

Supporting Information:

**Fabrication of Large-Area Patterned Nanostructures for Optical
Applications by Nanoskiving**

Qiaobing Xu¹, Jiming Bao², Robert M. Rioux¹, Raquel Perez-Castillejos¹, Federico
Capasso², George M. Whitesides^{1,*}

*¹Department of Chemistry and Chemical Biology, Harvard University,
12 Oxford Street, Cambridge, Massachusetts, U.S.A. 02138*

*²Harvard School of Engineering and Applied Sciences, Harvard University,
29 Oxford Street, Cambridge, Massachusetts, U.S.A. 02138*

*Corresponding Author

Telephone Number: (617) 495-9430

Fax Number: (617) 495-9857

Email Address: gwhitesides@gmwgroup.harvard.edu

EXPERIMENTAL SECTION:

MATERIALS

The Araldite 502 epoxy was purchased from Electron Microscope Science (Fort Washington, PA). The epoxy was prepared by mixing different components included in the kit in the following amounts: 5 mL of the bisphenol-A diglycidyl ether (Araldite 502), 5.5 mL of dodecenyl succinic anhydride (DDSA), and 0.3 mL of benzyldimethylamine (BDMA). We used a number of substrates transparent in the mid-infrared to support arrays of both L-shaped and closed-loop nanostructure arrays. The infrared permissive substrates are submerged in water during the sample (epoxy slab) collection process and therefore must be resistant to attack or dissolution by water. Calcium fluoride (CaF_2 , Harrick Scientific, 19-mm diameter single-crystal disc, 2-mm thick) is insoluble in water and transmits light from 1.5 to 9 μm . Zinc selenide (ZnSe , International Crystal Laboratories, Garfield, NJ) is insoluble in water and transmits light from 0.6 to 16 μm . For polarization experiments, a KRS-5 polarizer (Reflex Analytical Corporation, Ridgewood, NJ) was placed in the path of the incident beam. KRS-5 (thallium bromide iodide) is optically transparent from 0.6-40 μm with an index of refraction of 2.37 at 11 μm .

MICROTOME SECTION ALIGNMENT

Correct alignment is critical for high uniformity across a mm^2 -area section. The alignment of the microtome requires several steps. Readers are referred to the following website for a complete set of instructions on the operation of a microtome.²⁹ We include

an abbreviated procedure for correct alignment of the knife with the sample block face. It includes three steps for correct alignment: (1) align bottom edge of the block face parallel with the knife edge; (2) align knife edge parallel to the block face across entire width of the block; and (3) align block face with the knife edge along length of the block.

Step 1: Align bottom edge of sample block face parallel with the knife edge: Move block slowly past knife with handwheel and observe shadow as it appears on bottom of block face and disappears at top of block. If top and bottom edges of the block are parallel to the knife edge, the shadow will appear across the entire width of the block at the lower edge and leave the top edge at the same time. If the shadow appears on the lower edge at one side of the block before the other side, the edge of the block is not parallel to the knife. To adjust, rotate holder with specimen rotation adjustment screw until shadow of knife appears on lower edge of block evenly across the block width. Care must be taken to ensure the knife is not hit by the sample block face when loosening and rotating the holder.

Step 2: Align knife edge parallel to the block face across width of block: Move block slowly past knife with handwheel and observe height of reflection across the width of the block. The shadow should be uniform in height across the width of the block face. If the shadow is higher on one side than the other, the block face is farther away from knife on the side with the shadow at the higher position. In order to adjust, carefully rotate knife holder toward this side of block with the stage rotation micrometer knob until the shadow is uniform in thickness across the width of the block. Care must be taken to ensure the knife is not hit by the sample block face when loosening and rotating the holder.

Step 3: Align block face with knife edge along length of block: Observe the shadow, while slowly moving the sample block face past the knife edge by turning the handweel. The shadow should maintain the same height from the bottom to the top of the block face. If the shadow decreases in height, the top of block face is closer to knife than the bottom of sample block face. Conversely, if the shadow increases in height from the bottom to the top of the sample block face, the bottom of the block face is closer to the knife than the top of the block face. To adjust, rotate arc with specimen slide adjustment screw on arc segment mount until the shadow remains even in height along the length of block.

OPTICAL MEASUREMENT

We used a Nicolet Fourier-transform infrared spectrometer in transmission mode to optically characterize the sample.^{16,17} We placed a piece of aluminum foil (~20 μm thick) with a punched hole (~ 1.5 mm diameter) directly in front of the sample. For all single beam measurements, 128 scans with a resolution of 4 cm^{-1} were averaged. A separate spectrum of the clean substrate was collected and used as a reference. The measured transmittance spectrum of the FSS surface was obtained by normalizing it to this reference.

FDTD SIMULATIONS

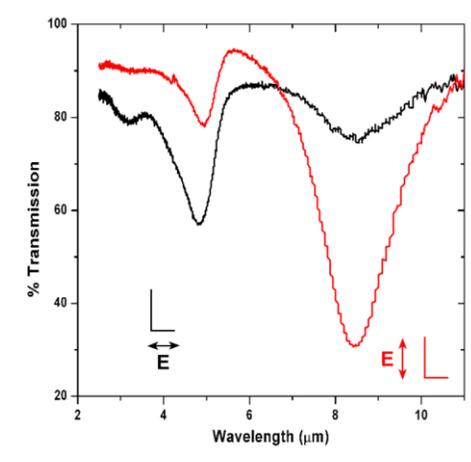
We used a commercial Finite-Difference Time-Domain (FDTD) software (xfdd, from remcom.com) to calculate the back-scattering (reflectance, R) spectra from an individual element nanostructure (closed loop, L-shaped or U-shaped nanostructures) in air. We account for the effect of the substrate by multiplying the simulated spectrum by n_{eff} . To calculate back-scattering spectra, an incident Gaussian pulse excites the structure, and the

back-scattered electrical field in time domain is obtained. The ratio of the power spectrum of scattered field to the power spectrum of the incident field yields the scattering spectrum in the frequency domain. The reflectance spectrum for an FSS array is linearly proportional to a single unit with the constant of proportionality dependent on the density of unit structure, if we neglect the weak interactions between the units. Transmittance (T) through the sample is related to reflectance (R) by the relationship, $T = 1 - R$. The reflectance spectra are plotted with y-axis values reversed and rescaled for comparison with the experimentally measured transmittance spectra. The objective of the simulation is not to provide absolute transmittance, but to confirm the main features of the transmission spectrum, such as its resonance position, and its line width. In the simulation, gold nanostructures are approximated by wire with a cross section of 50-nm width \times 100-nm height (as determined during fabrication). The dimensions of the nanostructure in the simulation are shown in Supporting Information Figure 3. The structures are approximated as an ideal rectangle; for L or U structures, the angle is set to 90° for adjoining arms. The dimensions for these structures in the simulation are set according to SEM measurements. The Debye mode is used to model the dielectric property of gold;^{30,31} the parameters for the Debye model are infinite dielectric constant = 1.001, static dielectric constant = -7499, conductivity = 8.84×10^6 S/m, and relaxation time = 7.5×10^{-15} s. These parameters give the best fit to the refractive index of gold for light with a wavelength of 2-10 μm . The $n_{\text{eff ZnSe}} \sim 1.8$ at 11 μm and the $n_{\text{eff CaF}_2} \sim 1.2$ at 7 μm are calculated from Eq. 2. We use $n_{\text{eff}} \sim 1.2$ for the Araldite epoxy (100-nm thick slab).

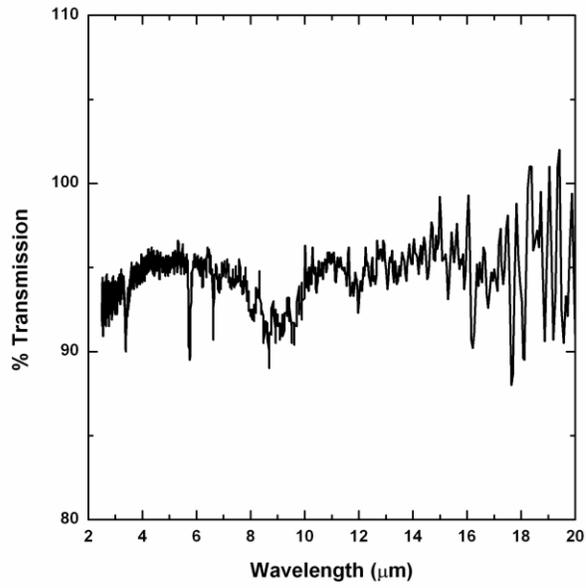
IMAGING

We imaged the nanostructures by SEM measurements using a LEO 982 SEM operating at 2 kV at a working distance of 2-6 mm. Bright-field and dark-field optical microscopy imaging was performed using a Leica DMRX upright optical microscope.

Supplementary Information Figure 1: Transmission spectra of the L-shaped nanostructure with polarization parallel to either of the two arms.



Supplementary Information Figure 2: Transmission spectrum of 100-nm thick epoxy film.



Supporting Information Figure 3: The dimensions of the nanostructures in the FDTD simulations. The width and the height of all three shaped nanostructure are set 50-nm and 100-nm respectively.

