Lithographically Designed Porous Plasmonic Nanostructures

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Direct-fabrication of synthetic nanoparticles by top-down physical routes, in which materials are vacuum deposited in a nano-patterned polymer template, enables exquisite control over material composition, multilayer structure, and particle size/shape.[1-3] This capability allows us to yield artificially designed nanoparticles with unique physical properties, such as the surface plasmon field enhanced Raman-active nanoparticles. Here, we report the lithographically designed plasmonic nanodisks and nanodishes containing high-density nanopores. The nanopores were utilized as internal Raman hot spots, where a local electromagnetic field enhanced by surface plasmon resonance reaches its maximum value.

For the incorporation of nanopores into Au nanostructures, dealloying process was applied; AuCu alloys were sputter-deposited to the lithographically patterned polymer templates, then Cu was selectively dissolved out with nitric acid, followed by lift-off. By applying different sputtering conditions and alloy compositions, Au nanodisks with four different internal structures were synthesized as shown in Figure 1(a). The surface enhanced Raman scattering (SERS) properties of the prepared Au disks were analyzed using a scanning confocal microscopy after modified with Rhodamine 6G at a concentration ranging from 1 nM to 1mM. Consequently, the maximum SERS intensities of Rhodamine 6G molecules were increased about five times by introducing nanopores into the Au nano-disks. This in turn led to the improvement of minimum molecular detection level by three orders of magnitude from 1 μM to 1 nM. In order to theoretically elucidate the impact of the nanostructures on SERS enhancement, electromagnetic simulation was carried out for the geometries based on the SEM images of Figure 1(a), and the calculated electromagnetic field contour in Figure 1(b) clearly demonstrates that the nanopores inside the Au disk function as multiple hot spots.

Considering the present results, we conclude that the porous Au nanostructures on the substrate are applicable as a highly sensitive molecular detection platform, and expect that such nanodisks released from the substrate can be useful as molecular imaging reagents.

[1] J. -S. Wi *et al.*, ACS Nano **5**, 6449 (2011).
[2] J. -S. Wi, S. Sengupta, R. J. Wilson, M. Zhang, M. Tang, and S. X. Wang, Small **7**, 3276 (2011).
[3] W. Hu *et al.*, Nanotechnology **22**, 185302 (2011).

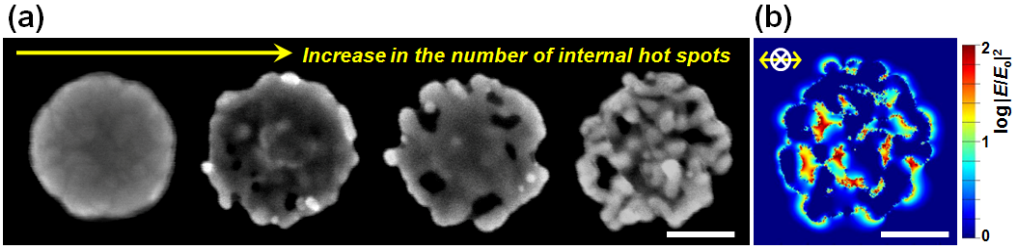

Figure 1 (a) SEM images of lithographically patterned Au nanodisks with controlled porosities. (b) Squared magnitude of the local electric field amplitude calculated using three-dimensional finite-difference time-domain simulation program (Lumerical FDTD Solution 6.5). Incident light having a wavelength of 530 nm enters in the z-direction and is polarized in the x-direction, as indicated by the white and yellow arrows, respectively. All the scale bars are 100 nm.