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## Characterization of complementary patterned metallic membranes produced simultaneously by a dual fabrication process

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An efficient technique is developed to fabricate optically thin metallic films with subwavelength patterns and their complements simultaneously. By comparing the spectra of the complementary films, we show that Babinet's principle nearly holds for these structures in the optical domain. Rigorous full-wave simulations are employed to verify the experimental observations. It is further demonstrated that a discrete-dipole approximation can qualitatively describe the spectral dependence of the metallic membranes on the geometry of the constituent particles as well as the illuminating polarization. © 2010 American Institute of Physics. [doi:10.1063/1.3504664]

During the past decade optical metamaterials have attracted much attention because they promise to exhibit optical properties that may not be readily available in nature.<sup>1-3</sup> A wealth of distinct meta-atoms<sup>4</sup> have been designed to generate different bulk properties of the corresponding metamaterials.<sup>5–7</sup> One valuable design guideline is Babinet's principle, which suggests that the magnetic and electric field are interchanged with respect to a perfectly conducting, planar, patterned screen, and its complement.<sup>8</sup> Babinet's principle has provided a valuable design tool for optical filters, metamaterials, and nanoantennas.<sup>9–13</sup> Strictly speaking, Babinet's principle is an exact theory only for perfectly conducting metal screens.<sup>8</sup> It has been applied with success for many years by the microwave community mainly because the conductivities of most metals are sufficiently large (nearly perfect) at radio frequencies. However, its application in the optical domain merits more careful consideration. For example, an analytical study of a metallic nanowire with subskin-depth thickness and its complement reveals that the nonzero resistivity of the metal produces large differences in the field enhancement between the nanogap and nanowire.<sup>14</sup>

In this letter, we present a dual fabrication process which is capable of simultaneously producing optical thin metallic nanorod arrays and their complementary structures. To study Babinet's principle in the optical regime, we fabricate three sets of gold membranes with subskin-depth thickness perforated with subwavelength patterns. Through detailed experiment-simulation comparisons, we show that under certain circumstances Babinet's principle nearly holds in the optical domain. We further demonstrate that a discrete dipole approximation can qualitatively explain the dependence of the spectral response on the geometry of the constituent particles and the illuminating wave polarization.

At the core of this enabling technology based on Babinet's principle is the dual fabrication process we developed.

Glass slides are first cleaned in standard "piranha" solution  $(1:3 \ 30\% \ H_2O_2: H_2SO_4)$  at 80 °C for 30 min, followed by an ultrapure (18.00 M $\Omega$  cm) water rinse. To produce a hydrophilic surface, the slides are then sonicated in 5:1:1 H<sub>2</sub>O:NH<sub>4</sub>OH: 30% H<sub>2</sub>O<sub>2</sub> for 30 min, followed by rinsing with large amounts of ultrapure water. Next, 140 nm of the e-beam resist ZEP 520 A (ZEON Corp.) is spun onto the freshly prepared slides. A 10 nm thick electron conductive layer of thermally evaporated Au is deposited prior to exposure in the e-beam lithography system. After exposure, the Au film is removed in Au Etchant TFA (Transene) for 30 s; patterns in the e-beam resist are obtained by developing the sample in n-Amyl Acetate (Sigma Aldrich) at 20 °C for 3 min, followed by immersing into an 8:1 methyl isobutyl ketone : isopropanol (IPA) solvent for 30 s and rinsing in IPA for 30 s. The deposition mask, as shown in Fig. 1, is obtained by descum in an O<sub>2</sub> plasma etch for 10 s. Au (30 nm) is later



FIG. 1. (Color online) Schematic for the fabrication of the nanoparticle and complementary hole structures, with SEM images of particle and hole arrays. The scale bar is 600 nm.

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FIG. 2. (Color online) [(a) and (b)] Experimentally measured and [(c) and (d)] numerically simulated transmission spectra for hole and particle arrays. The lattice spacing of the square lattice is 320 nm. The minor axis of the elliptical hole is fixed at 120 nm, while its major axis varies from 140 to 220 nm.

deposited by e-beam evaporation over the pattern. A thin Cr layer ( $\sim 2$  nm) is added to improve adhesion between the Au nanoparticles and the glass substrate. After deposition, the e-beam resist is then dissolved in N, N-Dimethylacetamide (Sigma Aldrich) solution at 60 °C for more than 20 min to ensure a complete separation of the top Au film and the substrate. The entire sample is slowly immersed into water at an angle slightly less than 30°, so that the perforated Au film, surrounded by hydrophobic N, N-dimethylacetamide residuals, is released from the substrate to float on the water surface. Another precleaned glass slide is used to fish out the film and transport it to a simple vacuum chamber. As water evaporates, the perforated film smoothes out and eventually sticks to the substrate.

Because the gold film is only 30 nm thick, i.e. much thinner than the metallic skin depth (around 140 nm at 800 nm wavelength), our samples are ideal for studying the applicability of Babinet's principle in the optical domain. Three pairs of complements were fabricated. The unit cells are arranged in square lattices with a lattice constant of 320 nm. The constituent particle is elliptical with a minor axis of 120 nm and a variable-length major axis, as shown in the insets of Fig. 2. Their spectra are measured with an Ocean Optics spectrometer (HR4000 CG-UV-NIR) using a deuterium-tungsten light source.

Figures 2(a) and 2(b) plot the measured transmission spectra. The incident plane wave is normal to the surface of the metallic film, with a polarization as indicated. Similar to previous reports, Fano-type interferences are observed in the hole arrays and Lorentz-type resonances are found in the complementary rod structures.<sup>15,16</sup> For each set of configurations, their spectra under complementary-polarization excitation are also complementary, which is consistent with Babinet's principle. More specifically, the hole array under vertically polarized illumination presents a transmission peak whose wavelength is almost identical to that of the maximal reflection from the rod array under horizontally polarized illumination. In addition, the sum of the complementary transmission spectra is roughly a constant, but smaller than unity due to the finite conductivity of Au. Using a rigorous full-wave Maxwell solver,<sup>17</sup> we numerically simulate the same structure (but taking the glass substrate to be infinitely



FIG. 3. (Color online) (a) Extinction cross-section of isolated gold cuboids with different lengths. (b) Comparisons between rigorous simulations (dotted) and analytical discrete-dipole approximations (solid).

thick for computational efficiency). The refractive index used for gold is similar to the experimental measurements presented in Ref. 18 with the imaginary part increased by 0.6 to account for increased electron scattering at the film surfaces. The results, plotted in Figs. 2(c) and 2(d), are in reasonable agreement with their experimental counterparts [Figs. 2(a)and 2(b)]. The wider resonances observed in the experimental spectra are likely caused by nonuniformities in the experimental samples, i.e., inhomogeneous broadening. Numerical studies of similar structures without glass substrates reveal that the substrates only slightly perturb Babinet's principle because the refractive index of glass is relatively close to that of air and the spectra of the complementary structures are mainly determined by the plasmonic resonances of the metallic unit cells.

Both experiments and simulations found that the unit cell geometry significantly affects the spectrum, especially the resonance. To qualitatively interpret this dependence, we use a discrete dipole approximation, modeling self-standing gold cuboids with geometrical parameters almost identical to those of the elliptical rods. The calculated extinction spectra of the isolated cuboids are plotted in Fig. 3(a).<sup>19</sup> Each cuboid presents an extinction peak associated with its first-order plasmonic resonance, i.e., the localized surface plasmon resonance.<sup>16</sup> Because the 30 nm height of the particles is much smaller than the incident wavelength, retardation effects can be neglected; thus the extinction cross-section is largely determined by the electric dipole of the gold nanoparticle. A Lorentz model can describe the dipole polarizability under horizontally polarized illumination

$$\alpha_h(\omega) = \frac{4\pi\varepsilon_0 f}{\omega_0^2 - \omega^2 - i\omega\tau},\tag{1}$$

where  $\omega_0$  is the resonant frequency, f is the oscillator strength, and  $\tau$  characterizes the phenomenological damping.<sup>10</sup> By fitting the numerical extinction spectra, we find that the parameters  $[\lambda_0, f/\tau, \tau/\omega_0]$  ( $\lambda_0$  being the resonant wavelength in units of nm) are [656, 3.1 × 10<sup>-6</sup>, 0.21] for the 140 nm particle, [744, 4.4 × 10<sup>-6</sup>, 0.27] for the 180 nm particle, and [836, 5.9 × 10<sup>-6</sup>, 0.31] for the 220 nm particle.

The gold cuboid array can be approximated by an ideal dipole array on a square lattice with a lattice constant of 320 nm. The resulting reflection coefficient at horizontally polarized incidence is given by  $^{16}$ 

$$r_h = \frac{i\omega\mu_0 c/2A}{1/\alpha_h - G_{\rm E}},\tag{2}$$

where *c* is the free-space light velocity, *A* is the area of the lattice unit cell, and  $G_{\rm E}$  represents the collectively scattered fields at a given dipole by the other dipoles in the array. The



FIG. 4. (Color online) The dependence of the transmission intensity, at a wavelength of 805 nm, for the 220 nm hole array on the incident polarization angle  $\theta$ . The solid curve is obtained from Eq. (4).

well-known expression relating reflection and transmission is  $t_h = 1 + r_h$ . The theoretical prediction of this simple model is plotted in Fig. 3(b) as solid curves. By comparing the resonant wavelength of the array with that of the individual particle, we see that the lattice contribution  $G_{\rm E}$  blueshifts the resonance. The dotted curves of Fig. 3(b) show the transmission spectra of the cuboid arrays, calculated with a finitedifference time-domain (FDTD) approach. The agreement between these models indicates that the simple discrete dipole theory can serve as a good first-order approximation. The differences between the numerical spectra and their analytical counterparts arise from nonvanishing higher-order multipoles, mainly the electric quadrupole.<sup>19</sup> Interestingly, the multipolar effects redshift the resonances, opposite to the lattice effect. These discussions regarding the rod array can also be easily extended to cover the complementary hole array.<sup>16,20,21</sup>

A strong dependence on the incident polarization of the transmission intensity for an elliptical hole array was experimentally observed in Ref. 22. A similar phenomenon is also seen here. For the elliptical hole with a major axis of 220 nm, the experimental polarization dependence of its transmission at 805 nm (the resonant wavelength under vertically polarized illumination) is plotted in Fig. 4 as the dotted curve. To explain this polarization dependence, we again employ the discrete dipole approximation. For a general metallic particle whose dipole polarizability  $\alpha_h \neq \alpha_v$  (with  $\alpha_v$ ,  $\alpha_h$  being the polarizability under vertically or horizontally polarized illumination), the polarization dependence of the reflection intensity of the particle array is

$$|r(\theta)|^2 = |r_h|^2 \cos^2 \theta + |r_v|^2 \sin^2 \theta, \tag{3}$$

where  $r_v = i\omega\mu_0 c/2A(1/\alpha_v - G_E)$  is the reflection coefficient for vertically polarized incidence,  $\theta$  is the polarization angle, and  $\theta = 0$  ( $\pi/2$ ) corresponds to horizontal (vertical) polarization. Obviously, the reflectivity is constant for an isotropic particle with  $\alpha_h = \alpha_v$ . On the other hand, if the dipole polarizability  $|\alpha_h| \ge |\alpha_v|$  at a horizontally polarized wave induced resonance, then  $|r_v|^2$  is much smaller than  $|r_h|^2$  and hence the resulting reflection exhibits a  $\cos^2 \theta$  dependence on the incident polarization. A similar dependence is expected for the transmission of the complementary hole array because of the relation  $|r(\theta)|^2 \leftrightarrow T_c(\pi/2 - \theta)$  suggested by Babinet's principle,

$$T_c(\theta) = T_c(0)\cos^2 \theta + T_c(\pi/2)\sin^2 \theta.$$
(4)

This relation is used to calculate the polarization-dependent transmission; Fig. 4 plots the results as a solid curve. The analytical expectations are in nearly perfect agreement with the experimental measurements. The discrepancy at large angle comes from errors in the polarization angle measurement.

To summarize, we demonstrate an efficient dual fabrication process to simultaneously produce optically complementary patterned metallic membranes. It is shown that Babinet's principle qualitatively holds to good approximation at visible and near-infrared optical wavelengths despite the finite conductivity of gold. It is further shown that the spectral dependence of the elliptical particle arrays on the incident polarization can be explained well with a discretedipole approximation. We believe that the dual fabrication process together with Babinet's principle can provide a pathway to creating better optical devices, including filters and metamaterials.

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