Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information for

Vertically Stacked Plasmonic Nanoparticles in Circular Arrangement: Key to Colorimetric Refractive Index Sensing

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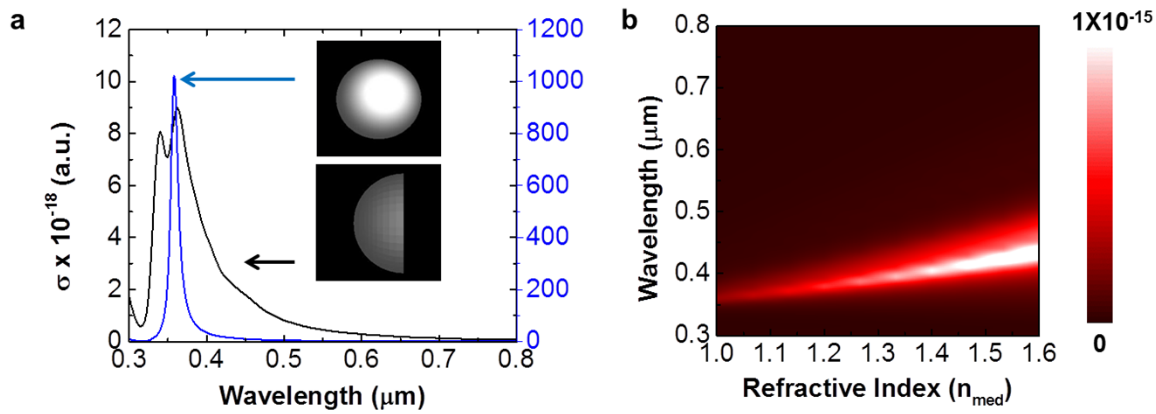
Supplementary Experimental

Fabrication of cup array pattern

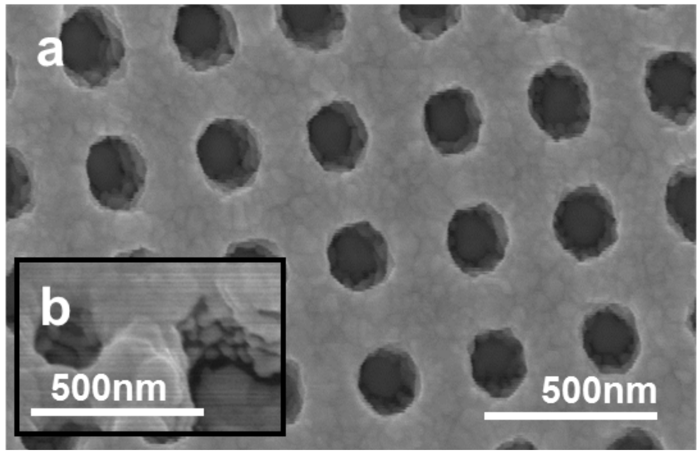
The hemispherical nanoparticles arranged in circle were fabricated on the cup array, which was produced from replica molding with the urethane based UV-curable polymer, NOA 61. The periodic embossed cup patterns of the mold were produced by the laser interference lithography on the quartz substrate and NOA 61 was cured on this mold to resemble the cup patterns as an intaglio print. After the deposition of 10 nm of Titanium and 80 nm of silver by electron beam evaporator, the nanoparticles arranged in circle were produced on the sidewall inside the cup patterns. The formation of silver nanoparticles on the sidewall was possible with a slanted sidewall angle of 82 degree to the device surface. The average particle size on the sidewall was 30 nm and approximately eight particles were formed in the same focal plane parallel to the device surface.

Computed scattering cross section spectra of a single silver spherical particle and a hemispherical particle and the surrounding refractive index dependent Mie scattering spectra of a hemispherical particle are presented.



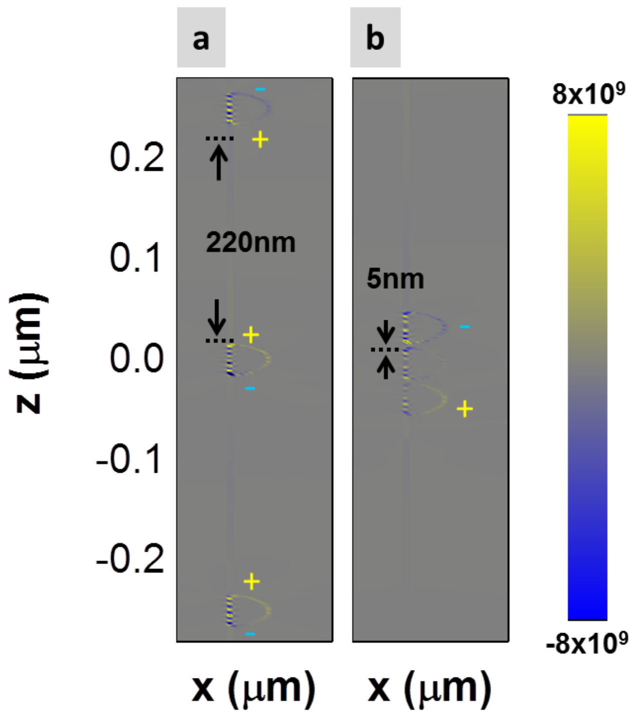
Supplementary Fig. S1. (a) The scattering cross section of a silver sphere and a hemisphere. Two scattering peaks are present for a silver hemispheric nanoparticle, whereas a single narrow peak is achieved by a perfect silver spherical nanoparticle with the same diameter of 30 nm. **(b) Refractive index dependent Mie scattering spectra of a single nanosphere with the diameter of 30nm.** There is broadening of the peak as the refractive index of the surrounding media increases, resulting in lowering quality (Q) factor from increased FWHM. The slope of the peak wavelength variation is similar to that of the stacked quintuple layer circular array in the cylindrical hole.

SEM images of silver nano-cup array fabricated by replica molding process are shown in the following figure.



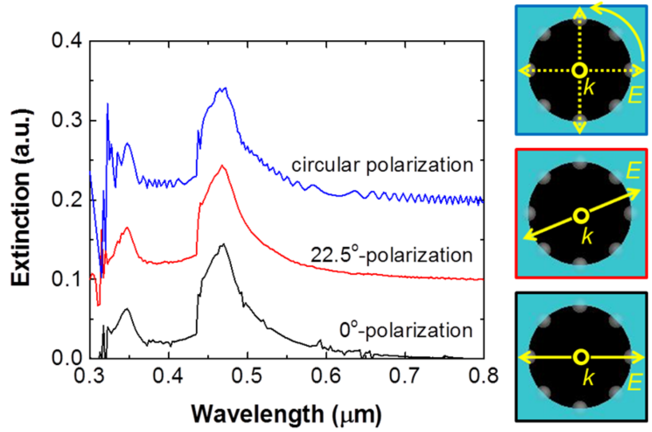
Supplementary Fig. S2. The nano-cup array device. (a) Top view of the nano-cup device taken from Scanning Electron Microscope (SEM). (b) 30 degrees tilted view of defect area on the device, showing nanoparticles formed in circular arrangement inside the hole.

Charge distribution among the triple layer stack of eight nanoparticle circular array is presented.



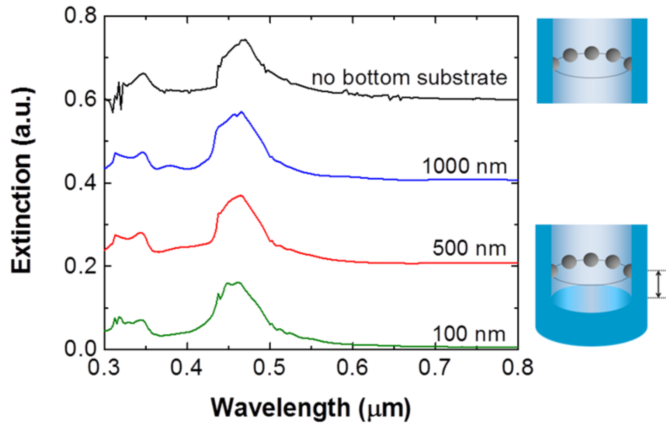
Supplementary Fig. S3. Derivative of electric field, which is proportional to surface charge, of the triple layer stack of circular arrays with eight nanoparticles. Two different edge-to-edge inter-layer distances which are (a) 220 nm and (b) 5 nm are calculated. When the inter-layer distance is 250 nm (layer center-to-center distance), each nanoparticle has an individual dipole oscillating out of phase with each other. On the other hand, shorter inter-layer distance produces single dipole formation along three vertically arranged nanoparticles in z-direction. Considering the net dipole strength along three layers, larger electric dipole built along the nanoparticles induces a larger magnetic field loop across the layers. This results in higher in-plane magnetic field in the nanohole as Fig. 4c shows.

The effect of the incident light polarization on a circular array of eight nanoparticles was studied.



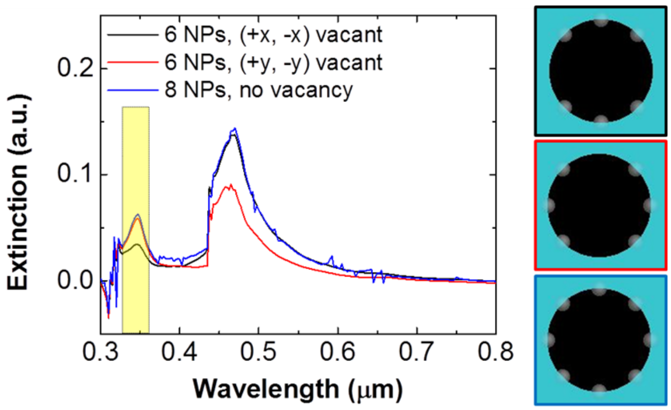
Supplementary Fig. S4. Effect of the polarization of incident light source. Electric fields polarized in x-direction (0°-polarization), orthogonal to inter-particle axis (22.5°-polarization) and in circle were imposed on a single circular array with eight nanoparticles attached on the sidewall of nanohoe. The overall intensity and shape of the extinction spectra for all three polarizations were identical except a small blue-shift of peak wavelength by 2.5 nm in the case of 22.5°-polarization. This addresses the model of the nanoparticle circular array can be utilized in a variety of applications without the limitation of polarizations of light source.

In the case of the presence of the bottom substrate under the nanohole, the extinction spectra with different height between the single circular array of eight nanoparticles and the bottom substrate surface are presented below.



Supplementary Fig. S5. Extinction spectra with different height difference between an array of nanoparticles inside the hole and the surface of the bottom substrate. The bottom substrate (with same refractive index as that of original substrate) has minimal effect on the resonance wavelength of the nanoparticle arrays. The single resonance peak in the visible light range purely comes from the nanoparticle circular array.

Actual fabrication of the circular array of nanoparticles can produce defects. The extinction spectra with vacant site in x- and y- directions were calculated.



Supplementary Fig. S6. Extinction spectra with vacancies in x- and y-directions, compared to the original circular array model with eight nanoparticles. The excited light was polarized in x-direction. Reduced extinction intensity at 347.5 nm with x-vacancies and at 470 nm with y-vacancies were observed.