Electronic Supplementary Material (ESI) for Nanoscale Horizons.

Supporting information for:

Transfer and Control of Orientation of 3D Nanostructures Fabricated by Nanoskiving

Chemicals and materials

Epofix epoxy prepolymer and harder were purchased from Electron Microscopy Science. Single-side polished silicon wafers were cut into 2 cm by 2 cm pieces and then cleaned in piranha solution (7 parts of H_2SO_4 and 3 parts of H_2O_2) for 5 h at 90 ^oC, rinsed repeatedly with Milli-Q water and ethanol and finally dried by a stream of nitrogen gas. Polystyrene (PS) spheres (700 nm and 1 μm) were purchased from Sigma-Aldrich. The polystyrene was purchased from Sigma-Aldrich and dissolved in toluene. Poly(dimethylsiloxane) (PDMS) monomer was mixed with curing agent in a 10:1 (w/w) ratio (Sylgard 184, Dow Corning). Photoresist (BP212-37 positive photoresist, Kempur Microelectronics, Inc., Beijing, China) was spin-coated on clean silicon wafers at 3000 rpm. Trichloro-(1H,1H,2H,2H-perfluorooctyl) silane (PFS) was purchased from Sigma-Aldrich. The sodium dodecylsulfate (SDS), sulfuric acid, hydrochloric acid, hydrogen peroxide, toluene and ethanol were purchased from Beijing Chemical Works.

Preparation of two-dimensional colloidal crystals

Hexagonal close-pack monolayers of PS nanospheres were prepared by the interface method.[1] In brief, 0.1 mL of 5% PS spheres dispersion in a mixture of deionized water and absolute ethanol (v/v=1:1) was dropped onto the surface of water in a petri dish by a syringe, and then 20 μL of 8% SDS aqueous solution was dropped into water along the edge of the plate. Finally, the PS nanospheres assembled into close-packed monolayers and then were lifted onto the as-prepared substrates.

Fabrication of nanocrescent arrays

The nanospheres with diameter of 1 μm were etched using ICP-RIE system (Oxford

Plasma Technology Type 80Plus) with a mixture of O_2 (40 sccm) and CF_4 (10 sccm), 30 W RF power to ignite the plasma and provide anisotropic etching, and 300 W ICP power to help sustain the plasma and provide relatively more isotropic etching. The etching process was applied at a work pressure of 10 mTorr and a temperature of 10 ^{o}C. The etching duration is 100 s, leading to non-close-packed nanosphere arrays. A gold nanomesh was then produced by evaporating 5 nm Ag and 10 nm Au on the silicon substrate. After the gold was deposited, the PS nanospheres were removed by toluene with mild sonication. A metal-assisted chemical etching process was applied to fabricate the arrays of silicon cylindrical nanoposts.[2, 3] The gold nanomesh-covered silicon substrates were immersed into an etching mixture consisting of HF (49%), H_2O_2 (30%) and ethanol (5:1:1 of HF: H_2O_2: ethanol). The etching duration is 15 min. Using a PDMS mold as an intermediate, these arrays of nanoposts were replicated from silicon to epoxy. A 50 nm-thick gold film was deposited only partially around the epoxy nanoposts by shadow evaporation. The substrate was placed at a 45^{o} angle from the source of evaporation. This structure was embedded in more epoxy to form a block that was then sectioned to yield epoxy slabs containing the array of nanocrescents.

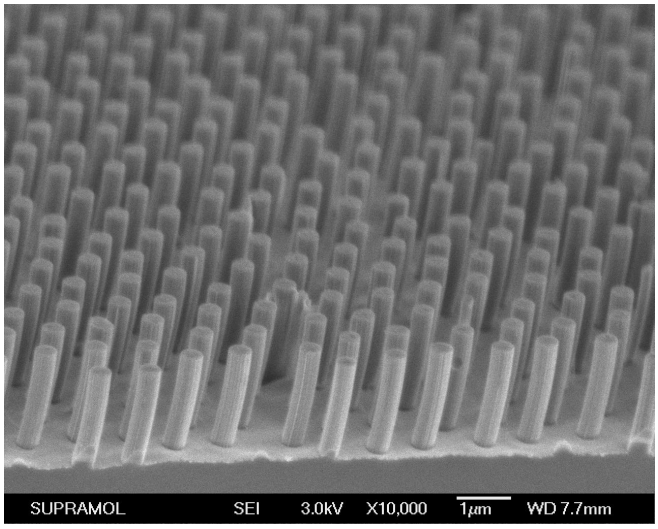

Fig. S1 SEM image of the array of silicon nanoposts. The PS nanospheres with a diameter of 1 μm were etched 90 s, and the metal-assisted chemical etching was performed 15 min.

Fabrication of nanohole arrays

After the monolayer of 700 nm PS nanospheres was transferred onto aluminum substrate, the same conditions of etching were performed on these nanospheres. The etching duration is 80 s. A 30 nm-thick film of gold was then deposited on the nanospheres and the substrate. After the samples were immersed into toluene with slight ultrasonication to remove the PS nanospheres, gold nanohole arrays were generated.

Fabrication of nanowire arrays

Photoresist was patterned using photolithography with a stripe-patterned mask, and then the patterned silicon surface was passivated with PFS. Using soft lithography, the patterns were replicated in epoxy through a PDMS mold. After the patterned epoxy substrate was obtained, a 100 nm-thick layer of gold was deposited on the patterned epoxy substrate at a glancing angle of 45^{o}. This structure was embedded in more epoxy to form a block, and then the block was sectioned to yield epoxy slabs containing the array of nanowires.

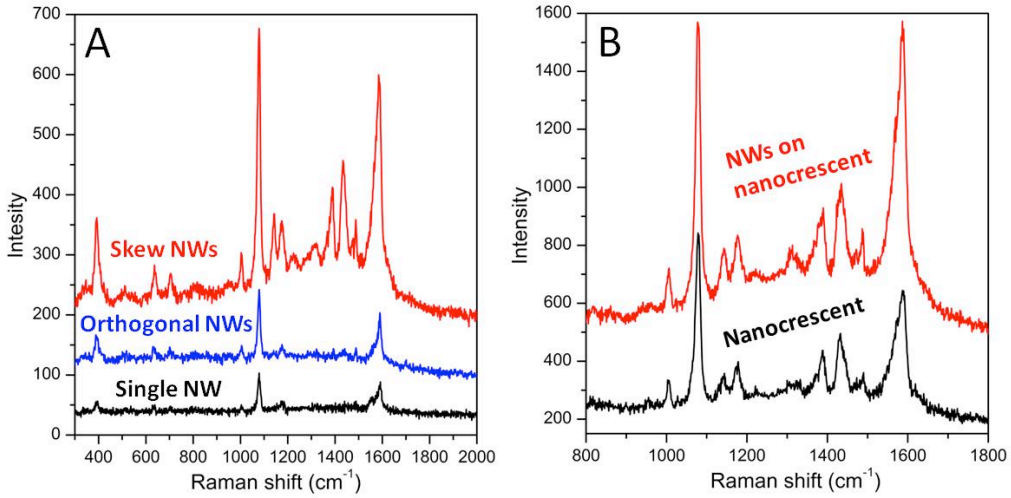

Figure S2 SERS spectra obtained from (A) the single nanowire and the crossing points of orthogonal nanowires and skew nanowires; (B) nanocrescent and nanowires on nanocrescent. The incident laser wavelength, laser transmission, and accumulation time were set to 633 nm, 5%, and 15 s, respectively.

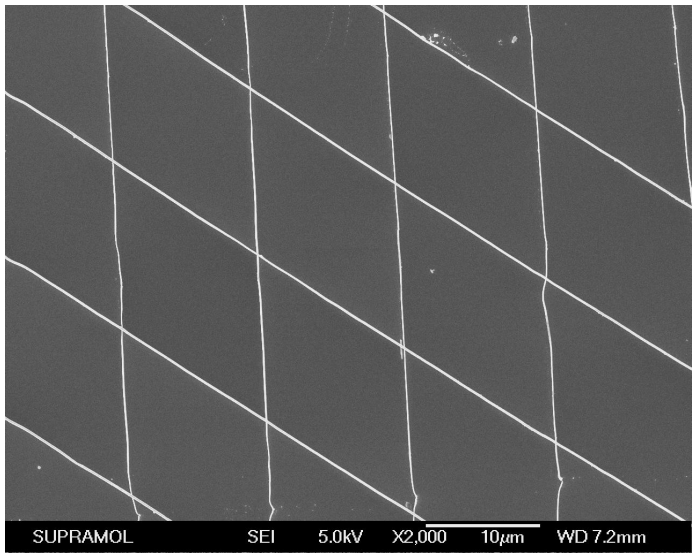

Figure S3 A zoomed-in SEM image of the gold nanogrid with intersection angle of 45^{o}.

References

1. J. Rybczynski, U. Ebels, and M. Giesig, *Colloids Surf. A*, 2003, **219**, 1-6.
2. J. Yeom, D. Ratchford, C. R. Field, T. H. Brintlinger, and P. E. Pehrsson, *Adv. Funct. Mater.*, 2014, **24**, 106-116.
3. S.-M. Kim, and D.-Y. Khang, *Small*, 2014, **10**, 3761-3766.