Tunable and augmented plasmon resonances of $Au/SiO_2/Au$ nanodisks

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The plasmon resonance of Au/SiO_2 multilayered nanodisks was studied using light scattering spectroscopy and numerical calculations. Compared to single layered Au nanodisks, multilayered nanodisks exhibit several distinctive properties including significantly enhanced plasmon resonances and tunable resonance wavelengths which can be tailored to desired values by simply varying dielectric layer thickness while the particle diameter is kept constant. Numerical calculations show that slicing one metal layer into metal multilayers leads to higher scattering intensity and more "hot spots," or regions of strong field enhancement. This tunable and augmented plasmon resonance holds a great potential in the applications of surface-enhanced Raman scattering (SERS). © *2006 American Institute of Physics*. [DOI: 10.1063/1.2172712]

The interaction of light with noble metal materials exhibits extraordinary optical resonances in their visible-infrared spectra due to the excitation of collective motions of conduction electrons, a phenomenon denoted as surface plasmons (SP) or particle plasmons.[1] The resonant excitations of surface plasmons cause enhancement of both far and local electromagnetic fields. The potential of using surface plasmons is of interest due to their application in subwavelength lithography,[2] surface-plasmon coupled power generators,[3] nonlinear optical devices,[4] optical corrals for the manipulation of local density of states,[5] nano optical waveguides,[6] and molecular trapping and sensing.[7–10] Especially, recent discoveries of single molecule sensitivity in surface-enhanced Raman scattering experiments (SERS) have stimulated renewed interest in its applications for molecule detection.[11,12]

For practical applications, it is imperative to develop SERS active substrates with reproducible and controllable SERS enhancements. Previous studies on plasmon resonances have been mostly focused on particles of single metal materials, where the resonance frequency is determined by the particle size, and by the particle shapes which can be varied from spheres, to prisms,[13] and to nanorings.[14] Recent studies have also shown unique properties of composite nanoparticles such as core-shell nanospheres[15] and nanobarcodes.[16,17]

In this letter, we present experimental and numerical studies of a type of multilayered nanodisks. The multilayered nanodisks are consisted of alternatively stacked metal/dielectric disks. We show that the plasmon resonances of such nanodisks are augmented with resonant wavelengths tunable over a wide range. In comparison to single layered nanodisks with the same diameter and the same metal volume, numerical results show that layered Au/SiO_2 nanodisks exhibit significantly stronger light scattering at plasmon resonance wavelengths. Numerical calculations also show that accompanying this enhancement in scattering intensity is an increase in regions with enhanced local fields or "hot spots." This augmented plasmon resonance is explained as a result of the increased geometrical singularities or sharp edges in multilayered nanodisks.

The multilayered nanodisks were prepared on quartz substrates by electron beam lithography (EBL), and electron beam evaporation followed by the standard lift-off process. We fabricated singlets and doublets of three layered $Au/SiO_2/Au$ nanodisks with three different SiO_2 thicknesses: 5 nm, 15 nm, and 25 nm and with the gold layer thickness fixed at 15 nm. The disks size and shape were characterized by using a scanning electron microscope (SEM). Figures 1(a) and 1(b) show typical SEM images of the three-layered nanodisk singlet and doublet. It can be seen that the size and shape of disks for singlets and doublets are uniform. The disks are elongated with a 101 nm diameter long axis and a 75 nm diameter short axis. The thicknesses

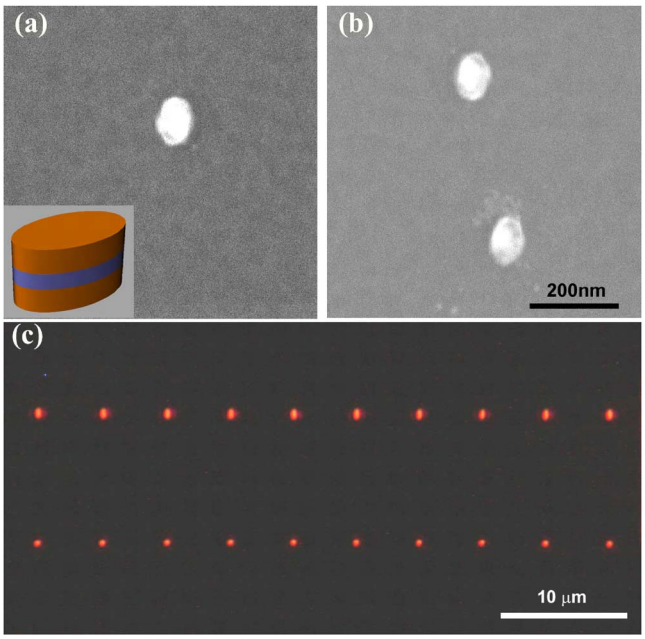

FIG. 1. (Color online) (a), (b) SEM pictures of $Au/SiO_2/Au$ three layered nanodisk singlet (a) and doublet (b). (c) Real color picture of nanodisks illuminated by evanescent white light waves taken with a digital camera. The top row contains doublets, and the bottom row contains singlets. The thicknesses of Au and SiO_2 disks are 15 nm and 15 nm, respectively, in all pictures here.

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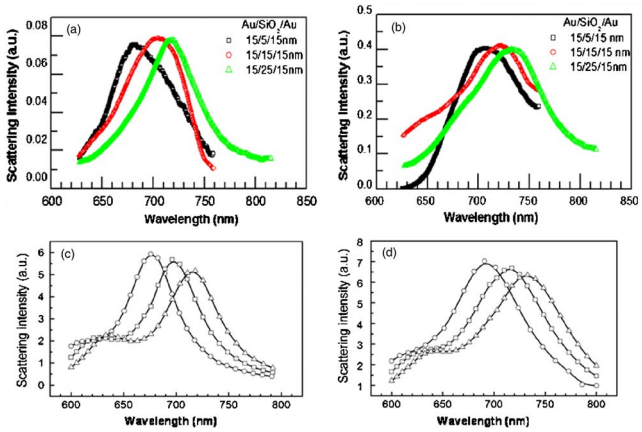

FIG. 2. (Color online) Measured scattering spectra for singlet (a) and doublet nanodisks (b) with different SiO_2 layer thicknesses: 5 nm (□), 15 nm (○), and 25 nm (△), respectively. The disk center-center spacing is 250 nm for doublets. (c), (d) Simulated scattering spectra for single nanodisks of identical sizes as in the experiments. The SiO_2 layer thickness is 5 nm (○), 15 nm (□), and 25 nm (△), respectively.

of these nanodisks have been measured by an atomic force microscope (AFM), and the results show that the deviations from the designed nominal values are less than 1 nm. The AFM measured thickness can be used to distinguish the multilayered nanodisks with different thicknesses of SiO_2.

In order to measure their optical properties, we illuminated these layered nanodisks with evanescent light waves produced by a collimated white light beam undergoing total internal reflection (TIR). Under an optical microscope, these nanodisks, as shown in Fig. 1(c), are distinctively visible due to the strong scattering of light at resonant wavelengths. An experimental setup, which, as detailed in previous papers,[18,19] consists of an optical microscope coupled with an imaging spectrograph, was used to measure the scattering spectra of individual layered nanodisk singlets and doublets.

Measured light scattering spectra are shown in Figs. 2(a) and 2(b) for layered nanodisk singlets and doublets, respectively. For these measurements, the polarization direction of the illuminating light was set to be parallel to the disk plane, and to the center-center direction in the case of doublets. With increasing SiO_2 layer thickness from 5 nm to 25 nm, the resonant peak wavelengths of individual nanodisks was observed to be significantly redshifted from 675 nm to 725 nm. This peak shift can be attributed to the variation of the near-field plasmon coupling between individual Au layers with the change of the dielectric layer thickness.

To gain a better understanding of these experimental results, we performed numerical calculations by using the discrete dipole approximation method (DDA).[20] Figures 2(c) and 2(d) present the calculated spectra for layered nanodisk singlets and doublets corresponding to experiment parameters (101 nm × 75 nm in diameters) obtained from SEM and AFM measurements. The permittivity of Au is taken from the literature measured for bulk Au material,[21] and the permittivity of SiO_2 is set to 2.13 assuming a bulk refractive index of 1.46. The substrates, which have significant effects on the plasmon resonance, are taken into account by embedding the disks in a homogeneous medium with a refractive index of 1.4 which is the averaged refractive index of air and ITO.[22] A comparison with the experimental results shows good agreements on the resonant peak wavelengths and the resonance wavelength shifts with the variation of SiO_2 layer thickness.

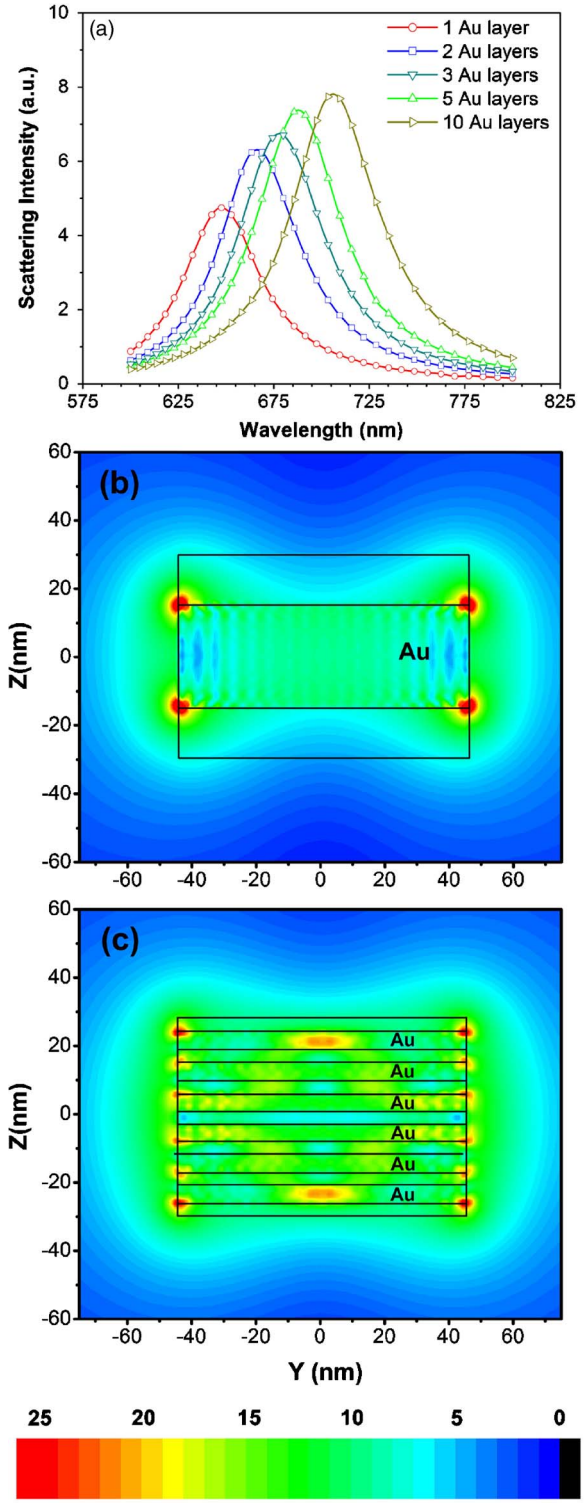

FIG. 3. (Color online) (a) Simulated scattering spectra for single nanodisks with various metal layers. The nanodisk is circular with a 90 nm diameter, while the total thicknesses for metal layers and SiO_2 layers are kept both at 30 nm. The polarization of the incident light is polarized in the *Y*-axis direction. (b) *Y*-*Z* plane cross section of local electrical field distribution for the single Au layer nanodisk (SiO_2/Au/SiO_2) at the resonant frequency. (c) *Y*-*Z* plane cross section of local electrical field distribution for the 6 Au layer nanodisks (SiO_2/Au)^6/SiO_2 at resonant frequency.

Previous studies have shown that for longitudinal plasmon coupling where the electrical field is parallel to the disk center-center axis, the resonance wavelength of doublets

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shifts to red compared to that of singlets, and the shift decays approximately exponentially with the gap between two disks and becomes minor when the gap is larger than 2.5 times that of the relevant disk diameter.[19] In contrast, as for transverse coupling where the electrical field is perpendicular to the disk center-center axis, the resonance wavelength of two coupled disks is always blueshifted.[23] The layered $Au/SiO_2/Au$ nanodisks can be considered as two Au nanodisks coupled vertically. The plasmon coupling is in transverse mode since the excitation electrical field is horizontal. Therefore, it can be expected that with the decrease of the SiO_2 layer thickness, the plasmon coupling strength increases, and the peak resonant wavelength shifts to the blue [Fig. 2(a)]. It can be argued that the resonant wavelength red-shift may also be ascribed to the increase of the effective refractive index of surrounding medium when the SiO_2 layer thickness is increased. This effect, however, turns out to be minute. We simulated the 30 nm thick single Au disk with a SiO_2 disk of different thicknesses on the top, and the results show that the resonant wavelength shifts only about 3 nm when the SiO_2 thickness is varied from 5 nm to 15 nm. (Results are not shown here.)

When a second layered nanodisk is present in close proximity, the resonance peaks, as shown for the doublets with a fixed 250 nm center-center spacing [Fig. 2(b)], are shifted to the red. These redshifts can be ascribed to the longitudinal plasmon coupling between two layered nanodisks, in contrast to the blueshift observed in singlet layered nanodisk.

The observed large range of the resonance wavelength tuning provides a unique way of tailoring the plasmon resonance with high accuracy. This plasmon tuning through thickness control is superior to that obtained through disk size control, since the layered nanodisk sidewalls of different materials allow for attaching different probe molecules at the same nanodisks, opening up possibilities for integrating multifunctionalities into single disks.

We also calculated and compared the scattering spectra and local field distribution for nanodisks of single and multi metal layers with the same diameter and the same total volume of metal and dielectric materials (Fig. 3). The results show that by "slicing" a 30 nm Au layer evenly into 10 layers, the scattering intensity is increased by twofold. In addition, spots of enhanced local electrical fields are increased for the layered nanodisk as a result of increased sharp corners (or singularities) [Figs. 3(b) and 3(c)].

Furthermore, the electrical fields inside the Au layers for layered nanodisk are intensified, and as a result, the electrical field within the SiO_2 disks is also enhanced in comparison to the single metal layer disk. It can be seen that different layers are oscillating in different multipolar modes. The location of the enhanced fields varies from layer to layer and is symmetrical in the Z direction. This unique electrical field distribution may be employed for nonlinear optical applications. It can be expected that if a nonlinear material is used to replace SiO_2, this layered nanodisk should exhibit enhanced nonlinear effect.

In summary, we demonstrated a type of multilayered nanodisks with precisely tunable surface plasmon frequency and augmented spots of strongly enhanced local field, both of which are important for SERS active substrates. It is observed that by changing the dielectric layer thickness between two metal nanodisks, the surface plasmon resonance can be precisely tuned as a result of coupling between plasmons of each metal layers. It is also found that by "slicing" the metal into multiple layers, the "hot spots" are significantly increased due to the increase of singularities in the system. In the future to reach single molecule SERS with these tunable layered nanodisks, plasmon coupling between two or more of these layered nanodisks should be employed by fabricating disks aggregates or arrays with gaps less than 10 nm.[16]

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