \( r_1 = 10 \) nm and increasing the QD size from 20 nm to 24 nm enhanced the LFEF from about 8, 434 to 12, 270. This enhancement is accompanied with a blue shift of the enhancement peaks from 579 nm to 555 nm in the outer interface of silver (Ag@SiO\(_2\)). Note that comparison of figures 3(a) and (b) shows that the LFEF is higher when the size of the core is reduced.
than when the thickness of the shell is increased. This might indicate that the quantum confinement is more significant than the plasmonic effect for the local field enhancement.

However, when both the core and the shell radii increase simultaneously \((r_1 = 5 \text{ nm} \text{ to } 9 \text{ nm} \text{ and } r_2 = 12 \text{ nm} \text{ to } 16 \text{ nm})\), the resonance peaks are significantly lowered from about 12, 270 at 555 nm to 6, 550 at about 603 nm at the interface of Ag@SiO\(_2\) (figure 4(a)). Also, when the sizes of both the core and the shell changes simultaneously by equal amounts \((i.e., \Delta r = 4 \text{ nm})\), the amplitudes of the resonance peaks are reduced from 3, 316 at 460 nm to about 918 at 446 nm at the interface of CdSe@Ag region.

For the nanoparticle considered under this section, the simultaneous increase in the radii of the core and the shell could not help to increase the local enhancement factor for the core/shell nanoparticle. This can be attributed to the fact that, when the shell size increases, charge separation distance also increases, leading to the decrease in the electric field inside the nanoparticle. In the other case, when the radius of the core is increased from 3 nm to 7 nm, while reducing the size of the shell from 17 nm to 13 nm, the local field enhancement factor is reduced from 42, 660 to 7, 237 (figure 4(b)). Whether the shell size is constant or decreased, increasing the core size led to lower field enhancement factor for the material under the study. Hence, it is observed that the core size of the nanoparticle is a crucial parameter to increase or decrease the field enhancement factor for the core and single shell CdSe@Ag spherical nanoparticle. All these results show that the LFEF of CdSe@Ag nanoparticle becomes controllable by carefully altering the size of the core radius.

3.2. Triple layered core@shell nanoparticle

In the second part of this study, ZnSe was placed as a spacer between the CdSe core and Ag shell and the local electric field enhancement was analyzed using equation (18). The size of ZnSe \((r_1 = 10 \text{ nm})\) is fixed and the sizes of the core \((r_1)\) and the QD \((r_2)\) were varied (figure 5(a)). As the core and the QD sizes increase \((r_1 = 5 \text{ nm} \text{ to } 9 \text{ nm}; r_2 = 12 \text{ nm} \text{ to } 16 \text{ nm})\), two sets of resonance peaks were observed. The two resonances are associated with the inner and outer interfaces of silver shell, respectively.

In the absence of the ZnSe spacer, the intensities of the local field enhancements decrease with increase in the core and the QD sizes \((i.e., \text{figure } 4(a))\). However, when the spacer was placed in between CdSe and Ag, the magnitudes of the resonance peaks showed increasing effect for the same increase in the core size and for the same size of the whole NP (figure 5(a)). This result reveals that the spacer has an increasing effect on the LFEF of core/shell nanoparticle even when the core size is increasing. Previous researches show that the thickness of the dielectric spacer controls the plasmonic response of the three-layered nanoparticles [40, 41]. Thus, one of the reasons for the increase in the local field enhancement in this study might be due to the decrease in the thickness of the spacer layer (ZnSe). As illustrated in figure 5(a), when the core radius and the shell thickness are increasing, the spacer layer is decreasing from 5 nm to 1 nm. That is, the decrease in the thickness of the spacer layer provides a platform for strong plasmonic coupling between the core and the outer metal shell nanomaterial leading to the enhancement of the local field. For all the dimensions indicated in figure 5(a), the second set of the resonance peaks show a blue shift within the visible range of electromagnetic spectrum.

In figure 5(b), the core and the QD sizes were fixed and the size of ZnSe was varied from \(r_2 = 10 \text{ nm} \text{ to } 10.8 \text{ nm}\). In this process, still two peaks were observed but the resonance peaks were found to decrease with an increase in the size of the spacer.

Among all the size combinations, comparatively the largest peak is obtained when the spacer size is the thinnest. Previous experimental studies show that when thin layer of ZnSe is deposited on CdSe, its emission efficiency increases [11]. When it becomes thicker, the defects on the ZnSe surface may induce the nonradiative
transitions, thereby decreasing the emission intensity [18]. Our theoretical and numerical analysis also show similar results that when relatively the thinnest ZnSe is used as spacer on the CdSe core, the LFEF increases. However, when the spacer thickness increases, the resonance peaks decreases and are red shifted (figure 5 (b)).

Comparison of figures 5(a) and (b) shows that the core and the spacer sizes have different effects on the field enhancement factor of core/shell spherical NPs.

In figure 6(a), the radii of the core ($r_1 = 10$ nm) and the spacer ($r_2 = 14$ nm) are fixed and the shell size was increased from $r_3 = 20$ nm to 24 nm. The result shows that the field enhancement factor increases with an increase in the metallic shell size which might be related to the surface plasmon resonance [31, 33].

This is similar to figure 3(b) in all aspects except the presence of the spacer (ZnSe). For the two layer NP (figure 3(b)), the resonance peaks are higher and are achieved at shorter wavelengths whereas in the triple layer case (figure 6(a)), the peaks are lower and are located at relatively longer wavelengths. When the core size increases and the spacer thickness decreases with constant NP (core + shell) size ($r_2 = 20$ nm), the field enhancement factor decreases (figure 6(b)). In this process, the resonance peaks in the outer interface of the metal shell were red shifted. Although the amplitudes were not the same, the peak positions of results in figure 6(a) were nearly reversed in figure 6(b).

In figure 7(a), the spacer and the metal shell thickness sizes are increasing with decreasing core size. This results in increased field enhancement factor.

In the two layer NP, a blue shifted and significantly enhanced local field can be obtained in the visible range of the spectrum by decreasing the core size (figure 3(a)). However, in the presence of spacer between the core and the metal shell of the same NP size, relatively smaller field enhancement is observed with significant blue shift from infra-red (IR) to the visible spectral region (figure 7(a)). Keeping the core size fixed and simultaneously increasing the spacer and the metal shell thicknesses also show enhancement of the LFEF with the blue shift of the resonance peaks (figure 7(b)). Nevertheless, the magnitudes of the peaks were more pronounced in the latter case.

Figure 6. LFEF of CdSe@ZnSe@Ag: (a) when shell size is increasing at fixed sizes of the core and spacer and (b) when core size is increasing and spacer thickness is decreasing at fixed NP size.

Figure 7. LFEF of CdSe@ZnSe@Ag: (a) when core size is decreasing and spacer thickness is increasing at fixed size of NP and (b) when spacer and shell thicknesses are increasing at fixed core size.
Comparing the results of double and triple layered nanoparticles explored in this study, LFEF was enhanced with increasing the core size in the presence of spacer (ZnSe). But this was not observed in the core and single shell nanostructure. Increasing the metallic shell radius (keeping others constant) show increased LFEF both in the double (figure 3(b)) and the triple (figure 6(a)) layered nanostructures except that the increment was larger for two layered NP than the triple layered NP by the factor of about 15.3 (i.e., 12, 270 to 800). When the core and the NP sizes increase simultaneously for double layered NP (figure 4(a)), the LFEF decreases accompanied with red shift while the LFEF increases and are blue shifted for the triple layered one (figure 5(a)). This indicates that in triple layered core/shell spherical nanoparticle, the enhancement of the local field can be achieved at higher energy.

4. Conclusions

In this study, the local field enhancement factor of CdSe@Ag and CdSe@ZnSe@Ag core/shell nanoparticles were studied theoretically and numerically by changing the sizes of each components. For a fixed size of the NP, the local field enhancement factor of CdSe@Ag was increased with the decrease in the size of the core. Moreover, the resonance peaks were red shifted and blue shifted, respectively, in the inner and outer interfaces. By increasing the size of metallic shell while keeping the core size constant, similar patterns of resonance peaks were obtained except that the degree of enhancements were larger in the former case. Increasing the core size produces lower field enhancement factor whether the shell thickness is constant or decreased in size. This may indicate that the core size is a crucial parameter to change the field enhancement factor of the dielectric core and metallic shell nanoparticle.

For triple layered spherical core/shell nanoparticle, setting the ZnSe radius constant, the resonance peak increases with an increase in the size of the core which was not observed in the case of two layered core/shell nanocomposites having the same core and NP sizes. In triple layered core/shell spherical nanoparticle, an increase in the size of the spacer led to a decrease in the field enhancement factor of the nanocomposite. For fixed sizes of the core and the NP, the lower the size of the spacer produces the higher the field enhancement factor. On the other hand, increasing the thickness of the shell size increases the magnitude of the resonance peaks. Similarly, increasing the thicknesses of both the spacer and the shell sizes also increased the field enhancement factor. In conclusion, the sizes of the core, the spacer, and the shell has vigorous effect on the local field enhancement factor of core/shell nanoparticles. The possibility of obtaining size dependent LFEF by adjusting the sizes of nanoparticles make these nanocomposites attractive for applications in optoelectronics and nonlinear optics.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Conflict of Interest

The authors have no conflicts to declare.

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