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Fabrication and optical properties of novel plasmonic cone-shell crystal

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ABSTRACT

Tweaking the shape, size, and material of metallic nanostructure enables researchers to engineer the scattering properties. In particular, by breaking the symmetry of the nanostructures, additional degrees of freedom to manipulate the optical properties can be obtained. In this work, we fabricate a novel large-area plasmonic cone-shell crystal (PCSC) via two-process physical deposition of dielectric and metallic materials on the self-assembled monolayer colloidal crystal (CC). In comparison with the enhanced optical transmission (EOT) spectrum of the conventional plasmonic semi-shell array, multiple plasmon resonances within a remarkably broadened spectrum are observed in this PCSC, which are the main results of the plasmon coupling and hybridization effects based on the increased symmetry-breaking structure. Our findings could develop the investigation on the plasmonic shell structures and hold potential applications in light modulation, surface-enhanced spectroscopy and optoelectronic detection.

1. Introduction

The excitation of surface plasmons in metal nanostructures has a strong impact on light scattering, transmission and absorption [1]. Periodic plasmonic structures have attracted considerable interest due to the observed impressive optical properties such as the enhanced optical transmission (EOT) [2–6] via the plasmon resonances and optical field coupling. Recently, a new emerging plasmonic crystal consisting of metallic semi-shells [7–11] has been demonstrated with novel applications including the redirecting scattered light modulation [12], unidirectional spacer [13], spectral and directional reshaping of fluorescence emission [14,15]. A variety of plasmonic crystals consisting of metallic nanorices, nano-eggs, nano-cups, semi-shells or perforated semi-shells [16] were fabricated via the dry etching of chemical synthesization or deposition of metal on the template colloidal crystal (CC) [17–19]. However, far less attention is conducted on the exploration of the efficient method to fabricate and tune the semi-shell geometry features in the vertical direction and further to develop new unique optical properties in the high symmetry-breaking system.

In this work, we develop a new plasmonic cone-shell crystal (PCSC) via a simple two-process deposition of dielectric and metallic layers on the self-assembled large-area CC. By tuning the thickness of the deposited dielectric layer, a PCSC with tunable geometry structure is obtained. In comparison with the EOT spectrum with only one main transmittance band of the conventional semi-shell structures, obviously broadened spectrum with multi-band plasmon resonances are observed due to the intensified plasmon coupling and hybridization in the high symmetry-breaking of the PCSC. Our findings might be helpful in the further exploitation of novel large-area and low-cost symmetry-breaking structures in sub-wavelength nano-optics, nano-plasmonics, and surface enhanced spectroscopies.

2. Experimental details

High-quality and large-area monolayer CCs are fabricated on the clean quartz substrates by the self-assembly of monodisperse silica (SiO_2) spheres (with diameters of 1.58 μm) [18]. A SiO_2 layer with controllable thickness (t) is then plasma sputtered on the surface of the CC to form a dielectric cap on CC (here denoted as hetero-colloidal crystal, HCC). Then, a 60 nm gold film is deposited on the surface of the HCC to form the plasmonic hetero-colloidal crystal (PHC). Finally, by etching the SiO_2 layer and SiO_2 CC with hydrofluoric acid, and further transferring the remaining shell array onto a clean quartz substrate, the plasmonic shell crystal could be achieved. Numerous simulations are performed using the finite-difference time-domain method [20]. The dielectric constants of SiO_2 colloids and SiO_2 layer are assumed to be $\varepsilon = 2.13$. The Drude model is used to describe the dielectric constant of the gold to fit the experimental data [21].

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3. Results and discussion

Fig. 1(a) shows the schematic of the monolayer CC, which could be used to form a metal-coated CC via depositing metal material on the top surface of the CC (Fig. 1(b)). By etching the CC and transferring the rest of metallic semi-shell array onto a quartz substrate, a conventional plasmonic crystal consisting of semi-shell can be obtained (Fig. 1(c)). On the other hand, by firstly depositing dielectric material onto the CC to form the HCC, and then depositing a metal layer on this HCC (Fig. 1(d)), a novel PHC is obtained (Fig. 1(e)). Based on this PHC, a novel PCSC could be fabricated through a simple etching and transferring procedure (Fig. 1(f)).

Fig. 2(a) presents the scanning electron microscopy (SEM) images of the fabricated ellipsoidal PHC with a 450-nm-SiO_2 layer between the top metal and the bottom CC. The cross-view image as the inset shown in Fig. 2(a) confirms the reshaped CC with an ellipsoidal geometry feature at the vertical direction. After etching and transferring the remaining cone-shell crystal onto a dielectric substrate, a large-area PCSC could be achieved (Fig. 2(b)). A clear crystal diffraction pattern obtained by the laser irradiation onto the PCSC verifies the high-quality of the obtained hexagonal-close-packed crystal structure. Cross-view SEM images of the conventional semi-shell crystal and the new PCSC are shown in Fig. 2(c) and (d), respectively. Different from the standard half-sphere shell geometry achieved for the former, a highly reshaped cone-like shell is obtained for the latter.

Fig. 3(a) presents the measured EOT spectrum curves of the conventional metal-coated CC (dashed line) and the PHC (solid line). Modulated optical properties for the PHC with double enhanced transmittance peaks are observed due to the reshaped metallic shells and geometry features of the HPC, which could produce additional plasmonic coupling channels [4,16] and hybridization modes [7–10]. After simply etching the PHC with hydrofluoric acid and further transferring the remaining shell array onto a clean substrate, the plasmonic shell crystals could be obtained. Fig. 3(b) presents the EOT spectrum curves of the conventional semi-shell crystal (dashed line) and the novel cone-shell crystal (solid line). In contrast to the only one EOT peak at 1.352 μm for the semi-shell crystal, a broadened spectrum with an obvious triple-peak (named as $\lambda_1=1.197$ μm, $\lambda_2=1.366$ μm, $\lambda_3=1.481$ μm) response is achieved for the PCSC. The observed multispectral EOT behavior confirms the high modulation of the optical properties of the plasmonic shell crystal via reshaping the structural geometry [16]. The intensified symmetry-breaking of the cone-shell crystal could produce multi-dipolar plasmon resonances and plasmonic coupling [8,9,22]. These findings could hold potential applications in the multiplexing redirecting fluorescence emission, spacer and other optoelectronic devices [13–15,23].

For the observed triple-band (λ_1–λ_3) EOT response of the PCSC, the calculated normalized electric and magnetic field distributions are presented in Fig. 4. At λ_1, obvious optical field confined at the outer metallic shell surface is observed (Fig. 4(a) and (b)), which suggests the sphere-like plasmon resonance excited [4,5]. The sphere-like plasmon resonance could also been excited in the conventional semi-shell crystal [24]. For the emerged resonances at λ_2 and λ_3, the electric field distributions are the results of the cooperative effects of the sphere-like plasmons and the resonances occurred at the tip edge of the cone-shells. For instance, at λ_2, strong optical field distributions are observed both at the areas of the top metallic shell and the tip edge of the shell (Fig. 4(c) and(d)), which suggest the hybridization of the plasmon resonances [8–10]. At λ_3, the optical field is mainly confined at the tip edge of the cone-shell (Fig. 4(e) and (f)), which suggests the contribution of the resonances at the tip edge of the shell to the EOT [8].

4. Conclusions

We have proposed and fabricated a novel PCSC via a two-process deposition method based on the self-assembled CC. In contrast to the conventional metallic semi-shell crystal, the high symmetry-breaking cone-shell array has been demonstrated to produce multispectral EOT response due to the enhanced plasmonic coupling and hybridization

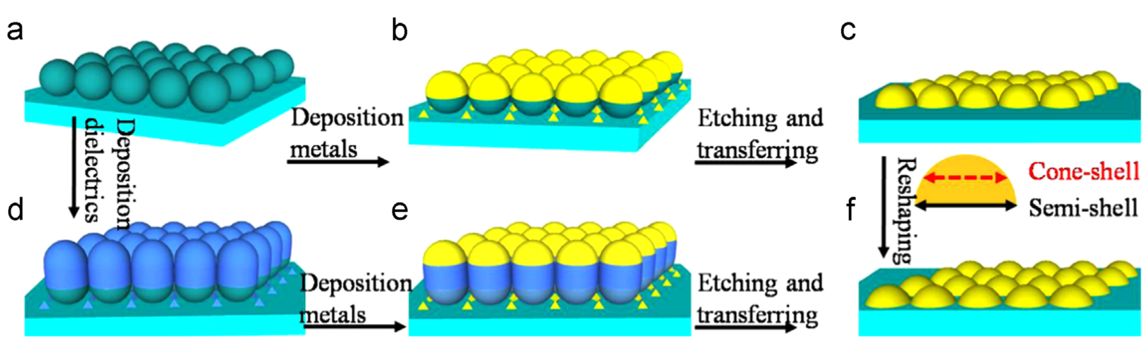

Fig. 1. Schematic diagrams of the proposed fabrication programs for the conventional metallic semi-shell array ((a)–(c)) and the PCSC ((d)–(f)).

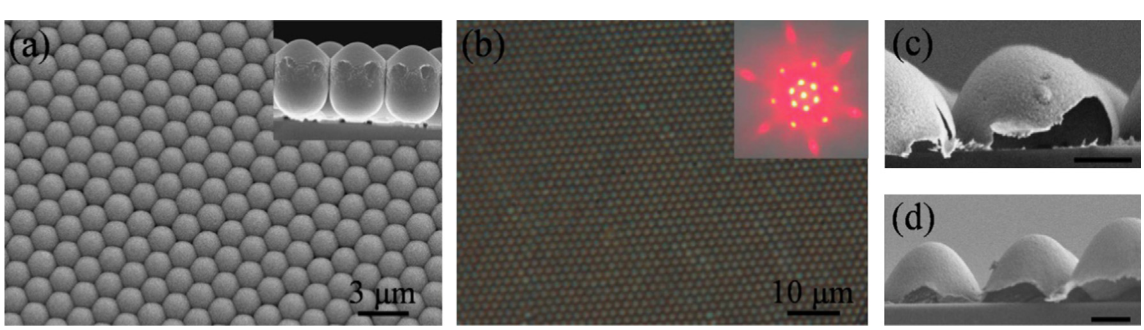

Fig. 2. SEM images of the fabricated ellipsoidal PHC (a) and the PCSC (b). Cross-view SEM images of the semi-shell crystal (c) and cone-shell crystal (d). The scale bar in (c) and (d) is 0.5 μm.

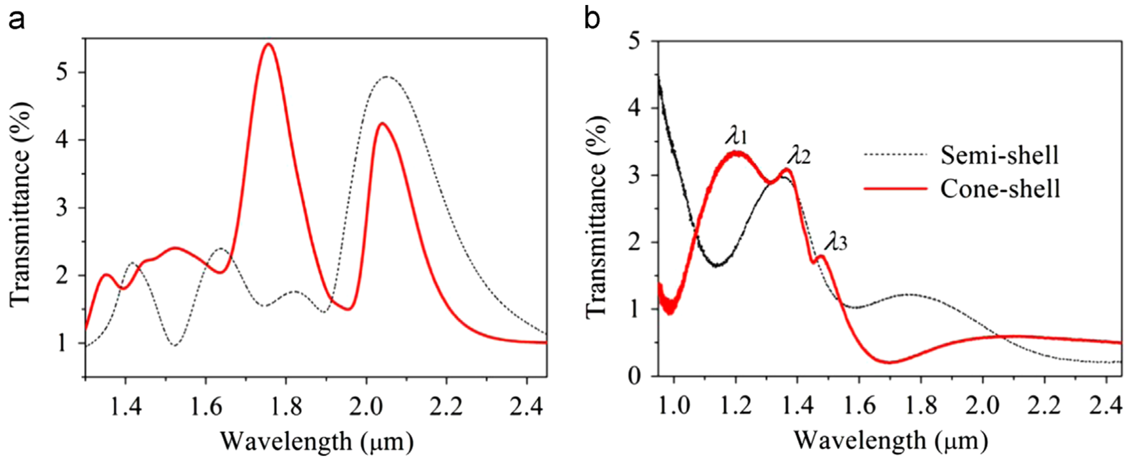

Fig. 3. Normalized transmittance spectra of the fabricated PHCs (a) and the plasmonic shell crystals (b).

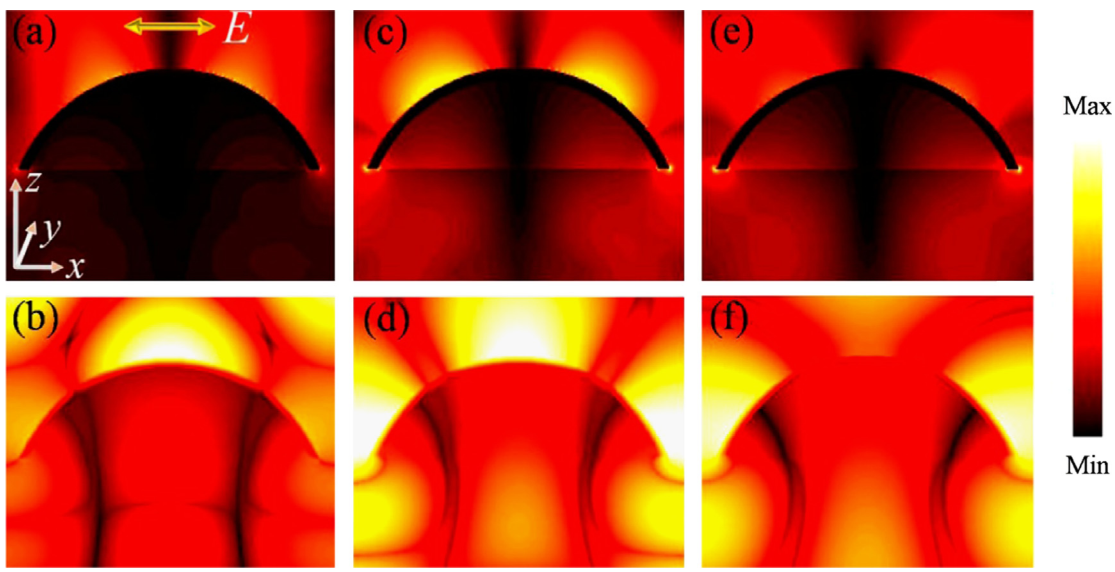

Fig. 4. Normalized electric ((a), (c) and (e)) and magnetic ((b), (d) and (f)) field distributions of the PCSC at λ_1–λ_3, respectively.

effects. This investigation could provide a new way to achieve novel plasmonic shell crystal with tunable structural geometry by controlling the dielectric deposition process. Our findings might be helpful to develop the investigation on the optical properties in these reshaped metallic shell structures, and also to further exploit large-area and low-cost structures in sub-wavelength optics, plasmonics, and surface enhanced spectroscopies.

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