Sensing response of dielectric-coated spherical metal nanoshells

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Localized surface plasmon properties of dielectric-coated spherical metal nanoshells embedded in different surrounding environment were computed theoretically, and the effect of the dielectric coating on the sensing response of metal nanoshells was analyzed accordingly. It was found that the sensibility of the metal nanoshells depends on the thickness and refractive index of the coating layer. The sensitivity can be decreased from 257 nm/RIU to about 90nm/RIU after coated with 9 nm coating for [10, 15] nm Ag nanoshell. However, dielectric Coating may improve the figure of merit of the sensing response of metal nanoshells with large size. The FOM of [30, 36] nm Ag nanoshell can be increased from 2.3 RIU^{-1} to about 2.8 RIU^{-1}.

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1. Introduction

The research on metal nanostructures has increased remarkably in the past decade due to their fascinating properties resulting from localized surface plasmon (LSP) resonances [1-2]. Strong enhancement in the optical absorption, scattering, and near-field arising from LSP resonance of noble metal nanoparticles allow their use in numerous applications such as biological imaging, biochemical sensing, selective photothermal therapy and surface-enhanced Raman scattering (SERS) [1-4]. The LSP resonance also shows strong tunability. Its resonance wavelength depends not only on the size, the metal type, the geometry of the nanostructure, but also on the surrounding dielectric environment. Sensing applications of plasmonic nanostructures are based on such tunability, in which case the plasmon resonance band is shifted linearly with the increase of the refractive index of the surrounding environment.

In certain circumstance, bare metal nanostructures are not acceptable in applications. They are always coated with a dielectric layer, by which not only metal nanoparticles are protected from photochemical degradation by absorbed species, but also in some cases the coatings on the metal nanoparticle is indispensable, such as surface decoration in imaging, sensing field etc. [5-12]. For example, many investigations has found that the strong Joule absorption loss accompanying metal nanostructures is detrimental to some applications such as light trapping in solar cells and luminescence enhancing of emitting nanodots. Dielectric medium coating on the metal nanoparticles is believed a possible approach to tackle the problem [11, 12]. Therefore, the research on the dielectric-coated metal nanostructures is indispensible. Several groups have prepared protected Ag surfaces by coating metal islands with dielectric medium such as SiO_x, TiO_2 and other oxide, and the role of this overlay in tuning SPR has been paid attention. Theoretical work have also been done to explore the influence of the dielectric-coating on the LSP properties of metal nanostructures [13, 14].

Metal nanoshells, which consisting of a dielectric core and a metallic shell, exhibit attractive features due to the hybridization of the plasmons supported by the nanoscale sphere and a cavity in the surrounding medium [15]. It exhibits a wide-range tunability of the SP resonance through the UV to IR with varying the radius ratio between core and shell. Many groups have reported excellent performance of metal nanoshells in many application fields such as in sensing [16, 17]. The sensitivity of the metal nanoshells is found far exceed that of compact nanoparticles of the same size. To our knowledge, however, no report on the sensing response of dielectric-coated metal nanoshells is available. In our previous report, we have found that dielectric coating affects not only the LSP resonance band position but also the damping width of metal nanoshells [14]. In this article, we aim at the sensing characteristics of dielectric-coated Ag nanoshells. Extinction spectra of Ag nanoshells coated with dielectric layer of varying thickness and refractive index in different environment were simulated theoretically in detail. The sensing characteristics were compared with those of bare nanoshells, and the effect of dielectric coating on the sensing response of metal nanoshells was deduced.

2. Theoretical modeling

The geometry of the dielectric-coated nanoshells is illustrated schematically in the inset of Fig. 1. Inner and outer radii of r_1, r_2 are used to characterize the size of the metal core-shell, which is denoted as [r_1, r_2] in this paper. The dielectric coated metal nanoshell is denoted as [r_1, r_2, r_3], in which case the thickness t of the coating layer is determined by r_3-r_2. The dielectric coating was selected as dielectric materials and the refractive index is kept as a constant. The core material is selected as silica due to that silica microspheres are usually used as template in metal nanoshell preparation. The refractive indexes of metal Ag used in the computation were theoretical fitting results using Lorentz-Drude model to the experimental values from Ref. 18. Finite Difference Time Domain (FDTD) method was used in the numerical computation of the extinction efficiency of the metal nanoshell.

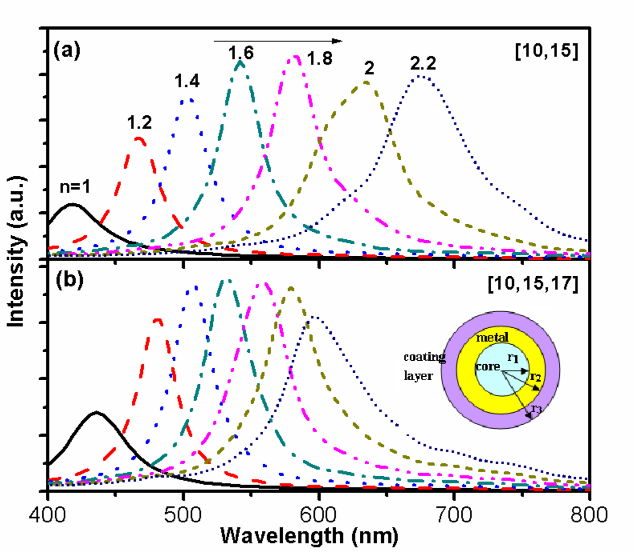

Fig. 1. LSP extinction spectra of [10, 15] nm Ag nanoshells in different dielectric environment. (a) bare Ag nanoshell; (b) after coated with 2 nm layer. Inset: Structure schematics of the dielectric-coated metal nanoshells

3. Results and discussion

3.1. Sensing response of Ag nanoshells with different coating thickness

Fig. 1 (a) show the extinction spectra of [10, 15] nm Ag nanoshells embedded in different dielectric environment. As demonstrated, the LSP resonance band redshifts with the increase of the refractive index n of surrounding environment from 1 to 2.2. Fig. 1 (b) show the extinction spectra of the nanoshell after coated with dielectric layer of 2 nm thickness ([10, 15, 17] nm nanoshell). The refractive index n_0 of the coating layer is deemed as 1.45 which is the same as that of the core material silica. When the Ag nanoshell is situated in atmosphere (refractive index n=1), the LSP band red-shift from 425 nm to about 435 nm after dielctric coating. With the increase of the refractive index of environment, the LSP band of dielectric coated Ag nanoshell also shows redshift, but the shift is slow than that of the [10, 15] nm nanoshell without coating. In addition, the position and width of the LSP band of the coated nanoshell are different from those of the bare Ag nanoshell.

To compare the LSP band characteristics and the sensing response of the metal nanoshell, the peak positions and the FWHMs (full width at the half maximum) of the LSP extinction spectra in Fig. 1 are summarized in Fig. 2. Apart from those of [10, 15, 17] nm nanoshell, the spectra positions and FWHMs of Ag nanoshells coated with thicknesses of 5 nm and 7 nm ([10, 15, 20] nm and [10, 15, 22] nm nanoshell respectively) are also presented. It is observed that the LSP peak positions of the coated Ag nanoshells are always red than those of the bare Ag nanoshell when the refractive index of the environment is lower than 1.45, and it is the opposite case when the refractive index is higher than 1.45. When the refractive index of the environment is 1.45, which is equal to the reafractive index of coating silica, the peak positions are the same for bare and coated nanoshells. It is due to that the environment surrounding the metal nanoshell is uniform at this time. The behavior of the sensing response can also be divided into two zones by $n = 1.45$. For $n < 1.45$, though the slope of the response curve of coated Ag nanoshell is lower than that of bare nanoshell, the contrast is minute. For $n > 1.45$, however, the contrast is apparent and becomes more tremendous as the coating gets thicker. Note that the slope of the curve is related to the sensitivity. So the behavior can be explained as the dielctric coating induced inert of the metal nanoshell to the outer environment. The thicker is the coating layer, the more insensitive is the nanoshell to the environment.

All the FWHMs of bare and coated nanoshells in Fig. 2 (b) show a trend of narrowing first and then widening with the increase of environment refractive index. The width narrowing behavior when environment refractive index is low can be ascribed to a small refractive index difference Δn between core silica and outer environment surrounding the metal nanoshell [14]. When the coupling strength between inner cavity SP mode and outer sphere mode in metal nanoshell is strong, the small refractive index difference Δn may lead to weak electron oscillation phase incoherence. For $n > 1.8$, all the FWHMs become wider due to the increased loss of electron phase coherence induced by the increased environment refractive index [19]. Comparing the FWHMs of bare and coated metal nanoshells, it can be found that for environment refractive index $n < 1.8$ the FWHMs of coated nanoshells are narrower than those of bare except $n = 1$, but the FWHMs differences between the bare and dielectric-coated Ag nanoshell are minor. While for $n > 1.8$, the FWHMs difference becomes apparent. The thicker is the coating layer, the narrower is the FWHM. The FWHM of the extinction spectra is another index for evaluating the sensing performance of LSP sensor. A figure of merit (FOM) is defined as $FOM = \frac{\Delta\lambda / \Delta n (nm\, RIU^{-1})}{FWHM\,(nm)}$ to quantitatively evaluate the refractive index sensibility of various sensing platform [20]. Here $\Delta\lambda / \Delta n$ is the sensitivity which is also the slope of the refractive index-dependent band position curve. Then it seems that though $\Delta\lambda / \Delta n$ is decreased for dielectric coated metal nanoshells, the *FOM* may be improved by dielectric coating due to the narrow spectra FWHM.

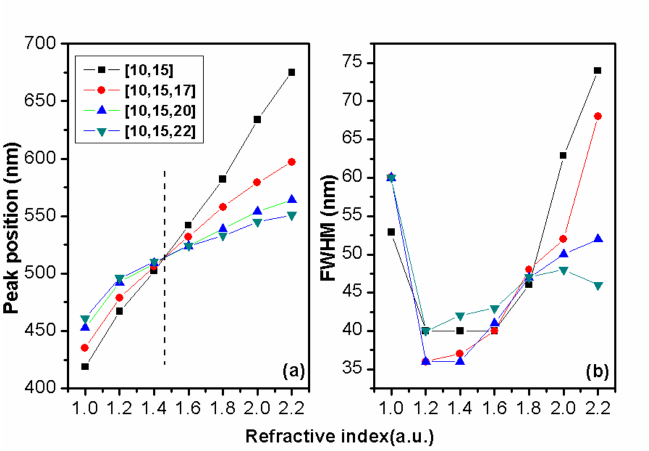

Fig. 2. Sensing responses of [10, 15] nm Ag nanoshells before and after coated with dielectric layer of different thicknesses. (a) peak positions of extinction spectra vs refractive index of the surrounding environment; (b) FWHMs vs refractive index of the surrounding environment

3.2. Sensing response of coated Ag nanoshells of different refractive index

Fig. 3 (a) and (b) show the sensing responses of [10, 15] nm Ag nanoshells coated with dielectric layer of different refractive index. The thickness of the coating layer is set at 2 nm and the refractive indexes are varied from 1.45 to 2.5 which are close to the refractive index of common coating materials. As shown in Fig. 3 (a), the curve slope ($\Delta\lambda / \Delta n$) of the bare nanoshell is still the maximum. However, with the increase of refractive index of the coating layer, the gap between the $\Delta\lambda / \Delta n$ value of the coated and that of the bare nanoshell became smaller. Notice that the curve of [10, 15] nm nanoshell intersects with the curves of [10, 15, 17] nm at $n_0 = 1.45$ and *2* when the refractive indexes of the environment is nearly equal to that of the coating layer. It also ensures that the FDTD calculation used in this work for coated nanoshells shows excellent agreement with the results for bare nanoshells for the limiting case: vanishing refractive index difference between coating layer and outer environment.

From Fig. 3 (b), similar trends of FWHMs change are observed for all the nanoshells: decreasing with the increase of the refractive index of the environment first and then increasing. Comparing with the bare nanoshell, most FWHMs of the coated nanoshells are a little narrower when *n* is small. And the FWHMs of coated nanoshells may be wider than those of the bare nanoshells for big *n*, especially for the coating layer with high refractive index. On the whole, changing the coating refractive index n_0 does not have a remarkable effect on the FWHMs. Coating with low n_0 seems have minor advantage over that with high n_0.

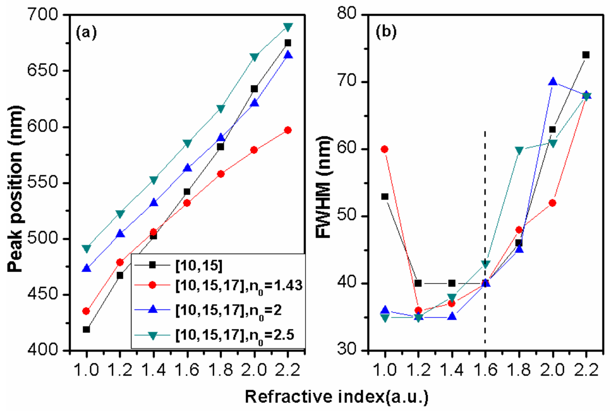

Fig. 3. Sensing responses of [10, 15] nm Ag nanoshells before and after coated with 2 nm dielectric layer of different refractive index. (a) peak positions of extinction spectra vs refractive index of the surrounding environment; (b) FWHMs vs refractive index of the surrounding environment

3.3. Effect of coating on the sensing response of Ag nanoshells with different size

A. Ag nanoshell with different outer radius

To study the effect of dielectric coating on the sensing response of Ag nanoshells with different size, we first compare the LSP peak positions and FWHMs of bare and coated Ag nanoshells with the same inner radius r_1 and varying outer radius r_2. Inner radius r_1 is set at 10 nm and r_2 is varied from 12 nm to 20 nm. The thickness and refractive index of the coating layer are set at 2 nm and 1.45 respectively. As Fig. 4 (a) shown, for the bare metal nanoshell, with the increase of outer radius, i.e. thickness of the metal shell, the LSP peak blushifts due to the decreased interaction between cavity mode and sphere mode [21], whereas the curve slope does not change perceptibly. After dielectric coating, the sensitivity of the nanoshell decreases and the change is related to the nanoshell size. The thicker is the Ag shell, the less is the effect of coating on the sensitivity change. The change in the FWHMs in Fig. 4 (b) also have similar trend. With the increase of outer radius r_2, the discrepancy between the FWHMs of bare and that of coated nanoshells becomes small gradually.

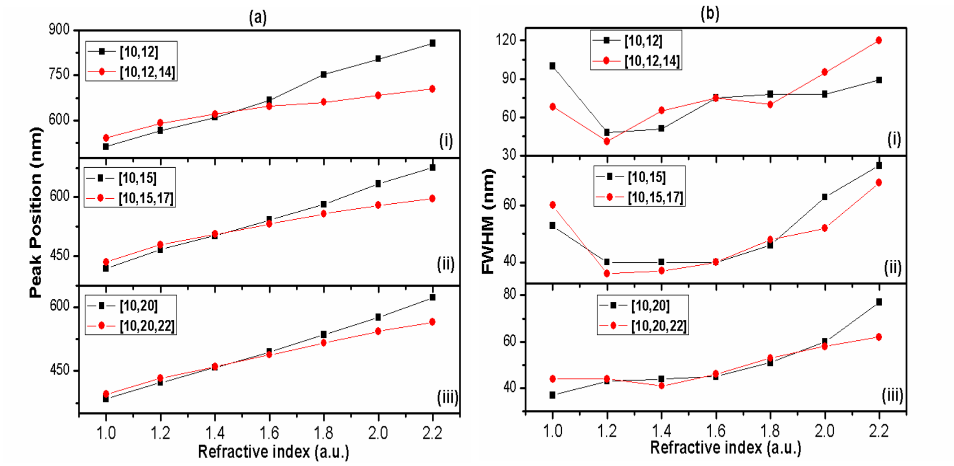

Fig. 4. Sensing responses of Ag nanoshells with different radius ratio before and after coating with 2 nm dielectric layer. (a) peak positions and (b) FWHMs vs refractive index of the surrounding environment. i) [10, 12] nm; ii) [10, 15] nm; iii) [10, 20] nm

B. Ag nanoshell with different inner radius

The size of the Ag nanoshell is also changed by keeping the radius ratio at a constant but changing the inner and outer radius. Fig. 5 shows the effect of dielectric coating on the spectral peak and FWHM change of Ag nanoshell. In this case, the radius ratio between r_1 and r_2 is kept at 10/12, and the inner radius r_1 is varied from 10 nm to 30 nm. The thickness and the refractive index of the coating layer are 2 nm and 1.45 as previous. As demonstrated in Fig. 5 (a), the coating has a slight effect on the curve slope of the bigger size Ag nanoshells such as [20, 24] nm and [30, 36] nm. Most of the FWHMs in Fig. 5(b), however, are narrowed by dielectric coating. Especially for [30, 36] nm Ag nanoshell, the reduction of FWHMs is the most apparent. It is estimated that the sensitivity of [30, 36] nm Ag nanoshell is about 339 nm/RIU. After dielectric coating the sensitivity does not change but the FOM can be increased from 2.3 RIU^{-1} to about 2.8 RIU^{-1}.

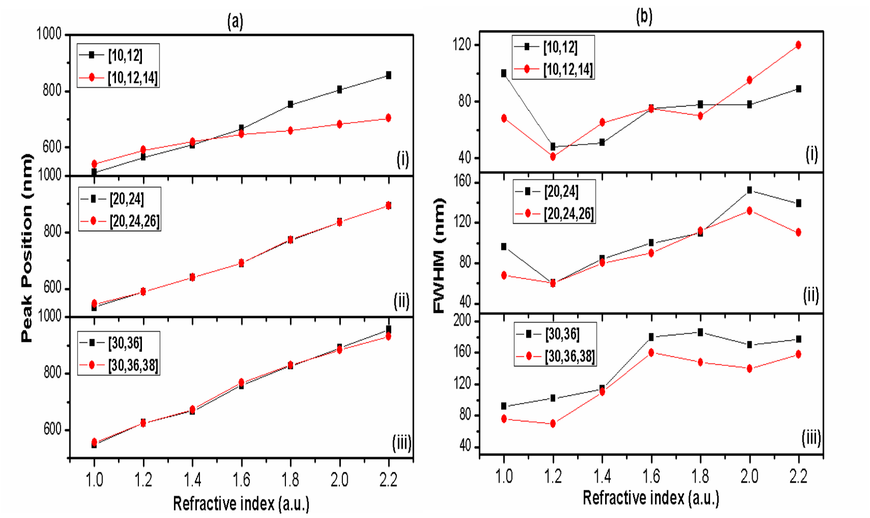

Fig. 5. Sensing responses of Ag nanoshells with different size before and after coating with 2 nm dielectric layer. (a) peak positions and (b) FWHMs vs refractive index of the surrounding environment. i) [10, 12] nm; ii) [20, 24] nm; iii) [30, 36] nm

From the computation results, it is inferred that the dielectric coating may influence the sensibility of the metal nanoshells. i) The thickness of dielectric coating affects the sensitivity significantly. The sensitivity can be decreased from 257 nm/RIU to about 90nm/RIU after coated with 9 nm coating for [10, 15] nm Ag nanoshell. ii) Increasing the refractive index of the dielectric coating may decrease the sensitivity difference between the coated and bare Ag nanoshell, but the change is slight. iii) Coating on the larger size Ag nanoshell may not raise the sensitivity, whereas it can improve the *FOM*. While some of the thicknesses and refractive indexes of the dielectric coatings used in this theoretical study is not yet experimentally achievable, the behavior and trends predicted here should give an instruction to the metal nanoshell based plasmon sensor designing.

4. Conclusion

Optical extinction spectra of dielectric coated metal nanoshells of varying geometric parameters embedded in different media were calculated using FDTD method. The sensing characteristics were compared with those of bare metal nanoshells. For all cases it is shown that the sensitivity can be decreased by dielectric coating but the FOM may be improved by properly coating for metal nanoshells of large size. The results obtained in our calculations can save a lot of experimental work needed for the preparation of metal nanoshells for sensing applications.

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