Supporting Information

Three-Dimensional Electrochemical Axial Lithography on Si Micro- and Nanowire Arrays

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Table S1. Si@metal wire array dimensions.

The dimensions of all the Si@metal wire array synthesized and shown in both the main text and the supporting info are reported here. The smallest dimensions achieved to date in terms of Si diameter (~ 160 nm, Fig. S13), ring height (~ 40 nm, Figure S9), gap length (~ 5 nm, Figure S9), and ring thickness (~ 30 nm, Figure S11) are shown in bold and red.

The Si wire diameter, height and thickness of the ring, and gap length were measured on one Si@Au structure (TEM image).

| Figure | S1 Length | S1 Diameter | Array Pitch | Ring Metal | Ring Height | Ring Gap | Ring Thickness | Location from bottom |
|--------|-----------|-------------|-------------|------------|-------------|----------|----------------|---------------------|
| 1b, 1c | 6642 ± 112| 945 ± 26    | 1500        | 1 * Au     | 263 ± 33    | -        | 59 ± 18        | 1443 ± 195          |
| 1d     | 5765 ± 79 | 958 ± 28    | 1500        | 1 * Au     | 290 ± 25    | -        | 39 ± 20        | 2596 ± 238          |
| 2a, S8 | 3551 ± 97 | 229 ± 15    | 590         | 7 * Au     | 61 ± 6      | 22 ± 3   | 47 ± 8         | 299 ± 35            |
| 2b     | 2210 ± 55 | 311 ± 19    | 590         | 2 * Au     | 91 ± 26     | 215 ± 26 | -              | 736 ± 41            |
| 2c, S10| 3560 ± 190| 295 ± 1     | 590         | 1 * Ni     | 136 ± 29    | -        | 37 ± 1         | 408 ± 45            |
| 2d, S11| 3483 ± 107| 265 ± 5     | 590         | 1 * Fe     | 208 ± 38    | -        | 30 ± 4         | 2539 ± 50           |
| 2e, S12| 5492 ± 61 | 259 ± 15    | 590         | 2 * Ag     | 264 ± 25    | 162 ± 16 | 64 ± 10        | 1326 ± 100          |
| 2f, S13| 1781 ± 108| 159 ± 18    | 590         | 1 * Fe     | 277 ± 33    | 302 ± 10 | 507 ± 22       | 453 ± 43            |
| 3, S14 | 2765 ± 58 | 183 ± 10    | 590         | 1 * Au     | 63 ± 10     | -        | 44 ± 7         | 1731 ± 49           |
| 3, S15 | 2875 ± 99 | 214 ± 25    | 590         | 2 * Au     | 64 ± 13     | 30 ± 11  | 49 ± 15        | 1485 ± 48           |
| S5b    | 757 ± 28  | 658 ± 22    | 1100        | 1 * Au     | 63 ± 11     | -        | 34 ± 10        | 111 ± 8             |
| S5d, e, f | 792 ± 69 | 630 ± 16    | 1100        | 1 * Au     | 102 ± 21    | -        | 154 ± 33       | 345 ± 53            |
| S7     | 1860 ± 86 | 527 ± 21    | 1100        | 2 * Au     | 144 ± 15    | 115 ± 16 | 558 ± 25       | 771 ± 53            |
| S9*    | 2328 ± 135| 232 ± 59    | 590         | 2 * Au     | 43 ± 4      | 5        | 42             | 1305 ± 47           |

* The Si wire diameter, height and thickness of the ring, and gap length were measured on one Si@Au structure (TEM image).

Materials and chemicals

All chemicals and solutions were used without further processing, unless noted otherwise. Commercially available plating solutions (Cyless for Ag, Orotemp 24 Rack for Au) were purchased from Technic Inc., USA. PS spheres with 1500 nm diameter (2.5 w%) were purchased from Polysciences Inc., USA. Boric acid (99 +%), iron(II)sulfate heptahydrate (99.0 %, ACS grade), nickel(II)sulfate hexahydrate (98.0 %, ACS grade), nickel(II)chloride hexahydrate (98.0 %) were purchased from Alfa Aesar, USA. Benzene-1,4-dithiol, L-ascorbic acid (99.0 %, BioXtra), phosphoric acid (99 %), Triton X-100 (laboratory grade), iodine (99.8 %), and potassium iodide (99.8 %) were purchased from Sigma Aldrich, USA. Styrene (99.0 %), acrylic acid (99.0 %) and ammonium persulfate (98.0 %) were purchased from Sigma Aldrich, USA. Styrene (Sigma Aldrich, 99 %) was purified by adding a 10 wt-% NaOH solution in a volume ratio 1:1. After vigorous shaking, the aqueous was discarded and the
styrene phase purified by passing through an aluminium oxide powder column. The water used was double deionized using a MilliQ system with a resistivity of 18 MΩ. Acetone (technical grade), ethanol (euro denaturated 96 %), ethanol absolute (TechniSolv, 99.5 %), methanol (99.8 %, ACS grade), ammonia (25 %, GPR RECTAPUR), dichloromethane (GPR RECTAPUR) were purchased from VWR, Europe. Glycerol, hydrofluoric acid (40 %, EMSURE), hydrogen peroxide (30 %, ACS grade), nitric acid (65%, EMSURE), tetraethyl orthosilicate were purchased from Merck, Germany. Conducting silver paste ACHESON G3692 was purchased from PLANO GmbH, Germany. N – doped Silicon wafers ((100) resistivity 0.1 – 10 Ω cm) were gratefully provided by Infineon, AT. N – doped Silicon wafers ((111) resistivity 55 – 60 Ω cm) and polycarbonate makrolon were gratefully provided by Sony DADC Inc., AT.

**Synthetic protocols**

**Polystyrene colloid synthesis**

PS colloids with 590 nm and 1100 nm diameter were synthesized by a surfactant – free emulsion polymerization. 250 mL of MilliQ water were heated to 80 °C in a 500 mL triple-neck round-bottom flask with reflux-condenser. Nitrogen gas was bubbled for 30 min for degassing. For 590 nm colloids 20 g styrene (40 g styrene for 1100 nm colloids) was added to the water phase under constant stirring. 0.4 g of the comonomer acrylic acid was dissolved in 5 mL MilliQ water and added to the mixture. After 5 min 0.1 g ammonium persulfate, dissolved in 5 mL MilliQ water, was added. The reaction was carried out for 24 h at 80 °C. After cooling to room temperature the dispersion was filtered and purified by centrifugation and redispersion and dialysis.

**Colloidal lithography**

The PS colloids (d = 590 nm, d = 1100 nm) were assembled at the air/water interface using ethanol as spreading agent.¹ Prior to the interfacial self-assembly process, the PS colloids were cleaned and purified by three centrifugation-redispersion steps using 1:1 ethanol/water mixtures. For the spreading onto air/water interface, the 590 nm PS colloids (750 µL of PS colloid dispersion) were mixed with 250 µL ethanol. For the 1100 nm PS colloids, a mixture of 500 µL of PS colloid dispersion and 500 µL ethanol was used. The dispersion was filled into a syringe added to the water surface using a syringe pump (Landgraf HLL LA120) at a speed of 30 µL min⁻¹. N-type c-Si substrates were cut into 4 x 4 cm² and cleaned via sonication in acetone, ethanol and MilliQ water for 4 min each, followed by an oxygen plasma treatment. The silicon substrates were immersed in the water phase, elevated under a
shallow angle after monolayer deposition to transfer the monolayer, and left to dry in air. The procedure delivered large – area colloidal crystals with grains in the mm² range.

Colloids with a diameter of 1.5 µm were obtained from Polysciences. A cleaned, plasma treated c-Si substrate was coated by spin coating (3500 rpm for 3 min) of the 1.5 µm PS dispersion (10 wt%) mixed with 3 parts of methanol : Triton X100 (400:1).

After monolayer deposition, the polystyrene particles were reduced in size to produce a non-close packed architecture using oxygen plasma (FEMTO, Diener Electronic, 50 W, oxygen flow 4 mL min⁻¹). The etching time was adjusted to the desired size of the particles.¹

A thin adhesion layer of Al doped ZnO was sputtered directly on the PS sphere array on Si, using a Clustex 100M sputtering system from Leybold Optics: base pressure before deposition around 1.10⁻⁶ mbar, Ar pressure during deposition 3.10⁻³ mbar, 1 s deposition, power in the 75-175 W range depending on the PS colloid size (i.e. lower power for smaller diameters).² The samples were then immediately sputtered with a gold film using a Cressington Sputter Coater 108 auto (deposition at 40 mA during 300 s).² Finally the PS colloids were removed using adhesive tape.

Synthesis of Si micro- and nanowire arrays via MACE

MACE was used to prepare Si micro- and nanowires by immersing the Si/Au hole array substrates in an aqueous HF/H₂O₂ mixture.² Caution: Appropriate safety precautions have to be observed when working with hydrofluoric acid (HF): HF is a contact poison! The MACE solution was prepared fresh before etching. Typically, the 4 x 4 cm² substrates were placed on a home-made 3D printed polymer sample holder and immersed into the etching solution for the desired duration. The substrates were then rinsed three times with deionized water, once with ethanol and finally dried in air. For the synthesis of straight micro- and nanowires, n-doped Si wafers (100) were utilized and the MACE solution was composed of 10 mL of hydrofluoric acid, 10 mL of MilliQ water, and 1 mL of hydrogen peroxide. Typical etching durations were 1 - 7 minutes. Kinked nanowires were etched according to the literature.³ N-doped Si wafers (111) were etched with two different solutions: Solution A consisted of 20 mL MilliQ water, 2 mL H₂O₂ and 10 mL HF, while solution B consisted of 15 mL MilliQ water, 5 mL Glycerol, 2 mL H₂O₂ and 10 mL HF. The etching sequence was A-B-A for 1 – 3 – 1 min, respectively.
Si@SiO$_2$ core shell wire arrays were synthesized by growing a SiO$_2$ shell using a sol–gel process developed by Keating et al. for coating metal nanorods with SiO$_2$. The SiO$_2$ growth conditions need to be chosen to exclusively yield heterogenous nucleation of conformal SiO$_2$ shells around the Si wires without significant homogeneous nucleation of SiO$_2$ particles in solution. Briefly, 2940 µL of ethanol, 960 µL of MilliQ water, 240 µL of TEOS and 60 µL of NH$_4$OH were mixed together in a 100 mL beaker. After one hour, the samples were taken out, rinsed twice in MilliQ water, once in ethanol and dried in air. The procedure was repeated several times until the desired shell thickness was reached, with each step increasing the shell thickness by increments of ca. 10 nm (Figure S3). The Si@SiO$_2$ wire arrays were then embedded within a polycarbonate film via spin-coating (Laurell WS-650SZ-6NPP/Lite spin coater). The choice of polycarbonate as the membrane material was motivated by its stability in HF (used to dissolve the sacrificial SiO$_2$ shell), its good wetting by aqueous solutions as demonstrated by its previous use as an ion track etched membrane material for templated electrodeposition, and the fact that it can be easily dissolved in organic solvents.

The membrane synthesis was optimized to obtain a conformal polycarbonate film with a constant height over the whole sample area, i.e. ~ 38 mm$^2$. Typically 50 mg of polycarbonate were dissolved in 500 µL of dichloromethane (CH$_2$Cl$_2$) using sonication for 1 h. The 4 cm x 4 cm samples were cut into smaller pieces of ca. 1.5 cm x 2 cm. A small area on the side of each sample was protected by adhesive tape for the proper electrical connection of the gold film with silver paste in the later stages of the synthesis. The polycarbonate solution was left untouched for 30 s before spin coating at 6000 rpm during 5 s. The tape was removed afterwards. Subsequently, the samples were placed on a heating plate at 180 °C for 10 minutes to anneal the polycarbonate film. The excess polycarbonate was etched in the plasma etcher (Emtech K1050X) at 50 W with an oxygen flow of 10 mL/min to partially uncover the top of the Si@SiO$_2$ wires. Homogeneous etching was obtained by putting an Al plate perforated with a 7 mm diameter hole on top of the sample during plasma etching (see Figures S2 and S5 for images of the membrane at different stages of the synthesis). The etched area was used later for the electrodeposition. The sacrificial SiO$_2$ shell was removed using a 1:5 HF : MilliQ water solution and the substrates were then successively washed in MilliQ water and ethanol. Typical durations were 4-8 min. A very thin protective SiO$_2$ shell was then deposited during 20 min (~ 3 – 4 nm thick) around the embedded wire arrays before electrodeposition using the same procedure as for the SiO$_2$ sacrificial shell. This protective shell is necessary to avoid parasitic growth of metal particles on the silicon wires and can be
removed with HF once the metal deposition and selective etching is completed. Electrochemical deposition of metals was performed using a Keithley Sourcemeter 2400 operated with a three electrode configuration and a home-made electrochemical Teflon cell. A Pt mesh was used as counter electrode, Ag/AgCl as reference electrode, while the Au film at the bottom of the silicon wire arrays was used as the working electrode. Before electrodeposition an electrical contact was prepared on the samples by applying silver paste on the side of the sample as well as below the sample. The silver paste was applied on the region, which had been protected with adhesive tape during the spin coating of the polycarbonate and is in direct contact with the gold film. The sample was then laid on top of an aluminum foil, sandwiched within the electrochemical cell, and electrically connected to the working electrode of the potentiostat. Metals were deposited at constant potentials using aqueous plating solutions. The amount of metal grown was controlled with the duration. The electrochemical cell and electrodes were thoroughly washed in MilliQ water after each deposition step.

Au was deposited at -950 mV using Orotemp 24 Rack solution.
Ag was deposited at -940 mV using Cyless solution.
Ni was deposited at -900 mV using a homemade aqueous Ni solution (0.2 M NiSO₄ * 6H₂O, 0.1 M NiCl₂ * 6 H₂O, 0.15 M H₃BO₃).
Fe was deposited at -1000 mV using a homemade aqueous Fe solution (12 g FeSO₄ * 6 H₂O, 4.5 g H₃BO₃, 0.1 g ascorbic acid in 100 ml MilliQ H₂O).

NB: We found that homogenous crystalline arrays of Si wires (i.e., with constant height and pitch) are necessary for the proper synthesis of the membrane and the metal shell depositions. Such well-defined arrays are made possible by self-assembling the PS colloids at the air-water interface, leading to large crystalline defect-free hexagonal arrays with crystals in the mm² range (Figure S1).

Selective Etching
After the metal deposition, the area covered with the silver paste was cut away using a glass cutter. Afterwards the polycarbonate was dissolved in CH₂Cl₂ for 1 h and the sacrificial shells were etched in the appropriate solutions. A specific combination of sacrificial layer and etching solutions was used for each target shell material (table S2): Ni was used as the sacrificial material for both Au and Ag shells, but was etched in 1:1 H₂O:HNO₃ for Au and in 15% H₃PO₄ aqueous solution for Ag shells. Ag was used as the sacrificial material for both Ni and Fe and was etched in a 4:1:1 ethanol:H₂O₂:NH₄OH solution. The gold film layer was
selectively etched in a KI/I$_2$ solution (10 weight % KI, 5 weight % I$_2$) for 20 minutes to yield Si@Ni nanowire arrays without a metal base layer (Figure S16).

Table S2. Sacrificial shell material, etching solution and duration

| Target material | Sacrificial material | Etching solution | Duration |
|-----------------|----------------------|------------------|----------|
| Au              | Ni                   | 1:1 H$_2$O:HNO$_3$ | 45 min   |
| Ag              | Ni                   | 15 % aqueous H$_3$PO$_4$ | 6 h      |
| Ni, Fe          | Ag                   | 4:1:1 ethanol:H$_2$O$_2$:NH$_4$OH | 30 min   |
| Ni              | Au (metal base layer)| 10 weight % KI, 5 weight % I$_2$ | 20 min   |

Confocal Raman measurements

1,4-benzenedithiol (BDT) was used as the SERS target molecule. The substrates were incubated in a 1 mM ethanol solution of BDT for one hour and then washed several times with ethanol to remove physisorbed molecules. For Raman measurements a dispersive Thermo DXR2 Raman microscope (Thermo, USA) equipped with a confocal microscope BX41 (Olympus Corp., Japan) and controlled by Thermo Scientific OMNIC9 acquisition software, was used. The collection of the Raman signal was carried out in 180° backscattering geometry, with a laser excitation wavelength of 785 nm (≡ 1.58 eV) in combination with a “high resolution” diffraction grating (830 lines/mm), covering a wavenumber range from 600 – 1850 cm$^{-1}$. With a 50 µm confocal pinhole-like entrance slit to the spectrometer, this setup results in a spectral resolution of about 4 cm$^{-1}$. A laser power of 1 mW on the sample and a selected 10x microscope objective (NA = 0.25), with a laser spot diameter of approximately 2.5 µm, yields in an irradiance of around 200 µW µm$^{-2}$. All spectra were collected with an exposure time of 20 s and 3 accumulations each. For Raman mapping, the same parameters were set as for single spectrum collection. No photochemical or photothermal reaction was observed using these parameters. Unless mentioned otherwise in the text, the Raman spectra were not baseline corrected. The position of the Raman peaks observed on the Si@Au ring samples functionalized with BDT matched the literature values.$^{8,9}$ The standard deviation of the Raman signal measured at 1563 cm$^{-1}$ on the map was calculated based on 900 different spot locations.
**FDTD simulations**

Electric fields generated by the Si@Au ring nanowires were calculated using a commercially available finite-difference-time-domain (FDTD) simulation software package (Lumerical Solutions Inc., Vancouver, Canada). A plane wave source was injected above the wire, propagating in a direction parallel to the wire longitudinal axis with the electric field perpendicular to the wire longitudinal axis. The simulations were done in three-dimensions with a 0.1 nm resolution (mesh size) around the metal rings. The distance between the structures investigated and the simulation boundaries was at least half the simulation wavelength. The refractive index of the medium was set to 1 since the Raman measurements were done in air. The dielectric constants of gold and silicon were used directly from the Lumerical materials library: we used Johnson and Christy’s data for gold\textsuperscript{10} and Palik’s data for silicon.\textsuperscript{11}

**Microscopy**

**SEM.** Secondary electron (SE) and back-scattered electron (BSE) images of the arrays were acquired using a Zeiss Ultra Plus at a working distance of \(\sim 2.4 \text{ mm}\), equipped with an InLens SE detector, an InLens BSE detector (EsB), and an angle selective BSE detector (AsB) located below the pole piece. The accelerating voltage was adjusted between 1 and 5 kV depending on the sample (i.e. charging).

**TEM.** Secondary electron (SE mode) and high-angle annular dark-field (HAADF) imaging z-contrast scanning transmission electron microscope (STEM) images of the wires were acquired using a cold field emission gun JEOL F200 STEM/TEM operated at 200 kV equipped with a large windowless JEOL Centurio EDX detector \((100 \text{ mm}^2, 0.97 \text{ srad}, \text{energy resolution} < 133 \text{ eV})\). TEM grids were prepared by cutting out a small sample piece of about 1 mm x 1 mm. The sample was put into a 1.5 ml Eppendorf tube, filled up with \(\sim 500 \mu \text{L}\) of ethanol absolute (99.5 %) and sonicated for 4-5 min. The wires were then transferred by pipetting 2 \(\mu \text{L}\) of solution onto a holey carbon coated Cu TEM grid. Prior to TEM investigation, the TEM grids were cleaned in a gentle He plasma (Zepto, Electronic Diener) at 20W during 45 s (base pressure: 0.08 mbar, pressure during plasma cleaning: 0.3 mbar) to remove any remaining carbon contaminants.

**EDX.** EDX maps and spectra were acquired with a typical beam current of 0.1 nA and a beam diameter of 0.16 nm. The maps were acquired during ca. 5 minutes. The maps were obtained by integrating the counts over a specific transition: O K\(_\alpha\) line for O (integration: \(0.450 – 0.600 \text{ keV}\)), Si K\(_\alpha\) line for Si (integration: \(1.630 – 1.840 \text{ keV}\)), Au M\(_\alpha\) line for Au (integration:
2.020 – 2.220 keV), Ag Lα line for Ag (integration: 2.840 – 3.120 keV), Fe Kα line for Fe (integration: 6.240 – 6.560 keV), Ni Kα line for Ni (integration: 7.300 – 7.640 keV). Nb: the small Fe and Cr signals that can be seen sometimes in the EDX spectra are artifacts and originate from the TEM pole piece. The Cu and C signal originate from the TEM grids.

**AFM.** The height and smoothness of the Au rings was extracted by AFM using a JPK NanoWizard instrument in AC mode using a NCS-36 cantilever B (resonance frequency 130 kHz, spring constant 2 N/m). The images were post processed with Gwyddion, using flattening and median fits. The root mean square roughness was obtained by using the built in roughness function of Gwyddion on linescans going across the rings. The unprocessed linescans were used for the roughness measurement.
Figure S1. Self-assembly of PS colloids at the air/water interface

a) Self-assembly of the PS colloids ($d = 1100$ nm) at the air/water interface. The colloidal particles are added to the air/water interface as a 1:1 water-ethanol dispersion via a syringe attached to a syringe pump. b) Transfer of the hexagonal colloidal monolayer onto a Si wafer. c) 4x4 cm$^2$ Si substrate after transfer of the hexagonal colloidal monolayer showing prominent structural colours resulting from grating diffraction at the ordered colloidal lattice. Scale bar: 1 cm. d) Secondary electron SEM image of the hexagonally arranged PS colloids. Scale bar: 2 µm.

Figure S2. Synthesis of the Si@Au arrays: scheme and photographs

a-d) Initial PS colloid diameter: 1100 nm. e-h) Initial PS colloid diameter: 590 nm. Scale bars for all photographs: 1 cm. a) PS colloidal monolayer (in blue in the cartoon) after size reduction. b) Gold nanohole array (in yellow in the cartoon) after colloidal removal. c) Silicon wires (in grey in the cartoon) after MACE. d) Cutting of samples before 3D electrochemical lithography. e) Embedded nanowire array after sacrificial silica SiO$_2$ coating (in blue in the cartoon) and spin coating of polycarbonate (in orange in the cartoon). The area on the right side of the sample was protected by adhesive tape during spin coating. f) Sample ready for electrodeposition after gradual plasma etching of polycarbonate, removal of sacrificial SiO$_2$ shell, deposition of protective SiO$_2$ shell and deposition of silver paste for electric contact (on the right). g) Sample after electrodeposition of nickel and gold (nickel in black and gold in yellow in the cartoon). Here: gold ring dimer. h) Silicon nanowires with two gold rings after cutting of the silver paste, dissolution of polycarbonate and selective etching of nickel.
Figure S3. Control over SiO$_2$ shell thickness.

Top view SEM images of the Si nanowires as a function of the number SiO$_2$ deposition steps (each step lasts 1 hour). Scale bars: 1 µm. The total SiO$_2$ shell thickness can be tuned by increments of ~ 10 nm by adjusting the number of SiO$_2$ deposition steps used.

Figure S4. EDX map of conformal SiO$_2$ shell around a Si nanowire

a) Bright field STEM image of the Si@SiO$_2$ nanowires. b-d) EDX maps. b) Overlay (red: Si, green: O). c) Si and d) O.
Figure S5. Polycarbonate membrane synthesis around the Si@O₂ wire arrays.

a) Scheme showing the successive synthetic steps. Wire array after spin coating showing incompletely embedded wires. The following annealing step improves the formation of a conformal coating around the Si@SiO₂ core – shell wires. The tops of the nanowires are uncovered by gradual plasma etching of the PC membrane in order to dissolve the sacrificial SiO₂ shell. b-e) Corresponding secondary electron SEM images of different Si wire array geometries. b) After spin – coating. Scale bar: 200 nm. c) After annealing. Scale bar: 200 nm. d,e) After gradual plasma etching. Scale bar: 1 µm. d) Cross – section. e) Top – view. NB: All SEM images show different wire geometries.
Figure S6. Protective SiO$_2$ layer etching, EDX data.

Si@Au wires before HF (a and b) and after 4 minutes etching in 1:5 HF:MilliQ solution (c and d). a, c) HAADF STEM images. b, d) Corresponding EDX point spectra (120s live time). e, f) Comparison of the OK$_\alpha$ signal before (black curve) and after HF treatment (red curve) at the Au ring location (e) and at the bare Si wire (f). The curves were normalized for clarity. One can clearly see the disappearance of the O signal at both locations after HF treatment.
Figure S7. Control over the metal shell thickness.

The metal shell thickness is adjusted by the number of SiO_2 steps. a-b) Thin gold ring (thickness: 34 ± 10 nm) prepared using three SiO_2 deposition steps (3 hour deposition). a) Schematic of the synthetic pathway based on three SiO_2 deposition step. b) SE cross-sectional SEM image. c-f) Thick gold ring (thickness: 154 ± 33 nm) prepared using 15 deposition SiO_2 steps. c) Schematic of the synthetic pathway to make thick metal shell using thick SiO_2 sacrificial shells. d) SE cross-sectional SEM image. e-f) Top-view BSE images showing homogeneous ring thickness (obtained using the ESB in-lens detector).
Figure S8. SEM images of large homogenous Si@Au ring dimers arrays.

a-d) Tilted images. a,b) High magnification images. Scale bar: 100 nm. a) SE image, b) BSE image. c-d) Low magnification BSE images. Scale bar: 1 µm.
Figure S9. Au ring dimer with a 5 nm gap around a Si nanowire.

a) Dark-field tilt series STEM images of an Au ring dimer around a Si nanowire with a 5 nm gap showing continuous rings and gap. b) Point EDX spectrum in the gap region showing no residual nickel after etching of the sacrificial Ni segment. c) EDX line scan across the ring dimer (red line) supporting the presence of the gap between the two Au rings. d) EDX map of the ring dimer (blue colored map: Si and green colored map: gold).
Figure S10. Ni ring around a Si nanowire (EDX)

a) EDX point spectrum. b) EDX map (red: Si, green: Ni). The Cu signal originates from the Cu grid. c) SE cross-sectional SEM image.
Figure S11. Fe ring around a Si nanowire (EDX)

a) EDX point spectrum. b) EDX map (red: Si, green: Fe). The Cu signal is from the TEM grid. The Cr signal is from the pole piece. c) SE cross-sectional SEM image.
Figure S12. Ag ring dimer around a Si nanowire (EDX)

a) HAADF STEM image. b-d) EDX maps (red: Si, green: Ag). b) Overlay, c) Si and d) Ag. e) Integrated EDX spectrum at the Ag ring (selected area shown with a red rectangle in c-d) showing monometallic rings. The Cu signal is from the TEM grid. f) HAADF STEM image obtained after breaking the wires from the substrate. g) Low magnification SE cross-sectional image (SEM).
Figure S13. Si nanowire modified with two different metals.

a) HAADF STEM image. b-c) STEM images, EDX map (red: Fe, green: Ni) and integrated EDX spectrum at the Fe ring (b) and at the Ni ring (c) showing monometallic rings (the counts originating from the area outlined by the red rectangle were integrated). d) Low magnification SE cross-sectional images (SEM).
Figure S14. Single Au ring

a) HAADF STEM typical STEM images of the single Au ring used for the Raman experiments. The first image on the left is an SE image acquired in STEM mode showing the topography of the Au/Si structure. b) SE SEM cross-sectional image.

Figure S15. Au ring dimer with 30 nm gap

a) Top view secondary electron SEM image - inset: corresponding FFT showing hexagonal symmetry. b) HAADF STEM typical STEM images of the Au ring dimer (30 nm gap) shown in Figure 3 and used for the Raman experiments.
Figure S16. Selective etching of the metal base layer

a-c) Si@Ni wire arrays after 3DEAL (i.e. before etching the gold film). d-f) the same Si@Ni wire array after selectively etching the gold film in a KI/I$_2$ solution. a, d) Structure Scheme. b, e) SE cross-sectional SEM images. c, f) BSE cross-sectional SEM images, same area as the one shown in b) and e) respectively. Scale Bars: 200 nm.
**Figure S17. AFM characterization.**

a, b) AFM images of a Si@Au ring dimer wire. c) Linescan along the white line shown in b. These measurements show that the metal shells synthesized are very smooth (root mean square roughness of 0.6 nm) and therefore dominated by the surface roughness of the polycarbonate membrane pores. X-Y scale bars: 500 nm in b) and 50 nm in c). The color scales located on the right side of the images refer to the sample height.
Figure S18. Raman map data

a) Unprocessed Raman map (Raman intensity at 1563 cm⁻¹). b) Smoothed Raman map (Raman intensity 1563 cm⁻¹) used and shown in Figure 3 of the main text.
Figure S19. FDTD simulations of the complete Si@Au nanowire structures.

a-d) The plane wave source propagates along the y-axis (from top to bottom) and the electric field is polarized along the x-axis. The top of the wire is located at $y = 1500$ nm, the rings at $y = 0$ nm and the bottom of the wire at $y = -1500$ nm. a-c) E-field intensity enhancement maps of the Si@Au nanowires. Identical rainbow log scale for the three maps. a) Single Si nanowire. b) Si@Au ring nanowire. c) Si@Au ring dimer nanowire. d) Linescan of the E-field intensity along the center of the Si@Au nanowires ($x=0$, $z=0$) in the longitudinal direction from top to bottom, as indicated by the black arrows in a-c). Linear scale. Black curve: Si wire (no Au ring), blue curve: Si@Au ring wire and red curve: Si@Au ring dimer. The Au ring increases the amount of light reaching the top half of the Si wire (above the rings), while suppressing it in the bottom half (below the ring) in comparison to the nanowire with no gold rings. The effect is even more pronounced in the case of the Au ring dimers.
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