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Shaping the photoluminescence from gold nanoshells by cavity plasmons in dielectric-metal core-shell resonators

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We report experimental investigation of the photoluminescence (PL) generated from the gold nanoshells of the dielectric-metal core-shell resonators (DMCSR) that support multipolar electric and magnetic based cavity plasmon resonances. Significantly enhanced and modulated PL spectrum is observed. By comparing the experimental results with analytical Mie calculations, we are able to demonstrate that the observed reshaping effects are due to the excitations of those narrow-band cavity plasmon resonances. We also present that the variation on the dielectric core size allows for tuning the cavity plasmon resonance wavelengths and thus the peak positions of the PL spectrum. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). [http://dx.doi.org/10.1063/1.4961727]

I. INTRODUCTION

Since the pioneering work of Mooradian in the late 1960s,¹ photoluminescence (PL) from gold nanostructures has shown great potential in many fields, such as cell imaging,²–⁵ bio-sensing,⁶,⁷ and plasmonic mode mapping,⁸–¹⁰ due to its characteristics of non-bleaching, non-blinking and high-solution imaging. The PL from gold nanostructures has been attributed to the radiative recombination of conduction band electrons below the Fermi energy with d-band holes,¹¹ which is a very inefficient process. A possible way to enhance the PL intensity of gold nanostructures is to utilize the localized surface plasmon resonances (LSPRs). For example, the roughened gold surface has been reported to allow for enhancing the PL intensity,¹² where the PL enhancement is gained from the improvement of both excitation and emission efficiency by enhancing the local electric fields associated with the excitations of the LSPRs. Over the past few years, the plasmon-enhanced PL has been extensively investigated in various gold nanostructures such as nanospheres,¹³,¹⁴ nanorods,⁷,¹⁴,¹⁵ nanoflowers,¹⁶ nanobipyramids,¹⁷ nanodisk arrays,¹⁸ silver nanowire on a dielectric spacer/gold surface,¹⁹ and gold nanobeam-silver nanowire cross-like nanostructure,²⁰ with the main research focus having been placed on the mechanism of radiative recombination of electrons and holes, the PL intensity maximization, and even controlling the polarization of PL emission. Owing to the strong coupling between the excited electron-hole pairs and the LSPRs, the position and shape of the plasmon-enhanced PL spectra have been demonstrated to be modulated by the LSPRs.¹¹,¹⁴,²¹–²⁴ However, LSPRs supported by those gold nanostructures usually exhibit low quality factors,⁷,¹⁴,²¹ and consequently, only the reshaped PL spectra with broad linewidths are observed.
In this work, we investigate the PL generated from the gold nanoshells of the dielectric-metal core-shell resonators (DMCSRs). We demonstrate that the coupling of the excited electron-hole pairs in gold nanoshells to a set of sharp electric and magnetic based Mie cavity plasmon resonances supported by DMCSRs are enabled. As a result, the spectral reshaping of the PL spectrum from the gold nanoshells is experimentally observed. Furthermore, we also demonstrate that the resonance wavelengths of the cavity plasmon resonances and thus the peak positions of the PL spectra are tunable through the variation of the dielectric core size in DMCSRs.

The manuscript is organized as follows: in Sec. II, we introduce the various experimental techniques we used, the results are presented and discussed in Sec. III, and Sec. IV is our conclusion.

II. EXPERIMENTS

A. Fabrication of DMCSRs with a nearly perfect gold shell layer

A monolayer hexagonal-close-packed (HCP) array of polystyrene (PS) spheres was self-assembled on the water/air interface using a modified Langmuir-Blodgett method. The purchased water suspension of monodisperse PS spheres with different diameters of $D = 1000$ and 1060 nm (coefficient of variation less than 3%, Duke Scientific) were concentrated or diluted to 10 wt% depending on its initial concentration and then mixed with equal volume of ethanol. The prepared PS sphere suspension was carefully spread onto a confined area at the water surface via a conduit plate. After a monolayer HCP array of dielectric spheres was completely formed on the water surface, it was then transferred onto a substrate with through-holes to form freestanding monolayer colloidal crystal membranes by exploiting the strong interparticle van der Walls interactions and the interactions between the particles and the grid substrate as well. The freestanding area is $\sim 20 \times 55 \mu m^2$ for $D = 1000$ and 1060 nm. Thin gold films with an identical thickness were successively deposited (5 nm/min, HHV Auto 306) onto both half surfaces of the prepared freestanding monolayer membranes to form core-shell particles with an almost complete gold shell layer. The thickness was monitored by a quartz crystal microbalance.

B. Reflection measurement

The reflection spectra within the visible range were measured using a home-built setup based on a commercial microscope (Olympus, BX51) equipped with a spectrometer (Acton SP2760, spectral resolution is 0.2 nm). The measured spectra were normalized with a reflection spectrum collected on a silver mirror.

C. PL measurement

The PL spectra of the samples were acquired using a Princeton spectrometer, in which the spectra were dispersed by a 300 lines/mm grating and collected using a liquid nitrogen-refrigerated CCD (PyLoN 400BR, Princeton Instruments). The microscope contains a high resolution spectrograph (0.175 nm/pixel), which gives an accuracy of the peak positions in the spectrum of within $\pm 0.5$ nm. During the PL measurement, a laser with a wavelength of 488 nm and power of 5 mW was focused on the surface of the sample through a Nikon objective (60×, NA = 0.70). All PL spectra were obtained with an integration time of 3s after focusing the laser at the given region of interest.

III. RESULTS AND DISCUSSION

The inset of Fig. 1(a) shows a schematic of a DMCSR consisting of a dielectric sphere surrounded by a thin gold shell layer. In order to produce high-quality DMCSRs with a nearly perfect gold shell, a recently developed simple two-step approach is employed here, which allows for the creation of core-shell structures with various core sizes consisting of virtually any metal and dielectric materials. In brief, a monolayer hexagonal-close-packed (HCP) array of polystyrene...
FIG. 1. (a) Top-view scanning electron microscopy (SEM) image of the DMCSRs with a 1000-nm-diameter PS sphere core and a 40-nm-thick gold shell. The inset shows a schematic of a DMCSR consisting of a dielectric sphere surrounded by a thin gold shell layer. (b) The PL spectra generated from the gold nanoshells of the DMCSRs (red line) and a 40-nm-thick planar gold film (black line).

(PS) spheres was self-assembled on the water/air interface using a modified Langmuir-Blodgett method, and then transferred onto a substrate with tens of micrometer-sized through-holes to form a monolayer of self-supporting PS spheres. After that, thin gold films were successively deposited onto the upper and lower half-surfaces of the PS spheres to form core-shell particles with an almost complete gold shell layer. A representative top-view scanning electron microscopy (SEM) image of the resultant DMCSRs with a 1000-nm-diameter PS sphere core and a 40-nm-thick gold shell is shown in Fig. 1(a).

In order to excite the PL of the gold nanoshells, light from a continuous 488 nm wavelength diode laser with ~5 mW power is used as pump source. The pump beam is directed into a microscope objective (60×, 0.7 N. A.) via a dichroic mirror and focused onto the DMCSR sample. The PL light from the sample is collected by the same objective and passes through the dichroic and the emission filter. After a tube lens, an optical fiber is placed on its focal plane, where the real image of the sample appears, to guide the PL light into a cooled back-illuminated electron multiplying charged coupled device (EMCCD) imaging spectrograph. The energy-resolved PL spectrum with a wavelength range of 500-800 nm is measured for the prepared DMCSRs with a 1000-nm-diameter PS sphere core and is shown in Fig. 1(b). For direct comparison, Fig. 1(b) also shows the PL spectrum measured from a 40-nm-thick planar gold film deposited onto a quartz substrate, in which only a single broad emission peak locating at the wavelength of ~520 nm is expectedly observed (black line in Fig. 1(b)). This broad emission peak is attributed to the radiative recombination of electrons in the sp band at the Fermi level of gold with holes with the d band below the Fermi level. As compared with the planar gold film case, the intensity of the PL generated from the gold nanoshells of the DMCSRs is found to be greatly enhanced, and more interestingly the PL spectrum exhibits multiple emission peaks (red line in Fig. 1(b)).
In order to discover the origin of the observed multiple PL emission peaks, the reflection spectrum of the DMCSRs is measured at normal incidence and shown together with the PL spectrum in Fig. 2(a), in which several reflection dips are clearly observed (blue line in Fig. 2(a)). As indicated by vertical dashed lines, these reflection dips are found to practically coincide with the peaks 1-8 in the PL spectrum. Our previous experimental studies have already demonstrated that the DMCSRs with metal shell thickness beyond the optical skin depth of the metal could effectively act as a closed metallic cavity, and their plasmonic properties are dominated by a set of magnetic and electric-based cavity plasmons with their optical fields being tightly confined within the dielectric cores. Such highly localized nature prevents the cavity plasmons in adjacent DMCSRs from interacting with each other. Therefore, even though the DMCSRs are closely packed like in this study, the cavity plasmons are allowed to be analyzed using Mie theory, which has already been proven correct in our previous experimental work and also has been employed to analyze the cavity plasmon induced spectral reshaping of fluorescence emission of dye molecules. One of the main advantages of the analytical Mie solution is its ability to decompose the obtained spectra into separate multipolar contributions, characterized by electric TM$(l, m)$ and magnetic TE$(l, m)$ scattering coefficients, where $l$ is the index of angular momentum and $m$ is the order of the mode. Fig. 2(b) shows the results of this analysis on the absorption efficiency of an individual DMCSR composed of a 1000-nm-diameter PS sphere concentrically surrounded by a uniform 40-nm-thick gold shell. In the calculations, the permittivity of gold is taken from the experimental data by Johnson and Christy, and the dielectric constant of PS is assumed to be 2.46. It is clearly seen from Fig. 2(b) that each decomposed spectrum presents a sharp absorption peak, arising from the excitation of...
the cavity plasmon resonance because of the phase retardation effect.\textsuperscript{25,30,31} By comparing Fig. 2(a) and Fig. 2(b), it is directly seen that there is a very good one-to-one correspondence between theoretically predicted absorption peaks and experimentally observed PL (reflection) spectral features, demonstrating that the observed peaks 1-6 in the PL emission spectrum is due to the excitations of the Mie cavity plasmon resonances TE(3,1) TM(2,2), TE(4,1), TM(3,2), TE(2,2), and TM(4,2), respectively. It should be noted here that cavity plasmon resonances TE(3,2) and TM(2,3) are spectrally closed to each other, so that two corresponding PL peaks, and two reflection dips as well merge to one broad spectral feature around the wavelength of 525 nm.

Analytical Mie solution can also yield the near-field profiles at the selected wavelengths of interesting. In order to gain insight in the spectral reshaping of the PL emission, the optical field intensity distributions (normalized by the maximum value) are calculated at the cavity plasmon resonance wavelengths (corresponding to the absorption peaks in Fig. 2(b)) and summarized in Fig. 3(a)-3(h). In all cases, most of the optical fields are confined within the dielectric core of the DMCSRs, demonstrating typical features of the cavity plasmons. The electric field distributions within the cavity are found to exhibit four-fold symmetry for the resonances TM(2,2) and TM(2,3) (Fig. 3(a) and 3(b)), six-fold symmetry for the resonance TM(3,2) (Fig. 3(c)), and eight-fold symmetry for the resonance TM(4,2) (Fig. 3(d)), which confirm that these resonances correspond to the excitations of the electric quadrupolar, octupolar and hexadecapolar cavity plasmons, respectively. For the resonances TE(3,1) (Fig. 3(e)), TE(3,2) (Fig. 3(f)), TE(4,1) (Fig. 3(g)) and TE(2,2) (Fig. 3(h)), the magnetic field distributions within the cavity are also found to exhibit similar 2-fold symmetry, revealing that they are related to the excitations of magnetic-based multipolar cavity plasmon resonances.

So far, we have experimentally and theoretically demonstrated that both electric and magnetic based cavity plasmon resonances supported on the individual DMCSRs allow for an enhanced and spectrally engineered PL emission, which could be attributed to the relaxation of the electron-hole pairs excited from the interband transition of gold indirectly by excitations of the multipolar cavity plasmons that may subsequently decay via radiation in the form of PL.\textsuperscript{11,18,24,25,31,32} In the following, we will demonstrate that the modulated PL emission is spectrally tunable. It is well known

![FIG. 3. (a)-(d) The spatial distributions of the electric field intensity in the k-E central plane of the DMCSRs for the electric-based cavity plasmon resonances TM(2,2), TM(2,3), TM(3,2) and TM(4,2), respectively. (e)-(h) The spatial distributions of the magnetic field intensity for the magnetic-based cavity plasmon resonances TE(3,1), TE(3,2), TE(4,1) and TE(2,2), respectively.](image-url)
FIG. 4. (a) The normal-incidence reflection spectrum (blue) and the PL spectrum (red) measured from the DMCSRs composed of a 1060-nm-diameter PS sphere core wrapped by a 40-nm-thick gold shell. (b) Decomposed absorption spectra of an individual DMCSR consisting of a 1060-nm-diameter PS sphere core and a 40-nm-thick gold shell. Vertical dashed lines in (a) and (b) indicate a one-to-one correspondence.

that in the frame of Mie theory, the scattering coefficients corresponding to the cavity plasmons are dependent on the cavity size and also on the refractive index of the dielectric core. This makes it possible to tune the resonance wavelength of the cavity plasmon resonances and thus the spectral positions of the PL peaks by varying either the PS core size or the core refractive index. Here, we only show the structural tunability of the spectral reshaping of the PL emission. Figure 4(a) shows both the reflection and the PL spectra measured for the DMCSRs consisting of a PS core with a diameter of $D = 1060 \text{ nm}$ and a 40-nm-thick gold shell layer. As indicated by vertical dashed lines, the observed PL peaks (red line in Fig. 4(a)) are again found to match well with the reflection dips (blue line in Fig. 4(a)). In addition, a Mie theory based analysis of the absorption efficiency is performed for an individual DMCSR composed of a 1060-nm-diameter PS sphere concentrically surrounded by a uniform 40-nm-thick gold shell, and the resultant decomposed absorption spectra are shown in Fig. 4(b). By comparing Fig. 4(a) and Fig. 4(b), it is again seen that there indeed exists a one-to-one correspondence between theoretically predicted absorption peaks and experimentally observed PL emission peaks. Furthermore, the measured PL emission peaks, the reflection dips and the predicted multipolar cavity plasmon resonances for the DMCSRs with a relatively large core diameter of $D = 1060 \text{ nm}$ (Fig. 4) are clearly red-shifted by about 40 nm in comparison with the DMCSRs consisting of a 1000-nm-diameter PS core (Fig. 2(b)). Note that the magnetic octupolar cavity plasmon resonance TE(3,1) has shifted to the wavelength longer than 800 nm. Therefore, it is experimentally confirmed that the dependency of the cavity plasmon resonances on the core size provides an easy way to tune the spectral reshaping of the PL emission generated from the gold nanoshells.
IV. CONCLUSION

In conclusion, the PL generated from the gold nanoshells of the DMCSRs are experimentally investigated. By coupling the electron-hole pairs excited from the interband transition of gold to the sharp cavity plasmon resonances of the DMCSRs, the PL emission spectrum is strongly enhanced and modified, and has a good one-to-one correspondence with the theoretically predicted resonance positions. According to the Mie resonance nature of the cavity plasmons supported by the DMCSRs, the peak positions of the modulated PL emission from the gold nanoshells could also be tuned by controlling the dielectric core size of the DMCSRs.

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