Analysis of Localized Surface Plasmon Resonance in Ag/ITO/CdS/SiO₂ Multilayered Nanostructured Composite

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Multilayered nanoshells have attracted much attention due to their unique optical, electronic and magnetic properties. In this work, numerical calculation using discrete dipole approximation (DDA) is conducted to investigate the quad-layered metal nanoshell consisting of a particle with a dielectric silica (SiO₂) core, inner cadmium sulfide (CdS) shell, middle indium tin oxide (ITO) shell and outer metal silver (Ag) shell. The phenomenon is interpreted by plasmon hybridization theory and the Ag–ITO–CdS–SiO₂ multilayered nanoshells are studied by extinction spectra of localized surface plasmon resonance. The variation in the spectrum peak with nanoparticle thickness and refractive index of the surrounding medium is derived. The electric field enhancement contour around the nanoparticles under illumination is analyzed at the plasmon resonance wavelength. The \(|\omega^-\rangle\), \(|\omega^+\rangle\), and \(|\omega^\leftrightarrow\rangle\) modes red-shift with the refractive index of the surrounding medium and increase in the layer thickness causes either blue-shift or red-shift as shown by the extinction spectra. The mechanism of the red-shift or blue-shift is discussed. The \(|\omega^-\rangle\) mode blue-shifts and furthermore, the \(|\omega^-\rangle\) and \(|\omega^\leftrightarrow\rangle\) modes of the Ag coated multilayered nanostructure are noticeable by comparing the extinction efficiency spectra of the Au–ITO–CdS–SiO₂ and Ag–ITO–CdS–SiO₂ multilayered nanoshells.

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1. Introduction

Noble metal nanostructures have great potential in the areas of nanomedicine, biosensing and food safety due to their localized surface plasmon resonance (LSPR) properties.\textsuperscript{1–3} Surface plasmons are collective excitations of the electrons at the interface between a conductor and an insulator and are described by evanescent electromagnetic waves that are not necessarily located at the interface.\textsuperscript{4–6} The properties of LSPR depend largely on the shape and size of the nanoparticles as well as the refractive index of the surrounding medium.\textsuperscript{7,8} The optical responses associated with LSPR in metallic nanoparticles with different structures have been investigated\textsuperscript{9} and it is known that only one plasmonic resonance peak is generated from spherical nanoparticles, while two or more plasmonic resonance peaks can occur in other kinds of nanostructures such as nanodimers, nanorods and core/shell structures.\textsuperscript{10–12}

Recent research has focused on multilayered metallic–dielectric nanostructures that exhibit multiple resonance peaks capable of detecting various types of targets on one sample at the same time.\textsuperscript{7} The tunable intensity and peak wavelength of LSPR arising from layered metallic–dielectric nanostructures render them versatile by combining with different materials. Su\textsuperscript{13} studied the LSPR optical response of Au/SiO\textsubscript{2} multilayered nanodisks possessing distinct properties by controlling the dielectric layer thickness and Qian\textsuperscript{14} investigated the optical properties induced by dual symmetry breaking in the gold–silica–gold multilayered nanoshells. By controlling the two types of symmetry breaking, polarization-dependent multiple plasmon resonance is observed. Therefore, the LSPR properties of Ag-coated multilayered nanoshells with other materials are interesting. Among various types of dielectric materials, SiO\textsubscript{2} is one of the most extensively studied and used due to its unique optical and electrical properties.\textsuperscript{15} Indium tin oxide (ITO) has the advantages of near-metallic conductivity,\textsuperscript{16} environmental stability,\textsuperscript{17} and high transparency in the visible region\textsuperscript{18} and cadmium sulfide (CdS) is often utilized in luminescence probes and photosensors.\textsuperscript{19} However, the LSPR properties of nanoshells with multilayered structure of these materials are relatively not well known.

In this work, quad-layer metallic nanostructures consisting of metal Ag, ITO, CdS and SiO\textsubscript{2} are proposed and the effects of the layer thickness and the refractive index of the surrounding medium on the LSPR properties of Ag–ITO–CdS–SiO\textsubscript{2} multilayered nanoshells are studied by the discrete dipole approximation (DDA) method. In addition, the electric field enhancement contour around the multilayered nanoshells is analyzed on the basis of the plasmon hybridization theory.\textsuperscript{20}

2. Theory

The isolated concentric Ag–ITO–CdS–SiO\textsubscript{2} multilayered nanostructure is modeled as shown in Fig. 1. The core SiO\textsubscript{2} has a radius \( r_1 \) and the thicknesses of the inner shell, middle shell, and outer shell are \( r_2 - r_1, r_3 - r_2 \) and \( r_4 - r_3 \), respectively. The dielectric constants of the inner dielectric core, inner shell, middle shell and outer silver shell are \( \varepsilon_1, \varepsilon_2, \varepsilon_3 \) and \( \varepsilon_4 \). The surrounding medium has a refractive index of \( n \) and DDA is carried out to simulate the LSPR properties of multilayered nanostructures.

The numerical approach of DDA is widely used to calculate the electromagnetic field distribution of arbitrary structure, shape and size. The scattering spectra, absorption spectra and extinction spectra of these nanoparticles can be calculated by DDA as well. In DDA, the target can be measured by a cubic array of \( N \) polarizable points.\textsuperscript{21,22} Generally, the

![Fig. 1. Schematic representation of the concentric multilayered nanosphere.](image-url)
continuum target can be substituted by the discrete dipoles as long as the dipole number \( N \) is large enough. The polarization vector is generated by the interaction between the arbitrary point dipole and local electric field \( E_{\text{loc}} \) so that

\[
P_i = \alpha_i \cdot E_{\text{loc}}(r_i),
\]

where \( \alpha_i \) is the tensor of polarizability of the point dipole, \( r_i \) is the central position and \( E_{\text{loc}} \) consists of the electric field \( E_{\text{inc},i} \) at position \( j \) due to the incident plane wave and electric field stimulated by \( (N-1) \) other dipoles as shown in the following:

\[
E_{\text{inc},i} = E_0 \exp(i(k \cdot r_i - \omega t))
\]

\[
E_{\text{other},i} = -\sum_{j \neq i} A_{ij} \cdot P_j,
\]

where \( E_0 \) and \( k \) represent the amplitude and wave vector of the incident wave, respectively, \( |k| = \omega/c \), and \( -A_{ij} \cdot P_j \) is the contribution to the electric field at position \( i \) due to the dipole at position \( j \) as follows:

\[
A_{ij} \cdot P_j = \frac{\exp(ikr_{ij})}{r_{ij}^3} \times \left\{ \frac{k^2r_{ij} \times (r_{ij} \times P_j) + (1 - ikr_{ij})}{r_{ij}^2}, \right. \\
\left. \times [r_{ij}^2P_j - 3r_{ij}(r_{ij} \cdot P_j)] \right\},
\]

\( i \neq j \)

so that the scattering problem can be briefly described as a set of \( N \) inhomogeneous linear complex vector equations as follows:

\[
\sum_{j=1}^{N} A_{ij} \cdot P_j = E_{\text{inc},i}(i = 1, 2, \ldots, N).
\]

If the polarization \( P_j \) is known, the absorption cross section for the entire grain is

\[
C_{\text{abs}} = \frac{4\pi k}{|E_{\text{inc}}|^2} \sum_{i=1}^{N} \left\{ \text{Im}[P_i \cdot (\alpha_i^{-1})^* P_i^*] - \frac{2}{3} k^2 P_i \cdot P_i^* \right\},
\]

The extinction cross section is obtained by the optical theorem \( ^{23} \)

\[
C_{\text{ext}} = \frac{4\pi k}{|E_0|^2} \sum_{j=1}^{N} \text{Im}(E_{\text{inc},j} \cdot P_j).
\]

The extinction efficiency can be expressed as

\[
Q_{\text{ext}} = C_{\text{ext}}/\pi \alpha_{\text{eff}}^2,
\]

where \( \alpha_{\text{eff}} \) is the effective radius.

The number of polarizable points should be large enough to minimize the calculation error. In this study, the multilayered nanoshells consisting of Ag, ITO, CdS and SiO\(_2\) are represented by a finite array of polarizable points with the corresponding dielectric constants obtained from Ref. \( ^{24} \).

\section*{3. Results and Discussion}

\subsection*{3.1. Effects of refractive index of surrounding medium on extinction spectra}

The extinction spectra of LSPR are influenced by the refractive index of the surrounding medium. A detailed analysis is carried out to obtain the relationship between the extinction spectra and refractive index. Figure 2 shows the extinction spectra of the Ag–ITO–CdS–SiO\(_2\) multilayered nanostructure. Specifically, the parameters \( [r_1, r_2 - r_1, r_3 - r_2, r_4 - r_3] = [25, 5, 10, 10] \text{ nm} \) and \( [n_1, n_2, n_3, n_4, n_5, n_6] = [1.0, 1.16, 1.33, 1.41, 1.52, 1.67] \) of the Ag-coated ITO–CdS–SiO\(_2\) multilayered nanoshells are used in the calculation. The dipole resonance wavelength red-shifts from 595 nm to 790 nm when the refractive index varies from 1.0 to 1.67. Similarly, the quadrupole and octupole resonance wavelengths red-shift as the refractive index increases. However, the peak at 260 nm blue-shifts slightly due to the electronic transition of the Ag\(^+\) ions thus producing absorption bands at 200 nm and 230 nm, whereas the electronic transition of metallic Ag\(^+\) appears in the spectral range between 250 nm and 330 nm.\(^{25-27}\)

Figure 2 shows that there are three plasmonic resonance peaks in the extinction spectrum for a surrounding medium with a refractive index of 1.52, dipole resonance of 740 nm, quadrupole resonance of 570 nm and octupole resonance of 340 nm. Similar results have been obtained from a tunable plasmonic nanoparticle consisting of a metallic silver
shell and dielectric SiO$_2$ core.$^{28-30}$ The plasmon resonance of the Ag–ITO–CdS–SiO$_2$ multilayered structure can be visualized as hybridization between the outer Ag shell plasmon resonance and inner compound shell plasmon mode. The interaction between the inner and outer shells gives rise to two new plasmon resonances: a lower-energy mode $\omega_-$ and a higher-energy mode $\omega_+$, corresponding to the symmetric coupling mode and anti-symmetric coupling mode. Theoretically, four plasmon oscillation modes exist as the energy increases: a symmetric bonding mode $\omega_+^+/$ and an anti-symmetric bonding mode $\omega_-^-$, a symmetric anti-bonding mode $\omega_+^-$ and an anti-symmetric anti-bonding mode $\omega_-^+$.}

The total extinction spectrum including three types of plasmonic coupling modes with a surrounding medium refractive index of 1.52 is shown in Fig. 2(b). The differences in the dipole moments of the various plasmon modes influence the plasmon couples in the optical field, which is reflected by the magnitude of the extinction resonance for the various modes.$^{28}$ The resonance peaks attributed to the three plasmon modes ($\omega_+^-, \omega_-^+, \omega_-^-$) that are visible at approximately 3.62 eV, 2.17 eV and 1.67 eV or at a wavelength of 340 nm, 570 nm and 740 nm, respectively. However, it should be emphasized that the extinction peak corresponding to the $\omega_+^+$ mode is too weak to observe.

Figure 3(a) depicts the energy level diagram of the plasmon mode of the Ag–ITO–CdS–SiO$_2$ multilayered nanostructure further showing the interaction between the inner and outer nanoshell plasmons. The anti-symmetric plasmon mode $\omega_-^+$ has a lower energy and a smaller dipole moment than the symmetrically polarized hybrid plasmon $\omega_-^-$. The induced polarization of the concentric nanoshell modes is shown in Fig. 3(b). The $\omega_+^+$ mode has the highest energy due to the increased electrostatic repulsion at its internal adjacent interfaces for the plasmon excitation. Furthermore, for the $\omega_+^-$ mode, the sphere plasmon of the inserted sphere oppositely aligns the cavity plasmon with the sphere plasmon to further weaken the dipole moment in the $\omega_+^-$ mode.$^{31}$

### 3.2. Distribution of electric field

Figure 4 presents the contours of the electric field enhancement of the Ag–ITO–CdS–SiO$_2$ multilayered nanostructure at different resonance wavelengths for a surrounding medium with the refractive index of 1.52. At 260 nm, the electric field is concentrated in the region outside the multilayered nanostructure and CdS inner shell, whereas the electric fields in the SiO$_2$ core shell, ITO middle shell and Ag outer shell are low, as shown in Fig. 4(a). At 340 nm, the intensity of electric field is mainly distributed in the Ag outer shell, whereas the electric fields in the SiO$_2$ core–shell and ITO middle shell are weak as shown in Fig. 4(b). Owing to negative and
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Fig. 3. (a) Energy level diagram of the plasmon modes of multilayered nanoshell; (b) Induced polarizations of the concentric nanoshell modes.

Fig. 4. Electric field enhancement contour around Ag–ITO–CdS–SiO₂ multilayered nanostructure under illumination at plasmon resonance wavelength.
positive surface charges on the two interfaces of the outer silver shell, intense electric field enhancement occurs on both sides.\textsuperscript{32} Accordingly, the extinction peak at 340 nm corresponds to the $\omega^-$ mode derived from the symmetric coupling between the anti-bonding Ag shell plasmon mode and the inner plasmon.

Figure 4(c) describes the electric field enhancement with $\lambda = 570$ nm. The electric field spreads around the SiO$_2$ core shell and ITO middle shell. In contrast, the fields in the Ag outer shell and CdS inner shell are very weak. The same negative or positive charges are marked on the inner and outer surfaces of the core and middle shell because the electric field enhancement arises from the poles along the $y$-axis direction.\textsuperscript{7} The extinction peak at 570 nm corresponding to the $|\omega^+\rangle$ mode originates from symmetric coupling between the bonding Ag shell plasmon mode and inner plasmon. Similarly, as shown in Fig. 4(d), the electric field still spreads around the SiO$_2$ core–shell and ITO middle shell with $\lambda = 740$ nm and the contours of the electric field enhancement is pronounced outside the multilayered nanostructure. On the contrary, the fields in the Ag outer shell and CdS inner shell are very weak. Different negative or positive charges are assigned to the inner and outer surfaces of the core and middle shell because the electric field enhancement emerges in the poles along the $x$-axis direction. According to Fig. 4(b), it can be concluded that the extinction peak at 740 nm corresponds to the $|\omega^-\rangle$ mode ascribed to anti-symmetric coupling between the bonding Ag shell plasmon mode and inner plasmon.

3.3. Comparison of various metal-coated nanostructures

To compare the optical properties of various metal-coated multilayered nanostructures, the extinction spectra of the Au–ITO–CdS–SiO$_2$ and Ag–ITO–CdS–SiO$_2$ multilayered nanoshells are investigated as shown in Fig. 5. The parameters of Ag and Au coated ITO–CdS–SiO$_2$ multilayered nanoshells are: $[r_1, r_2 - r_1, r_3 - r_2, r_4 - r_3] = [25, 5, 10, 10]$ nm and

![Fig. 4. (Continued)](image)

![Fig. 5. Comparison of the extinction spectra: Au–ITO–CdS–SiO$_2$ and Ag–ITO–CdS–SiO$_2$ multilayered nanoshells as a function of refractive index of the surrounding medium.](image)
n = 1.52 in the calculation. The $|\omega^-\rangle$ mode of the Ag-coated ITO–CdS–SiO$_2$ nanoshells blue-shifts compared with Au coated ITO–CdS–SiO$_2$ nanoshells. However, the $|\omega^+\rangle$ and $|\omega^+\rangle$ modes of Ag–ITO–CdS–SiO$_2$ nanoshells are more sensitive and obvious than those of the Au–ITO–CdS–SiO$_2$ nanoshells, in which the specific $|\omega^-\rangle$ mode is invisible. The mechanism is likely the stronger and sharper surface plasmon resonance of Ag nanoparticles in comparison with that of Au nanoparticles. Based on this mechanism, the metal outer layer of nanoshells influences largely the total plasmon resonance of the multilayered nanoshells and consequently, the $|\omega^-\rangle$ mode of the Ag–ITO–CdS–SiO$_2$ nanoshells becomes intense and noticeable.8

### 3.4. Effects of shell thickness on extinction spectra

To obtain more accurate simulation results, DDA-based models that consider the effect of tuning the component thickness on LSPR are developed. The parameters of the Ag-coated ITO–CdS–SiO$_2$ multilayered nanoshells are $[r_2, r_3 - r_2, r_4 - r_3] = [15, 10, 10]$ nm and $n = 1.0$, with $r_1$ between 5 nm and 25 nm. Figure 6(a) shows that the $|\omega^-\rangle$ mode

![Fig. 6](image-url)

Fig. 6. Calculated extinction spectra of Ag–ITO–CdS–SiO$_2$ multilayered nanoshells as a function of refractive index of the surrounding medium with different (a) SiO$_2$ core thickness; (b) CdS inner shell thickness; (c) ITO middle shell thickness; and (d) silver outer shell thickness.
blue-shifts from 626 nm to 595 nm as the SiO₂ core radius increases. The resonance wavelength of the \(|\omega_+|\) mode shows a small blue-shift relative to the SiO₂ core radius.

The effect of different CdS inner shell thicknesses on extinction spectrum is examined by fixing \(|r_1, r_2, r_3 - r_4| = [5, 40, 10] \text{ nm}\), as shown in Fig. 6(b). The \(|\omega_-|\) mode blue-shifts from 640 nm to 595 nm when the thickness of the CdS inner shell increases from 5 nm to 30 nm, while the extinction efficiency diminishes gradually, indicating that the \(|\omega_-|\) mode is sensitive to the thickness of the CdS inner shell. In the \(|\omega_-|\) mode, the bonding metal shell plasmon is affected by hybridization of the SiO₂ core, ITO middle shell and CdS shell. By controlling the thickness of the CdS inner shell, the interaction between the SiO₂ core and Ag outer shell can be tailored arbitrarily.\(^{28}\) When the thickness of the CdS inner shell increases, the interaction of the metal shell plasmons decreases, leading to blue-shifted plasmonic bands. The parameters of the Ag–ITO–CdS–SiO₂ multilayered nanoshells are also defined as \(|r_1, r_2 - r_1, r_3 - r_2| = [5, 10, 50] \text{ nm}\). Increasing the ITO middle shell thickness leads to red-shift in the \(|\omega_-|\) mode from 428 nm to 760 nm, whereas the \(|\omega_+|\) mode blue-shifts, as shown in Fig. 6(c). The extinction spectra of the Ag–ITO–CdS–SiO₂ multilayer nanoshells with different Ag outer shell thicknesses are plotted in Fig. 6(d). The parameters are \(|r_1, r_2 - r_1, r_3 - r_2| = [5, 5, 10] \text{ nm}\). The \(|\omega_-|\) mode blue-shifts from 610 nm to 425 nm when the thickness of Ag shell changes from 5 nm to 30 nm, whereas the \(|\omega_+|\) mode red-shifts.

4. Conclusion

In summary, the optical properties of Ag–ITO–CdS–SiO₂ nanoshells are simulated by the DDA method and the following conclusions can be drawn:

1. The electric field enhancement contours of the surface resonance wavelength show the \(|\omega_+|\) mode at a shorter wavelength corresponding to the symmetric coupling between the anti-bonding silver shell plasmon mode and inner sphere plasmon, while the \(|\omega_-|\) and \(|\omega_+|\) modes at longer wavelengths are responsible for the symmetric or anti-symmetric coupling between the bonding of silver shell plasmon mode and spherical plasmon.

2. The \(|\omega_-|\), \(|\omega_+|\) and \(|\omega_+|\) modes red-shift with the refractive index of the surrounding medium increasing. The thicknesses have a large influence on the LSPR properties of the nanoparticles. Increasing the thickness of the SiO₂ core, CdS inner shell and Ag outer shell blue-shifts the LSPR peak. Although the SiO₂ core reduces the extinction efficiency, the CdS inner shell and Ag outer shell exhibit higher extinction efficiency. On the contrary, the thickness of the ITO middle shell causes red-shift of the peak of LSPR.

3. By comparing the extinction efficiency spectra of Au–ITO–CdS–SiO₂ and Ag–ITO–CdS–SiO₂ multilayer nanoshells, the \(|\omega_-|\) mode of the Ag-coated nanoshell blue-shifts. Simultaneously, the \(|\omega_+|\) and \(|\omega_+|\) modes of the Ag-coated multilayered nanostructure become intense and noticeable.

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