Study on the Plasmonic Properties of Ag-Coated Spherical Dielectric Nanoparticles by Finite-Difference Time-Domain Calculations

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Abstract

The optical properties of nanostructures are rather important for designing plasmonic devices. In this work, the plasmonic properties of Ag-coated spherical dielectric nanoparticles (NPs), namely, Ag-SiO$_2$-NPs, Ag-ZnO-NPs, and Ag-TiO$_2$-NPs, were studied using a method of finite-difference time-domain calculations. It was found that the Ag-coated dielectric NPs start to exhibit unique plasmonic properties different from Ag-NPs as the thickness of Ag shells is reduced to be less than a critical value, which is basically determined by the penetration depth of light in silver. On the other hand, the core-shell structures of Ag-coated dielectric NPs were found to be of benefit to the plasmonic resonance high-efficiently coupled with the incident light. In the extinction spectra of Ag-coated dielectric NPs with sufficient thin Ag shells, the dipole plasmonic resonance is predominant and exhibits a pronounced red-shift up to infrared band with increasing the NP sizes. In addition to the electromagnetic waves of emission towards the outside, the electromagnetic field in the dielectric NP inside is uniformly enhanced as well and both of dipole and quadrupole plasmonic resonances are identified. The Ag-coated dielectric NPs are suggested to have great potential in the plasmonic devices working in infrared band, such as the light emitters and SERS substrates for biosensing.

1. Introduction

Plasmonics has been developed into a relatively independent discipline involving the surface-enhanced Raman spectroscopy (SERS), near-field optics, nanophotonics, biosensing, and meta-materials, etc. [1, 2]. In the past decades, optical properties of metal nanoparticles (NPs) with a wide range of sizes, shapes and dielectric environments have been extensively investigated in theory and experiment [3–10] and thus extremely promoted relevant researches, such as single-molecules detection based on SERS and surface enhanced fluorescence (SEF) [11–15]. Up to date, it has been well known that the sizes, shapes and dielectric environments play a decisive role in tuning the optical properties of metal NPs and thus are important for optimizing the performance of SERS substrates as well as plasmonic devices. In comparison to the researches on the metal NPs or metal NPs coated by a layer of dielectric materials, there are a few reports involving the optical properties of metal-coated dielectric nanostructures, which are usually used as three-dimensional (3D) SERS substrates, such as Ag- or Au-coated nanostructured oxides [16–22]. The 3D SERS substrates based on metal-coated dielectric nanostructures have exhibited excellent performance capable of detecting single molecules, but it seems that we are still absent of a comprehensive understanding of SERS substrate optical properties.

In very recent, the plasmonic properties of Ag-coated ZnO nanorods (Ag-ZnO-NRs) were studied using a finite-difference time-domain (FDTD) method by this group [23]. It was found that the optical properties of Ag-ZnO-NRs are rather different from those of Ag NRs as the Ag layer is sufficient thin. For example, the dipole modes of localized surface plasmonic resonance (LSPR) are observed to have the low- and high-frequency two branches. At the same time, the thickness of Ag layer and the diameter of ZnO NRs were found to be capable of tuning the LSPRs in a wide range of frequency. In addition, the extinction spectra of Ag-coated nanocomposites are sensitive to the refractive index of dielectric materials. As such, the
nanocomposites of metal-coated dielectric nanostructures seem to have unique optical properties that need a systematical investigation, especially for the nanocomposites with thin Ag shells. In this work, the plasmonic properties of Ag-coated spherical dielectric NPs were studied using an FDTD method. The extinction spectra and local electromagnetic field in the vicinity of Ag-coated NPs were calculated, including Ag-coated spherical SiO$_2$, ZnO-, and TiO$_2$-NPs, which are referred to as Ag-SiO$_2$-NPs, Ag-ZnO-NPs, and Ag-TiO$_2$-NPs, respectively. The extinction spectra were studied as a function of Ag-shell thickness and dielectric NP radius with a comparison to those of spherical Ag-NPs. Excited by the incident light at plasmonic peaks, the local electromagnetic fields in the vicinity of Ag-coated NPs were calculated and the mode of plasmonic resonance was identified. Because the unique plasmonic properties of Ag-coated dielectric NPs are observable mainly in the case of Ag shells sufficiently thin, the Ag-coated dielectric NPs with Ag shells of 4 nm were specifically investigated as a function of dielectric NP radius and the electromagnetic enhancement was discussed in the regions of Ag-coated dielectric NP outside and inside.

2. Calculation Methods

The FDTD calculations of Ag-coated NPs were performed using a code of FDTD Solutions, which is able to accurately calculate the optical properties of metal-dielectric composites by solving the Maxwell equations. In the FDTD calculations, the radius of spherical SiO$_2$, ZnO, TiO$_2$ NPs varied mainly in the range of 20 to 72 nm and the thickness of Ag shells ranged from 4 to 44 nm. For comparison, we also calculated the extinction spectra of spherical Ag NPs with similar dimensions. The FDTD calculations were carried out using the dielectric functions of Ag and SiO$_2$ in the FDTD library and the refractive index and extinction coefficient of ZnO and TiO$_2$ taken from the literatures [24, 25]. The extinction spectra of Ag-SiO$_2$-NPs, Ag-ZnO-NPs, and Ag-TiO$_2$-NPs were calculated under the excitation of broadband total-field scattered-field source and the conditions of perfectly matched layer (PML) boundary, which were set at 250 nm of distance to the center. The local electromagnetic fields in the vicinity of Ag-coated spherical dielectric NPs were simulated in terms of electric field ($E^2$) under the excitation by the incident light in resonance with the given plasmonic peaks in the extinction spectra. The mesh interval of FDTD calculations was set to 1 - 2 nm and the auto shutoff minimum was set to $1 \cdot 10^{-6}$.

3. Results And Discussion

3.1 Optical properties of Ag-SiO$_2$-NPs

The extinction behavior of Ag-SiO$_2$-NPs was first studied by calculating the extinction spectra under the condition of PML boundary, as shown in Fig. 1a, in which the thickness of Ag shell is fixed at 20 nm and the radius of SiO$_2$-NP varies from 20 to 72 nm. For comparison, the extinction spectra of spherical Ag-NPs with similar sizes were calculated, as shown in Fig. 1b. The Ag-SiO$_2$-NPs exhibited the extinction spectra with the shapes similar to those of spherical Ag NPs, but the number of LSPR peaks is different.
In the extinction spectra of Ag-SiO$_2$-NPs, there are two plasmonic peaks having the similarity to those observed in the extinction spectra of Ag-NPs, which are referred to as D and Q peaks in this work. In addition, a new extinction peak is observed to appear at $\sim$ 345 nm, which is referred to as C peak. In previous study [5], it has been shown that the D peak of spherical Ag-NPs originates from the dipole plasmonic resonance and the Q peak is due to the quadrupole LSPR, which develops to be visible in the extinction spectra with the increase in the Ag-NP size, as shown in Fig. 1b. In the extinction spectra of Ag-SiO$_2$-NPs, the D and Q peaks exhibit the size dependences very similar to those of Ag-NPs while the C peak maintains nearly constant at $\sim$ 345 nm, as shown in the inset in Fig. 1b, suggesting that the D and Q peaks of Ag-SiO$_2$-NPs probably also originate from the dipole and quadrupole LSPRs, respectively, and the origin of C peak needs to be further identified. By plotting the peak energy as a function of Ag-NP or Ag-SiO$_2$-NP radius, the photon energies in resonance with D and Q peaks of Ag-SiO$_2$-NPs are found to be lower than those of same size Ag-NPs, respectively. In addition, the D and Q peaks of Ag-SiO$_2$-NPs are more rapidly shifted to the low-energy side with the increase in the sizes. At the same sizes, the Ag-SiO$_2$-NPs probably have relatively high extinction efficiency because of the relatively large extinction cross-section and the full width at half maximum.

To have a comprehensive understanding of the extinction behavior, the electromagnetic fields in the vicinity of Ag-SiO$_2$-NPs were calculated under the excitation by the incident light in resonance with the given plasmonic peaks, as shown in Fig. 2, which was presented in terms of electric field ($E^2$). Excited by the incident light in resonance with the C peak ($\lambda_{ex} = 343$ nm), the electromagnetic wave in the region of Ag-SiO$_2$-NP outside is basically of forward scattering, as shown in Fig. 2a. The electromagnetic enhancement can be identified to originate from a dipole plasmonic resonance caused by the incident light, as the $E^2$ pattern of y-z plane shown in Fig. 2a. In the Ag-SiO$_2$-NP inside, the electromagnetic field is enhanced as well and the energy seems to be restricted in the Ag-SiO$_2$-NP inside, as the $E^2$ pattern of z-x plane shown in Fig. 2a. As the Ag-SiO$_2$-NPs are excited by the incident light in resonance with the Q peak ($\lambda_{ex} = 413$ nm), the electromagnetic fields of emission toward outside becomes to have an approximately four-fold symmetry, as the $E^2$ pattern of x-y plane shown in Fig. 2b, though more emissions are forward. In the study of Ag-NPs, such an $E^2$ pattern was attributed to the quadrupole plasmonic resonance [5]. At the same time, the electromagnetic field caused by the dipole plasmonic resonance seems to be restricted in the area near the surface, as the $E^2$ pattern of y-z plane shown in Fig. 2b. In the Ag-SiO$_2$-NP inside, it is of interest that the electromagnetic field is observed to enhance extremely high in the area of back light, even stronger than those of emission toward outside, as the $E^2$ patterns of x-y and z-x planes shown in Fig. 2b. Excited by the incident light in resonance with the D peak ($\lambda_{ex} = 510$ nm), the electromagnetic fields of emission toward outside is obviously enhanced by the dipole plasmonic resonance, as the $E^2$ patterns of x-y and y-z planes shown in Fig. 2c, which are very similar to the observation of Ag-NPs [5]. In the Ag-SiO$_2$-NP inside, the electromagnetic enhancement is uniform while the intensity of electromagnetic field is lower than that of emission toward outside. It is evident that both of the inner and outside regions
of Ag-SiO$_2$-NPs can be used for electromagnetic enhancement, which should be linked to the thickness of Ag shells.

The extinction spectra were calculated as a function of Ag-shell thickness, as shown in Fig. 3, in which the radius of SiO$_2$ NPs were set to 24, 48, and 72 nm, respectively, and the thickness of Ag shells varied from 4 to 44 nm. With the decrease in the thickness of Ag shell, the D and Q peaks are observed to rapidly shift to the long-wavelength side and the C peak is blue-shifted slowly. Therefore, we are conceived that the C peak probably originates from the core-shell structure of Ag-SiO$_2$-NPs and is determined by the thickness of Ag shells. In addition, the C and Q peaks are observed to obviously depressed as the Ag shell is reduced to be sufficiently thin, thus leaving the D peak to be predominant in the extinction spectra. For the Ag-SiO$_2$-NPs with a radius of 72 nm and an Ag shell of 4 nm, the D peak is red-shifted to a wavelength larger than 1 µm, as shown in Fig. 3c. Therefore, such a kind of Ag-SiO$_2$-NPs have the optical properties much different from those of Ag-NPs. By plotting the wavelength of D peak as a function of Ag-shell thickness, a critical thickness of Ag shells could be taken in the range of 20 – 30 nm for the Ag-SO$_2$-NPs with SiO$_2$-NP radius of 24, 48, and 72 nm, as shown in the inset in Fig. 3a. As the thickness of Ag shells is less than the critical value, the Ag-SiO$_2$-NPs start to exhibit the extinction behavior obviously deviated from the Ag-NPs. For the Ag-SiO$_2$-NPs with Ag shell thicker than the critical thickness, the extinction spectra gradually approach those of Ag-NPs with the increase in the thickness of Ag shells. Therefore, we are conceived that the critical Ag-shell thickness is in association with the propagation of incident light in silver and thus is determined basically by the penetration depth of incident light.

3.2 Ag-SiO$_2$-NPs with 4-nm Ag shells

The FDTD calculations reveal that the Ag-SiO$_2$-NPs with sufficient thin Ag shells will exhibit unique plasmonic properties mainly in resonance with the incident light in infrared region and thus are probably significant for the plasmonic devices working in infrared band. For instance, metallic NPs and nanopatches have been used as the plasmonic antenna of enhancing the fluorescence emission [26–29], especially for the fluorescent centers of rare-earth ions, which usually have relatively long lifetime of optical emissions and low quantum efficiency, such as Er$^{3+}$, Yb$^{3+}$, etc. Therefore, extinction spectra of Ag-SiO$_2$-NPs with a Ag shell of 4 nm were specially studied as a function of SiO$_2$-NP radius, as shown in Fig. 4. In the wavelength range of 400 to 1400 nm, the D peak is almost linearly red-shifted with the increase in the SiO$_2$-NP radius, as shown in the inset in Fig. 4, and the contributions of other LSPRs are negligible. Such a kind of extinction spectra is very similar to that of thin Ag nanoprisms. For example, 16-nm thick triangular prisms with the edges of 100 nm also exhibited the extinction spectra dominated by the dipole plasmonic resonance and the extinction peak is gradually blue-shifted with the increase in the corner length of snipping [5]. By a more accurately fitting to the D-peak wavelength ($\lambda_{\text{peak}}$) as a function of SiO$_2$-NP radius, we have $\lambda_{\text{peak}} = 401.5 + 9.387x + 0.013 x^2$ (nm), where $x$ is the radius of SiO$_2$-NPs in nm. This fitting result suggests that there might be a maximum $\lambda_{\text{peak}}$ for the Ag-SiO$_2$-NPs, which was estimated equal to ~ 2.1 µm for the Ag-SiO$_2$-NP with SiO$_2$-NP radius of ~ 360 nm.
In comparison to the Ag-SiO$_2$-NPs with Ag shells of 20 nm, the electromagnetic fields in the vicinity of Ag-SiO$_2$-NPs with 4-nm Ag shells are substantially enhanced, either in the inner or the outside regions, as shown in Fig. 5, which was calculated by exciting the Ag-SiO$_2$-NPs by the incident light in resonance with the D peaks. For the Ag-SiO$_2$-NPs with SiO$_2$-NP radius of 48 nm, the $E^2$ value near the surface of 4-nm Ag shells is more than one order of magnitude higher than that of 20-nm Ag shells, as shown in Fig. 5a and Fig. 2c. Meanwhile, the electromagnetic enhancement in the Ag-SiO$_2$-NP inside is elevated by about two orders of magnitude. As such, we come to a conclusion that the electromagnetic fields are simultaneously enhanced as the thickness of Ag shells are reduced, probably in association with the magnitude of electron oscillation in the Ag shells. It is a common knowledge that the light propagation in silver is featured of decay, thus leading to the reduction in the magnitude of electron oscillation with the increase in the distance to the surface. If the Ag shells are sufficient thick, most of photon energy will be dissipated through heating the low-energy electrons instead of exciting the electron collective oscillation. As such, reducing the thickness of Ag shells will be in favor of generating plasmonic resonance high-efficiently coupled with the incident light and thus enhance the local electromagnetic fields.

As the SiO$_2$-NP radius is increased to 72 nm, the electromagnetic fields of emission toward outside are slightly reduced near the surface of Ag-SiO$_2$-NPs, as the $E^2$ patterns of $x$-$y$ and $y$-$z$ planes shown in Fig. 5b, but the intensity decay is relatively slow in comparison to that of small size Ag-SiO$_2$-NPs. One of reasons is that the decay of plasmon electromagnetic radiation ($E$) is proportional to $1/r$ in spherical NPs [5], where $r$ is the NP radius. As the $E^2$ patterns of $x$-$y$ and $y$-$z$ planes shown in Fig. 5b, the electromagnetic fields of emissions toward outside are basically due to the dipole plasmonic resonance, having the similarity to the Ag-NPs. In the Ag-SiO$_2$-NP inside, the electromagnetic enhancement becomes to have a two-fold symmetry in the $x$-$y$ and $y$-$z$ planes and a four-fold symmetry in $z$-$x$ plane. As such, we conclude that both of dipole and quadrupole plasmonic resonances are responsible for the electromagnetic enhancement in the Ag-SiO$_2$-NP inside. Despite that the inner electromagnetic enhancement is weaker than that near the surface of Ag-SiO$_2$-NPs, but more uniform within the whole volume. Therefore, both of the inner and the outside region can be used for designing plasmonic devices, differing from the solid metal NPs that the plasmonic devices are only relied on various forms of nanogaps. On the other hand, the SERS substrates of Ag-SiO$_2$-NPs with super-thin Ag shells seem more in favor of biosensing applications, since the plasmonic resonance has been red-shifted to the infrared band.

### 3.3 Ag-ZnO-NPs and Ag-TiO$_2$-NPs

It is well known that dielectric environment is one of important parameters of changing the plasmonic properties of metal NPs. Therefore, the extinction behaviors of Ag-coated dielectric NPs were further explored by replacing the SiO$_2$-NPs with ZnO- or TiO$_2$-NPs. For Ag-ZnO-NPs, the extinction spectra are very similar to those of Ag-SiO$_2$-NPs, as shown in Fig. 6a, which was calculated by fixing the radius of ZnO-NPs at 48 nm and varying Ag-shell thickness from 4 to 44 nm. As observed in the extinction spectra of Ag-SiO$_2$-NPs, the D, Q, and C peaks of Ag-ZnO-NPs also exhibit similar dependences on Ag-shell thickness,
but the D peaks are further red-shifted with respect to those of same size Ag-SiO$_2$-NPs. As shown in Fig. 6a, the D peak is located at ~ 961 nm for the Ag-ZnO-NPs with ZnO-NP radius of 48 nm and Ag-shell thickness of 4 nm, ~ 124 nm of redshift with respect to that of Ag-SiO$_2$-NPs. By plotting the wavelength of D peak as a function of Ag-shell thickness, the critical Ag-shell thickness for obviously changing the plasmonic properties can be taken between 32 and 36 nm, which is slightly increased in comparison to that of Ag-SiO$_2$-NPs, as shown in the inset in Fig. 6a. For the Ag-ZnO-NPs with Ag shells of 4 nm, the D peaks are almost linearly red-shifted as well with the increase in the radius of ZnO-NPs, as shown in Fig. 6b. As the ZnO radius reaches 84 nm, the D peak of Ag-ZnO-NPs is shifted to ~ 1254 nm, which ~ 156 nm longer that of same size Ag-SiO$_2$-NPs. As such, we come to a conclusion that relatively high refractive index of dielectric NPs is in favor of tuning the plasmonic resonance to the side of long wavelength. This conclusion was further substantiated by the FDTD calculations of Ag-TiO$_2$-NPs.

Figure 7a shows the extinction spectra of Ag-TiO$_2$-NPs calculated by fixing TiO$_2$-NP radius at 48 nm and varying Ag-shell thickness from 4 to 44 nm. A little different from the observations to the Ag-SiO$_2$-NPs and Ag-ZnO-NPs, the Q peak is observed to immerse in a new plasmonic peak, which is referred to as D’ peak in this work. By calculating the electromagnetic fields in the vicinity of Ag-TiO$_2$-NPs, the D’ peak was identified to originate from a dipole plasmonic resonance as the thickness of Ag shells is 20 nm, as shown in the left of inset in Fig. 7a, which were calculated by exciting the Ag-TiO$_2$-NPs by the incident light in resonance with D’ peaks. For the Ag-TiO$_2$-NPs with Ag shells of 44 nm, the $E^2$ pattern looks to have an approximately four-symmetry, as shown in the right of inset in Fig. 7a. At the same time, the electromagnetic field in the Ag-TiO$_2$-NP inside becomes very weak, about a few tenths intensity of incident light. In the thickness range of Ag shells varying from 4 to 44 nm, the extinction spectra of Ag-TiO$_2$-NPs are observed to smoothly change without a critical thickness of Ag shells, but the D peaks still exhibit an obvious red-shift with the decrease in the thickness of Ag shells. Therefore, we conclude that the optical properties of Ag-coated dielectric NPs are mainly determined by the thickness of Ag shells, which can be linked to the penetration depth of incident light in silver.

For the Ag-TiO$_2$-NPs with Ag shells of 4 nm, a nearly linear red-shift is observed with the increase in the radius of TiO$_2$ NPs, as shown in Fig. 7b. Because the refractive index of TiO$_2$ is higher than that of ZnO, the D peak reaches ~ 1600 nm as the radius of TiO$_2$ NPs is increased to 84 nm, which is more than 300 nm larger that of Ag-ZnO-NPs. It is of interest that the D’ peak is observed to red-shift to ~ 520 nm as well, suggesting that the Ag-TiO$_2$-NPs are capable of simultaneously enhancing electromagnetic fields in both of visible-light and infrared regions. Figure 8 shows the electromagnetic fields in the vicinity of Ag-ZnO-NPs and Ag-TiO$_2$-NPs with Ag shells of 4 nm, which were calculated by fixing ZnO-NP and TiO$_2$-NP radius at 72 nm. The Ag-ZnO-NPs and Ag-TiO$_2$-NPs exhibit the $E^2$ patterns similar to those of Ag-SiO$_2$-NPs (Fig. 5b), while the electromagnetic enhancement is observed to become weaker and weaker with the increase in the refractive index.
It should be emphasized that most conclusions in this work do not limit to Ag-coated spherical dielectric NPs, which can be varied into the NPs with various shapes, such as nanorods, nanosheets, and various nanostructured crystals, glasses, and polymers, etc. It is important that this work will enlighten us to pay much more attention to the nanostructures coated with a thin metal layer, which would exhibit unique optical properties much different from the nanostructures consisting of solid metals. In the past decades, 3D SERS substrates were fabricated by coating Ag or Au layers on various dielectric nanostructures, such as Ag-coated ZnO nanorod arrays [20–22]. Though pretty good SERS performances have be achieved, it is necessary to comprehensively understand the 3D SERS substrates by exploring the plasmonic properties. According to this work, the composites of dielectric nanostructures with thin metal layers are probably more useful for designing the plasmonic devices working in the infrared band, such as the light emitters based on the fluorescent center of rare-earth ions and the SERS substrates for biosensing. To achieve this purpose, a key problem to overcome is how to prepare a thin metal layer on the dielectric nanostructures, with a good uniformity and as thin as possible, which is still a great challenge to the various techniques of film growth. A promising candidate is atomic layer deposition, which are able to prepare thin films controlled within an accuracy as small as a few atomic layers.

4. Conclusions

In summary, the optical properties of Ag-SiO$_2$-NPs, Ag-ZnO-NPs, and Ag-TiO$_2$-NPs were studied using an FDTD method. Besides the commonly observed D and Q peaks in the extinction spectra of Ag-NPs, a new plasmonic peak is observed to appear in the region below 400 nm and related to the thickness of Ag shells. As the thickness of Ag shells is reduced to be less than a critical value, the Ag-coated dielectric NPs start to obviously deviate from the extinction behavior of Ag-NPs and the dipole plasmonic resonance gradually becomes predominant in the extinction spectra. For the Ag-coated dielectric NPs with Ag shell of 4 nm, the plasmonic peak is red-shifted up to infrared band with the increase in the NP dimension. At the same time, relatively large electromagnetic enhancement is observed to occur in the regions of Ag-coated dielectric NP outside and inside. The enhanced electromagnetic fields in the region of Ag-coated dielectric NP outside is similar to those emitted by Ag-NPs while the inner electromagnetic enhancement is relatively uniform and both of dipole and quadrupole plasmonic resonances have contributions to the inner enhancement. The Ag-coated dielectric NPs are suggested to be useful for designing plasmonic devices working in infrared band, such as the light emitters.

Declarations

- Ethical Approval: Not applicable
- Consent to Participate: Not applicable
- Consent to publish: Not applicable
- Author Contributions: All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Qing-Wei Sun, Qi Sun, and Qing-Yu
Zhang. The first draft of the manuscript was written by Qing-Wei Sun and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Availability of data and materials: The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

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Figures
Figure 1

(a) Extinction spectra of Ag-SiO₂-NPs calculated by fixing the thickness of Ag shell at 20 nm and varying SiO₂-NP radius from 20 to 72 nm. (b) Extinction spectra of Ag-NPs calculated by varying the radius from 24 to 72 nm. The inset shows the peak energy of plasmonic resonances plotted as a function of Ag-SiO₂-NP or Ag-NP radius. All the extinction spectra were collected at the cubic PML boundaries at 250 nm of distance to the center.

Figure 2
Electric fields (E2) in the vicinity of Ag-SiO2-NPs excited by the incident light in resonance with the C, Q, and D peaks, respectively. The simulations were carried out by fixing the thickness of Ag shell at 20 nm and the radius of SiO2-NPs 48 nm. The color bar represents the intensity of E2 varied in logarithmic scale and the intensity of incident light is set to 1.0.

Figure 3
Extinction spectra of Ag-SiO2-NPs calculated by varying the thickness of Ag shells from 4 to 44 nm and fixing the radius of spherical SiO2-NPs at 24 nm (a), 48 nm (b), and 72 nm (c). The inset shows the wavelength of D peak plotted as a function of Ag-shell thickness for the three series of Ag-SiO2-NPs. All the extinction spectra were collected at the cubic PML boundaries at 250 nm of distance to the center.

Figure 4

Extinction spectra of Ag-SiO2-NPs with Ag shells of 4 nm in the wavelength range of 400 to 1400 nm. The inset shows the wavelength of D peak plotted as a function of SiO2-NP radius. All the extinction spectra were collected at the cubic PML boundaries at 250 nm of distance to the center.
Electric fields (E2) in the vicinity of Ag-SiO2-NPs with Ag shells of 4 nm excited by the incident light in resonance with the D peaks. The radius of SiO2-NPs is 48 nm (a) and 72 nm (b). The color bar represents the intensity of E2 varied in logarithmic scale and the intensity of incident light is set to 1.0.

Figure 5
Figure 6

Extinction spectra of Ag-ZnO-NPs calculated by fixing ZnO-NP radius at 48 nm and varying the Ag-shell thickness from 4 to 44 nm (a) and by fixing the Ag-shell thickness at 4 nm and varying ZnO-NP radius from 24 to 84 nm (b). The inset shows the wavelength of D peak plotted as a function of Ag-shell thickness. All the extinction spectra were collected at the cubic PML boundaries at 250 nm of distance to the center.
Figure 7

Extinction spectra of Ag-TiO2-NPs calculated by fixing TiO2-NP radius at 48 nm and varying the Ag-shell thickness from 4 to 44 nm (a) and by fixing the Ag-shell thickness at 4 nm and varying TiO2-NP radius from 24 to 84 nm (b). The inset shows the E2 patterns of Ag-TiO2-NPs with 48-nm TiO2-NP radius excited by the incident light in resonance with the D' peak. All the extinction spectra were collected at the cubic PML boundaries at 250 nm of distance to the center.
Figure 8

(a) and (b) Electric fields (E2) in the vicinity of Ag-ZnO-NPs and TiO2-NPs with Ag shells of 4 nm excited by the incident light in resonance with the D peaks, respectively. The radius of ZnO- and TiO2-NPs is 72 nm. The color bar represents the intensity of E2 varied in logarithmic scale and the intensity of incident light is set to 1.0.

Supplementary Files

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- fig9.png