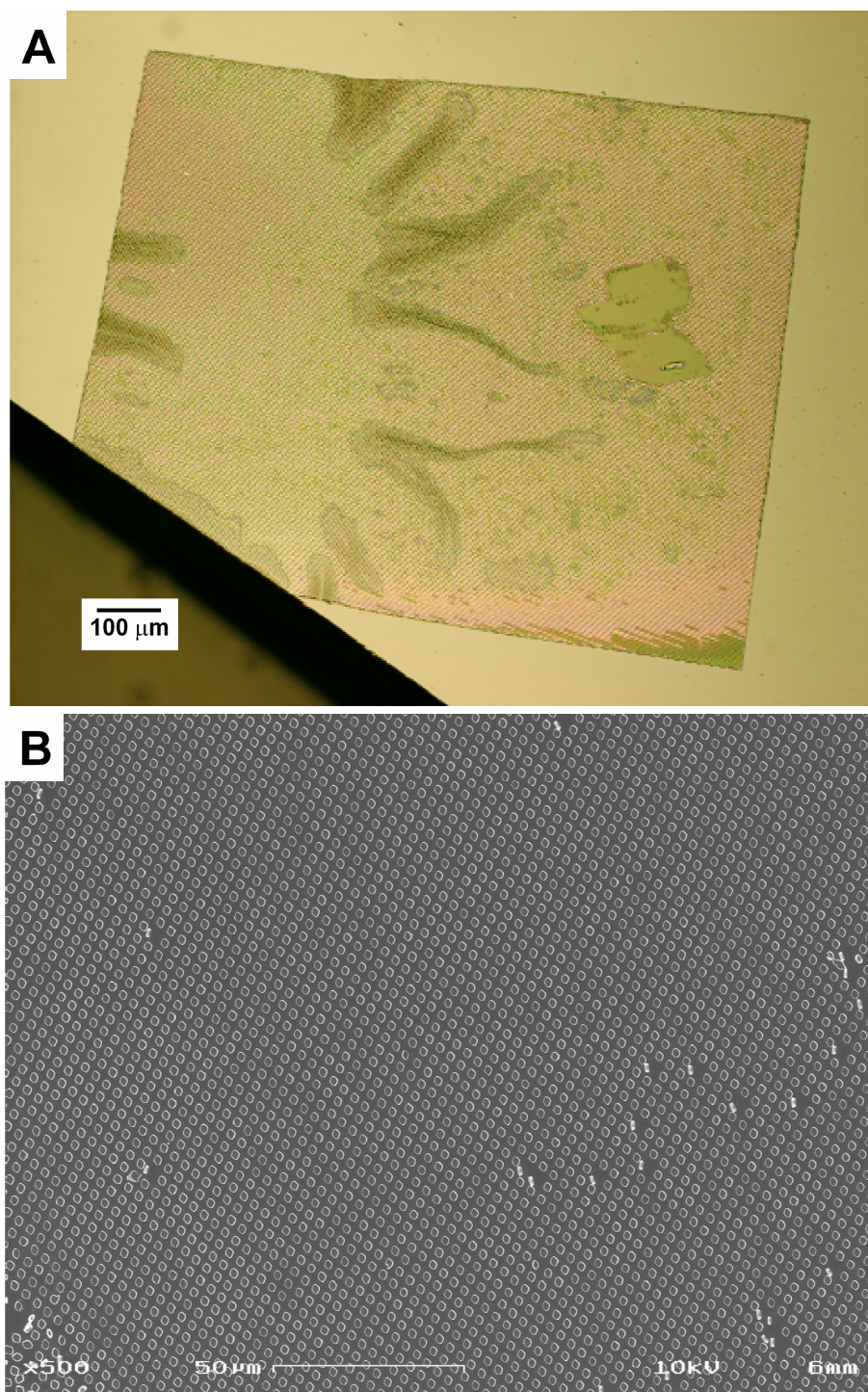


Supporting Information: Fabrication of High Aspect-Ratio Metallic Nanostructures

Using Nanoskiving

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Supporting Figure 1: (A) optical image of a 500-nm-thick epoxy section on a silicon substrate before the epoxy was etched. (B) SEM image of the nanorings with a square shape after the epoxy has been removed by etching with an oxygen plasma.

Experimental Section:

Fabrication of Epoxy Slab Containing Patterned Gold Films:

We obtained a poly(dimethyl siloxane) (PDMS) master by molding PDMS against a patterned substrate, which was fabricated by conventional photolithography using standard procedures for soft-lithography.¹ Typically, we coated the silicon wafers (<100>, N/phosphorus or P/boron doped, 1-10 Ω -cm, from Silicon Sense; Nashua, NH) with an adhesion promoter first (hexamethyldisilazane or HMDS), and then, with S1813 photoresist (MicroChem Corp., Newton, MA) by spin-coating at 3000 rpm for 30s. We patterned the films of S1813 by photolithography, coated the surface with a release layer (Tridecafluoro-tetrahydrooctyl trichorosilane, United Chem. Tech, Bristol, PA), and molded with PDMS (Dow Corning's Sylgard 184 kit, mixing catalyst and prepolymer in a ratio of 1:10).

We replicated this pattern into an Araldite-based epoxy by molding the epoxy precursor against the PDMS master on a 15 nm-thick gold coated silicon substrate.² This gold layer was used to facilitate separation of the epoxy from the silicon substrate: gold adheres poorly to the silicon substrate. The epoxy was cured at 60 °C for 12 h. The epoxy composed of a diglycidyl ether of bisphenol-A (isopropylidenediphenol) was purchased from Electron Microscope Science (Araldite 502 kit; Fort Washington, PA). The epoxy was prepared by mixing the different components of the kit in the following amounts: 5 mL of diglycidyl ether of bisphenol-A (isopropylidenediphenol) (Araldite 502), 5.5 mL of dodecenyl succinic anhydride (DDSA), and 0.25 mL of benzyldimethylamine (BDMA). After carefully removing the PDMS mold, we coated the molded epoxy with a gold film by sputtering. We then embedded the gold-coated epoxy substrate in a thick layer of the same prepolymer epoxy (Araldite 502). In order to make epoxy layers of the thickness required by the sample holder of the microtome (~ 1 cm), we punched a hole (~ 5 mm in diameter) through a 1 cm-thick PDMS slab and covered it on the previously gold coated substrate. We filled the hole with the same epoxy prepolymer. After curing, we peeled off the epoxy from the silicon substrate together with the gold.

Microtome sectioning: We initially trimmed the epoxy slab with a razor blade to an area

of $\sim 0.5\text{ mm} \times 0.5\text{ mm}$. The patterned plane was manually aligned parallel to the edge of the diamond knife with the aid of a microscope so that we could cut through the sample uniformly over relative a large surface area. A rough section with the same diamond knife was required in order to expose the embedded gold nanostructures. We then sliced thin epoxy film sections of the sample using a microtome (Ultra microtome, Leica MZ6) with water filling in the sample-collecting boat of the diamond knife (DiatomeTM). The section speed was set at 1 mm/s for a selected section thickness. The thin, sectioned polymer sections containing embedded metal nanostructures floated on the surface of water. We directly immersed the silicon wafer into water and pull it back carefully to let the floating polymer film sit on the solid substrate. The epoxy sections transferred onto a solid substrate were etched by oxygen plasma (0.9 Torr, 70 W barrel etcher) for 5 to 40 min depending on the thickness of the epoxy sections: 70nm to 500 nm, respectively.

Imaging: We observed the nanostructures by means of SEM measurements using a LEO 982 SEM operating at 2 kV.

References:

1. Xia, Y.; Whitesides, G. M. *Angew. Chem., Int. Ed.* **1998**, *37*, 550-575.
2. Xu, Q.; Gates, B. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **2004**, *126*, 1332-1333.