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Study on Extinction Properties of Nanoparticles with Hybrid Core-Shell Structure

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Based on the discrete dipole approximation (DDA) method, we studied the effects of different materials and thicknesses on extinction properties of the nanoparticles with a hybrid core-shell structure. The different core-shell structures can be used as sensors or to enhance sensitivity of sensors. For those uses, this article describes the application of DDA simulations to establish the extinction properties of hybrid nanoparticles fabricated with different materials associated with the different core-shell structures. The extinction efficiencies of core-shell structures were stronger than those of hybrid nanoparticles with other combinations of structures or of the single metal nanoparticles. As the shell's thickness was increased, the absorption properties in extinction spectra of different hybrid nanoparticles were changed from that of elemental core metals to that of shell metals, and the absorption peaks of extinction spectra widened. In addition, the DDA method was used to analyze absorption properties in extinction spectra of core-shell nanoparticles with different materials (silver, gold, silicon, and silicon dioxide). We found that the properties of the shell materials were the key factors in influencing the extinction properties of the hybrid nanoparticles with core-shell structures.

1. Introduction

Nanoparticles made of precious metals such as gold and silver have superior performance, in that the two conventional metals can be used in studying such phenomena as the quantum size effect, the surface effect, and the macroview tunnel effect. In recent years the research activities in the fields of nanomaterials, in optoelectronics, surface enhanced spectroscopy, biological chemical engineering, and environmental protection have offered the prospect of broad applications.[1–3] Core-shell structure composite nanoparticles, because of their special electronic structure and surface properties, are of increasing interest in applications in these fields.[4] Compared with the traditional two-element components, precious metals, and alloy nanoparticles, nanoparticles with a core-shell structure composite contain both a nuclear layer with the physicochemical properties of the metals and also a metal shell. Therefore, using methods of physical and chemical synthesis to produce different thicknesses of precious metals in the core and shell to make full use of the nuclear shell metal's characteristics will promote the development of nanometer materials in the 21st century.[5]

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The discrete dipole approximation (DDA) method is one of the most efficient computational numerical algorithms, and it can be used to simulate localized surface plasmon resonance (LSPR) for nanostructures with arbitrary shapes and dimensions. This method has the significant advantages of occupying fewer computation resources while calculating the interaction between the light and the metal nanostructures. Both theory and experiment suggest that a change in the thickness of the shell has a sizable influence on the spectral properties of LSPRs. For example, the effect of shell thickness on an Au–Ag core–shell nanorods-based plasmonic nanosensor[6] has been used to investigate the tunable properties of surface plasmon resonances; namely, the influence of core–shell thickness and dielectric environment.[7] To the best of our knowledge, thus far, there have been no reports on investigating the effect of both shell thickness and materials on the extinction properties of core-shell nanoparticles.

Hydrogen peroxide sensors are of practical importance in chemical, biological, clinical, environmental, and fuel cell applications, and we believe that the Au/Ag bimetallic composition in hybrid core-shell structure nanoparticles can be used for the electrocatalytic reduction of hydrogen peroxide.[8] Tang *et al*. found that the fluorescence intensity of [2,7-ylenevinylene-co-alt-1,4-phenylene dibromide] (PFV) after assembly on Ag@SiO_2 core-shell NPs was enhanced 1.3-fold compared with the fluorescence intensity of PFV assembled on silica NPs without silver cores for the metal-enhanced fluorescence (MEF) property of Ag@SiO_2 nanostructures.[9] From these studies we know that the hybrid core-shell structure nanoparticles can be used as sensor materials or used to enhance the sensitivity of sensors under development. In this study, the DDA method was used to simulate the extinction properties of hybrid core-shell structure nanoparticles. The influence of the variations in thickness of cores and shells and in materials used as the core and shell on extinction spectra of hybrid core-shell structure nanoparticles was explored.

2. DDA Method

DDA theory is a finite difference time domain calculation method, and it is the most effective numerical algorithm to simulate the LSPR properties of nanostructures with arbitrary shapes and sizes. DDA theory also provides a convenient method for the simulation and calculation of interactions between light and metal nanoparticles. To calculate the absorption, scattering, and extinction properties of nanoparticles with arbitrary shape, DDA theory firstly considers the particles as composite of an N set square lattice, and each lattice point is considered as a dipole approximation. Such an arbitrary dipole interaction with a local field can be expressed as

$$\boldsymbol{P}_i = \alpha_i \cdot \boldsymbol{E}_{\mathrm{loc}}(\boldsymbol{r}_i), \tag{1}$$

where α_i is the dipole polarizability. For isolated particles, $\boldsymbol{E}_{\mathrm{loc}}$ includes the incident optical field and others formed by the dipole in the dipole field and can be represented as

$$\boldsymbol{E}_{\mathrm{loc}}(\boldsymbol{r}_i) = \boldsymbol{E}_{\mathrm{inc},i} + \boldsymbol{E}_{\mathrm{other},i} \tag{2}$$

$$= E_0 \exp(i\boldsymbol{k}\boldsymbol{r}_i) - \sum_{j \neq i} A_{ij} \cdot p_j, \tag{3}$$

where, E_0 is the amplitude of the incident optical field, and $\boldsymbol{k}$ is the wave vector. The dipole–dipole interaction matrix e is normally expressed as follows.

$$A_{ij} \cdot p_i = \frac{\exp(ikr_{ij})}{r_{ij}^3}\left\{ k^2 r_{ij} \times (r_{ij} \cdot p_j) + \frac{(1 - ikr_{ij})}{r_{ij}^2} \times \left[r_{ij}^2 p_i - 3r_{ij}(r_{ij} \cdot p_j) \right] \right\} \quad (j \neq i) \tag{4}$$

Substituting Eqs. (3) and (4) into Eq. (1), we can generate the system of equations

$$\boldsymbol{A}' \cdot \vec{\boldsymbol{P}} = \vec{\boldsymbol{E}}, \tag{5}$$

where $\boldsymbol{A}'$ is a transposed matrix of $\boldsymbol{A}$. For a system containing N polarizable points, $\vec{\boldsymbol{E}}$ and $\vec{\boldsymbol{P}}$ are a $3N$ dimensional vector, and $\boldsymbol{A}'$ is a $3N \times 3N$ matrix. Solving this set of $3N$ complex linear equations, the polarizations $\vec{\boldsymbol{P}}$ are determined, and from this we can calculate the cross section of the extinction as

$$C_{\text{ext}} = \frac{4\pi k}{|E_0|^2}\text{Im}(E_{\text{inc},i}^* \cdot p_j). \tag{6}$$

3. Results and Discussion

Using the DDA method, we simulated the extinction properties of Ag@Au core-shell nanoparticles with different radii. In the calculation, we first fixed the nuclear radius of the core materials and changed the radius of shell materials. To facilitate analysis, we set the core's radius as R_1 and the shell's radius as R_2. To investigate the differences in the properties of extinction spectra between hybrid core-shell structure nanoparticles and elemental metal nanoparticles, we simulated the extinction spectra of two different core-shell structures and the elemental extinction spectra of the noble metal nanoparticles. Extinction is a term used in physics to describe the absorption and scattering of electromagnetic radiation. Any change in the parameters of metal nanoparticles could lead to the optical drift in extinction spectrum and thus influence the optical applications in practice.[10–13] As Fig. 1(a) shows, if only the elemental metal nanoparticles were used for simulation, the silver and gold nanoparticles gave absorbance peaks at around 409 and 518 nm, respectively. For comparison, the radii of shell nanoparticles for simulation were fixed as R_2 = 20 nm and the radii of core nanoparticles for simulation were changed from R_1 = 0 nm to R_1 = 20 nm. The simulated results are shown in Figs. 1(b) and 1(c).

From the results shown Fig. 1(b), as the silver shell's thickness was fixed at R_2 = 20 nm, when the thicknesses of the gold nuclei was increased from R_1 = 0 nm to R_1 = 20 nm, the absorbance peaks of Ag@Au hybrid nanoparticles shifted gradually from the elemental silver nanoparticle peak to the elemental gold nanoparticle peak. Similarly, as the results in Fig. 1(c) shows, when the gold shell's thickness was fixed at R_2 = 20 nm and the thicknesses of the silver nuclei increased from R_1 = 0 nm to R_1 = 20 nm, the extinction curve shifted gradually from the elemental gold nanoparticle peak to the elemental silver nanoparticle peak for Au@Ag hybrid nanoparticles. Figures 1(b) and 1(c) also show that, when R_1 was in the range of 0–10 nm ($R_1/R_2 \leq 1/2$), the extinction properties of core-shell hybrid nanoparticles were primarily dominated by the properties of the metals in the external shell. When R_1 was in the range of 10–15 nm ($R_1/R_2 \geq 1/2$), the extinction properties of core-shell hybrid nanoparticles were primarily dominated by the properties of the metals in the inner nuclear layer, because the value of R_2 is definite and the weight ratio of core metal decreases as the thickness of hybrid core-shell nanoparticles increases. When the core is thin, as the thickness

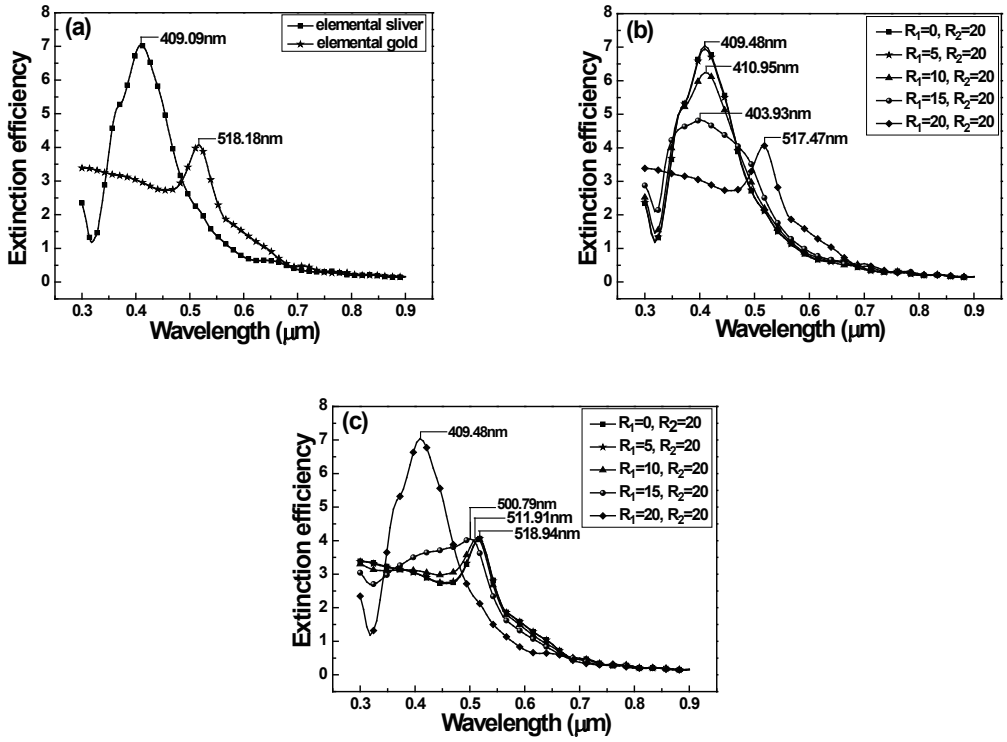

Fig. 1. Extinction spectra of (a) elemental gold and elemental silver nuclear shell models with shell radius R_2 = 20 nm; (b) gold-silver core-shell model with shell radius R_2 = 20 nm; and (c) silver-gold core-shell model with shell radius R_2 = 20 nm.

of the shell increases, the characteristics of hybrid core-shell nanoparticles are dominated by those of the shell metal. But when the shell is thin, the core has the larger weight ratio, the external metal effect is relatively small, and the effect of the core metal increases.

To investigate the effect of the extinction properties of the shell made from elemental precious metal in hybrid core-shell nanoparticles, two kinds of core-shell structures and elemental extinction spectra of noble metal nanoparticles were used for simulation. For convenience, the radii of shells of the nuclear layer nanoparticles were fixed at R_1 = 5 nm and the radii of core nuclear layer nanoparticles were changed from R_2 = 5 nm to R_2 = 30 nm, as shown in Figs. 2(a)–2(d). As the results in Fig. 2(a) show, as the thicknesses of the shell increased, the intensity of absorption peaks of the extinction spectra and full width at half maximum (FWHM) of the extinction coefficient spectra decreased. The wavelengths with the maximum extinction efficiency of LSPRs were shifted to lower values as the thickness of shell was increased from R_2 = 5 nm to R_2 = 30 nm. The results in Fig. 2(b) show that, as the thickness of the shells was increased, the intensity of absorption peaks of the extinction spectra and FWHM of the extinction coefficient spectra also increased.

From the results in Figs. 2(c) and 2(d), as the radii of the nuclear layer was fixed at R_1 = 5 nm and the thickness of the shell was increased, the properties of the extinction spectra of hybrid core-shell nanoparticles were primarily dominated by the properties of the shell metal. If the core was gold and the shell was silver, as Fig. 2(c) shows, the properties of the extinction spectra of hybrid core-shell nanoparticles were similar to those of elemental silver. Otherwise, as gold

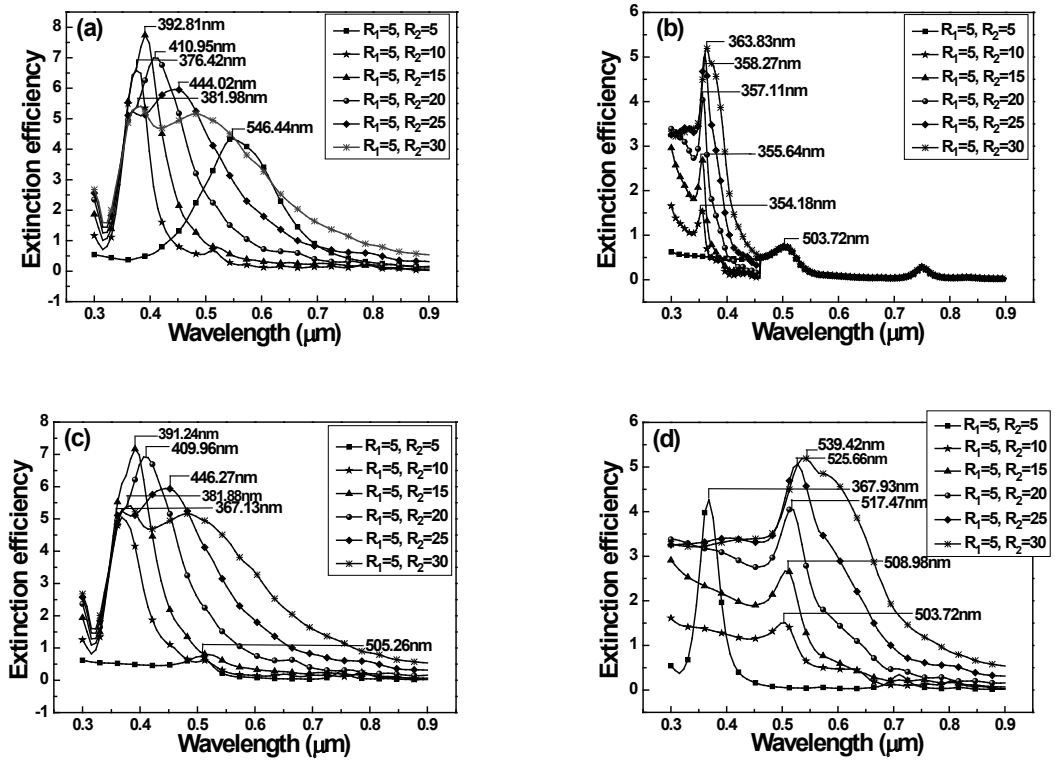

Fig. 2. Extinction spectra of core-shell nanoparticles with different shell thicknesses: (a) Ag@Ag, (b) Au@Au, (c) Au@Ag, and (d) Ag@Au.

and silver were used as the shell and core metals, respectively, as Fig. 2(d) shows, the properties of the extinction spectra of hybrid core-shell nanoparticles were not similar to the variations of elemental gold. The intensity of the absorption peaks in the extinction spectra first decreased and then increased, and the wavelengths with the maximum extinction efficiency in LSPRs showed no apparent changes when R_2 was equal to and larger than 10 nm. The results in Figs. 1 and 2 suggest that, as the ratio of R_1/R_2 decreases, the extinction properties of Au@Ag and Ag@Au core-shell hybrid nanoparticles become superior to those of elemental Ag@Ag and Au@Au hybrid core-shell nanoparticles.

The DDA method and experimental data were used to analyze the extinction properties of core-shell nanoparticles with different materials (silver, gold, silicon, and silicon dioxide) so that we may find the most suitable design model for LSPR sensors. On one hand, we can validate the experimental results of the performance of the LSPR probe. On the other hand, we can establish the reasonableness of the results of using core-shell structures.

As Fig. 3(a) shows, the absorption peaks of the extinction spectra of Ag@Ag and Au@Ag nanoparticles were located around a centered wavelength of 370 nm, with the former having the higher intensity of absorption peaks. However, their extinction intensities were similar to those of Ag@Au and Au@Au nanoparticles, for which the absorption peaks of maximum extinction

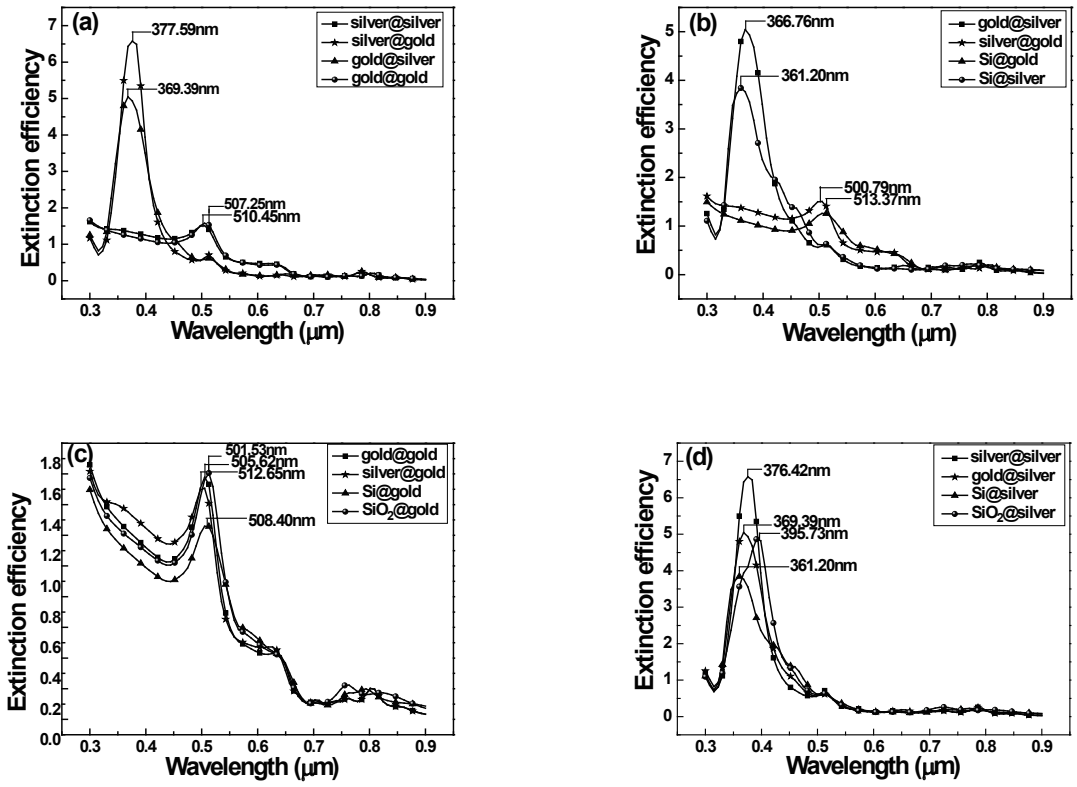

Fig. 3. Extinction spectra of core-shell nanoparticles with different structures (a) Ag@Ag, Ag@Au, Au@Ag, and Au@Au; (b) Au@Ag, Ag@Au, Si@Au, and Si@Ag; (c) Au@Au, Ag@Au, Si@Au, and SiO_2@Au; and (d) Ag@Ag, Au@Ag, Si@Ag, and SiO_2@Ag.

efficiency were located around a centered wavelength of 510 nm. The results in Fig. 3(c) are consistent with those in Fig. 3(b) for nanoparticle composite structures with silver and gold as the core. As Fig. 3(d) shows, the absorption peaks of maximum extinction efficiency were also around wavelengths of 370 and 510 nm for silver-core (Au@Ag and Si@Ag) and gold-core (Au@Ag and Si@Ag) nanoparticle, respectively. The maximum extinction efficiency of Au@Ag nanoparticles is higher than those of Si@Ag, although the maximum extinction efficiencies are similar to those of Ag@Au and Si@Au nanoparticles.

In summary, no matter what kind of metals are used, the extinction properties of core-shell nanoparticles are largely determined by the external layer of metal, but the thickness of the core materials can affect the extinction properties of core-shell hybrid nanoparticles. By comparing the results shown in Figs. 3(a)–3(d), we can say that, as the extinction efficiency and absorption wavelength range are compared, Ag@Au nanoparticles with a composite structure have better extinction properties than either other combinations of composite nanostructures or single metal nanoparticles. Note that, as can be seen from the extinction spectrum in Fig. 3, each curve has several peaks. This phenomenon not only relates to the hybrid gold and silver materials, but also relates to the optical properties of nanoparticles. For silver or gold nanoparticles, the extinction spectrum always shows several peaks due to the in-plane and out-of-plane polarization.

4. Conclusions

Using the DDA method, the properties of extinction spectra for nanoparticles with the silver-gold core-shell structure as the composite structures of different sizes and for the variations with different thicknesses of shell and core were reported in this paper. Research results showed that, as the thickness of the shell was increased, the spectral line of the composite nanoparticles gradually formed two extinction peaks, which were similar to those of elemental metal nanoparticles. The spectra gradually converged toward one extinction peak with a larger FWHM. Based on the extinction efficiency and absorption wavelength ranges, the nanoparticles with the silver-gold core-shell composite structure had better extinction properties than other combinations of composite nanostructures or single metal nanoparticles. Furthermore, the extinction properties of nanoparticles with the hybrid core-shell structure were primarily determined by the precious metal.

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