Supplementary information for: Large-area arrays of three-dimensional plasmonic nanostructures from azopolymer surface-relief gratings†

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Sample preparation and nanostructure fabrication

As the starting point, a thin film of a commercial azopolymer (poly(Disperse Red 1 methacrylate), Sigma-Aldrich) in an organic solvent (dichloromethane, Sigma-Aldrich) was spin-coated onto a glass substrate (film thickness around 300 nm) and subsequently annealed above the glass temperature of the polymer (to 110°C) to remove any residual solvent and to make the films as smooth as possible. The second fabrication step employs interference lithography, where the azopolymer film was exposed to an interference pattern of circularly polarized laser light ($\lambda = 488$ nm) in a Lloyd-mirror set-up[1] in two consecutive cycles. The interference pattern was generated by directing half of the incident beam directly onto the sample and by reflecting the other half from a mirror set at a right angle with the sample. In this geometry, the grating period can be conveniently tuned by adjusting the angle between the incident beam and the sample plane. In this work, the exposure conditions were adjusted to produce SRGs with modulation depths of the order of 80–130 nm and a periodicity of about 500 nm. The sample was rotated 90 degrees between the exposures to create a two-dimensional SRG pattern of two superimposed sinusoidal gratings. In the third step, a uniform gold layer with a thickness of 150 nm was deposited onto the polymer surface with an electron-beam evaporator. The final step employs a standard broad-beam (non-focused) ion milling device for milling away the peaks of the SRGs. For this purpose we used a Gatan Precision Ion Polishing System. Ion milling was performed while cooling the sample with liquid nitrogen in order to avoid heating-induced distortion of the polymer pattern during the milling process. The duration of milling was typically on the order of 5 to 10 minutes.

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Statistical image analysis

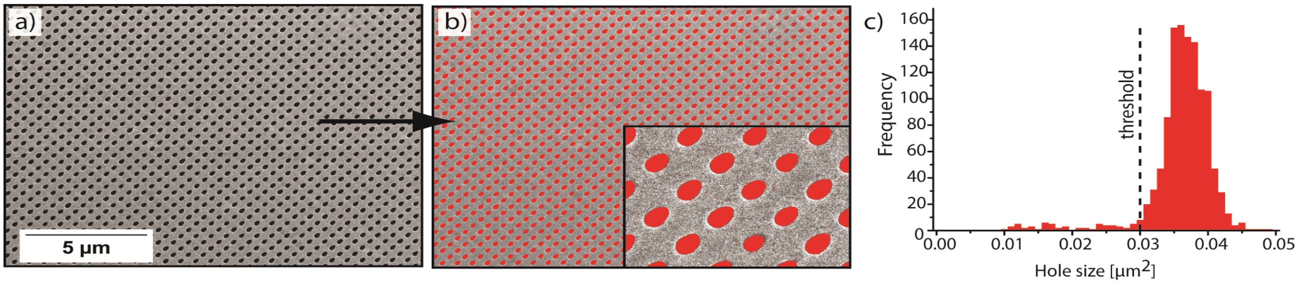
Digital image analysis of a SEM image of a gold nanohole array was performed to obtain statistical data on the average hole size and area. The SEM image shown in Fig. 3c in the main text was used for the analysis, which was performed with a free image processing software package, ImageJ[2]. The analysis was done with color-based thresholding in order to distinguish the holes from the gold surface. In the original SEM image shown in Fig. S1a the holes appear black, whereas in the color-thresholded image (Fig. S1b) the holes have been filled with red. From the color-thresholded image, the software determined the area of each individual hole. The resulting distribution of hole size is shown in Fig. S1c. The holes at the edges of the image were excluded from further calculations by setting a threshold for the minimum hole size to 0.03 μm^2 (A_{cr}). The threshold was determined from the hole-size histogram presented in Fig. S1c. The parameters are presented in Table S1.

Supplementary Table S1 Statistical parameters of the hole array calculated from the color-thresholded SEM image

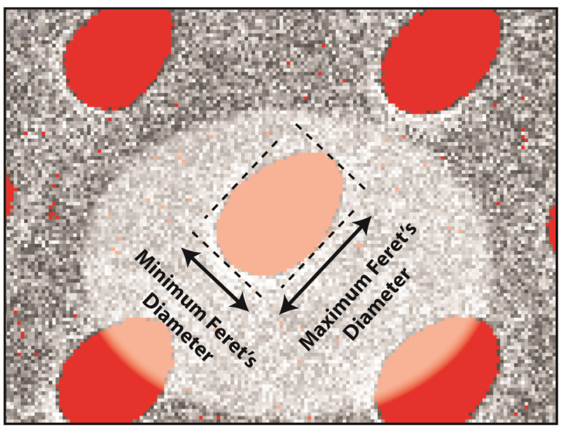
Parameter	Value
Total area of image (μm^2)	221.45
Number of holes ($A > A_{cr}$)	1108
Area of holes ($A > A_{cr}$) (μm^2)	40.96
Total area of holes (μm^2)	42.14
Percentage of holes ($A > A_{cr}$) (%)	97.20
Open-area fraction (all holes) (%)	19.00
Open-area fraction (holes $A > A_{cr}$) (%)	18.50
Average parameters of holes ($A > A_{cr}$)	
Average Size (μm^2)	0.036 ± 0.003 (1σ)
Average Max. Feret's diameter (nm)	268 ± 13 (1σ)
Average Min. Feret's diameter (nm)	185 ± 8 (1σ)

Optical transmission measurements

The transmission spectrum was recorded with an inverted optical microscope (Nikon TE-2000) coupled to a spectrometer



Supplementary Fig. S1 (a) The original SEM image of a gold nanohole array used for statistical image analysis, (b) color-based threshold-determination of the hole areas, and (c) size histogram of the threshold-determinated holes in image (b).



Supplementary Fig. S2 Maximum and minimum Feret's diameter determined from the color-thresholded hole areas.

(Acton SpectraPro-500i imaging monochromator coupled to a Princeton Instruments Pixis 400 CCD camera). The light source was a broadband halogen lamp. To ensure near-plane-wave illumination at normal incidence, the light was mildly focused with a lens-and-diaphragm system with an effective numerical aperture (NA) of less than 0.04. In all cases, the light was collected with a 0.25 NA objective from an area of about 940 μm^2, as determined by the diameter of the three fibers (200 μm) guiding the light and a 10x magnification of the microscope. In the case of the nanoparticle array (Fig. 5, main text), the sample was covered in index-matching oil and a glass cover slip was placed on top.

References

1 P. Rochon, E. Batalla and A. Natansohn, *Appl. Phys. Lett.*, 1995, **66**, 136–138.

2 ImageJ, `http://rsb.info.nih.gov/ij/`.