

Materials. Anodisc alumina membranes with a specified pore size of 200 nm and thickness of 60 μ m were purchased from Whatman (Catalog No. 6809-6022; Maidstone, UK). The pyrrole monomer was purchased from Sigma-Aldrich. The pyrrole was distilled regularly and stored at 4 °C. Gold targets (used to sputter the membranes) were purchased from Denton Vacuum (Moorestown, NJ). The gold and silver plating solutions (Orotemp 24 RTU RACK, and 1025 RTU @ 4.5 Troy/gallon) were obtained from Technic Inc. (Anaheim, CA). A 161 mM pyrrole in 200 mM NaCl solution was used for electropolymerizing the polypyrrole (PPy). All other chemicals were of analytical grade purity and were used as received. All solutions were prepared using nanopure water (18 M, ELGA purelab-ultra model, Ultra Scientific, Marlow, Buckinghamshire, UK).

Instrumentation. All controlled-potential experiments were performed with a CHI 621A potentiostat (CH Instruments, Austin, TX). Platinum wire and Ag/AgCl (3 M KCl, CH Instruments) served as the counter and reference electrodes, respectively. All working electrode potentials are given with respect to Ag/AgCl reference electrodes. Scanning electron microscopy (SEM) images and metal compositions were obtained with a FEI XL30 SEM instrument (FEI Co., Hillsboro, OR), equipped with an energy-dispersive X-ray analyzer (Amatek Inc., Mahwah, NJ) under an accelerating voltage of 30 kV.

Template Preparation of Multistep and Conical Nanowires. For all asymmetric nanowires, a thin film of gold was first sputtered on the branched side of the alumina membrane to provide an electrical contact for the subsequent electrochemical plating. For the asymmetric nanowires (not containing PPy), a copper base was plated first into the branched section of the membrane using a 1 M cupric sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) solution and a charge of 10 C; this was followed by 0.2 C of gold from an Orotemp 24 plating solution. Both plating steps were carried out at a potential of -0.9 V. Asymmetric gold nanowires containing PPy were grown using an initial gold base (1 C at -0.9 V), as opposed to copper and gold. The asymmetric step-cone nanowires were prepared on top of the previously mentioned bases by sequentially depositing (at -0.9 V) alloy segments (of 0.2 C) from gold/silver plating solutions of different ratios: 9/1, 8.5/1.5, 8/2, 7.5/2.5, and 7/3 (with intermediate rinsing with nanopure water). The nano-barbells were constructed by depositing alternately (at -0.90 V) alloy segments from gold/silver mixture plating solutions with ratios of 9/1 and 7/3 for five segments of 0.2 C each (starting with the 9/1 solution). The alloy sections of the nanowires were then dealloyed with the removal of the less noble silver component by placing approximately 1 mL of a 35% (v/v) nitric acid solution in the growth cell (containing the nanowires-embedded membrane) for 15 min and then rinsing with nanopure water and repeating the process once. The membranes were then “released” from the growth cells and rinsed with nanopure water to remove all residues. After rinsing, the membranes containing copper were swabbed (on the gold-sputtered side) with a cottontip applicator soaked in 0.1 M CuCl_2 in 20% HCl for *ca.* 2 min. This removed both the copper and the sputtered gold. The wires were then released from the alumina membrane as described below. The asymmetric cone-shaped porous nanowires were constructed on the previously mentioned copper and gold bases by growing nanowires from a continuously changing Au/Ag plating solution. The solution consisted initially of 5 mL of the gold plating solution, and its composition was varied gradually by adding the silver plating solution at a fixed flow rate while plating (at -0.9 V) until obtaining a final volume of 10 mL. Different flow rates of the silver solution led to conical nanowires of different sharpnesses. Nanobone nanowires were prepared using a constant-volume growth cell setup with solution mixer. The growth cell was connected to both a 7 cm premixing tube (that delivered the plating solution) and a waste tube (that removed extraneous plating solution from the cell to maintain the total volume of *ca.* 1.6 mL). The nanobone wires were plated (at -0.9 V) from the changing solution in the growth cell. The first conical segment of the nanobone structure was deposited while flowing the silver plating solution at 0.3 mL \cdot min⁻¹ into a continuously flowing (at 0.7 mL \cdot min⁻¹) gold plating solution for 300 s. To obtain the second inverse-cone segment, the flow of silver plating solution was stopped, and only the gold plating solution was allowed to flow (at 0.7 mL \cdot min⁻¹) for an additional 100 s. The cone- and nanobone-containing membranes were dealloyed as described earlier for the step-cone and barbell nanowires and were released from the membrane template as described below. The asymmetric PPy-covered step-cone nanowires were prepared atop the solid gold base by sequentially depositing at -0.9 V alloy segments of decreasing gold contents from Au/Ag solutions with descending composition ratios (87.5/12.5, 82.4/17.6, and 77.8/22.2). The silver was then removed from the alloy as aforementioned, and PPy was electropolymerized from a 160 mM pyrrole solution (in 0.2 M NaCl) for 12 s at a potential of -1.2 V. After removing the membrane from the growth cell and rinsing with nanopure water, the gold side of the membrane was polished with a standard 8-in. SEM sample polisher (South Bay Technology, Inc., San Clemente, CA) using 3-in alumina powder and a Final B polishing cloth (Electron

Microscopy Sciences, Washington, PA). The membrane was polished until the gold color (from the solid gold segment) on the back of the membrane was no longer visible. The wires were then released from the alumina membrane as described below. The release of the nanowires was carried out by first thoroughly rinsing the membrane with nanopure deionized water to remove any plating solution residue. This was followed by immersing the membrane in 3 M NaOH for 10 min with only slight agitation (owing to the delicate nature of the wires). The resulting nanowire-containing NaOH solution was removed to 1.5 mL Eppendorf tubes for precipitation. Nanowires were precipitated from the solution *via* centrifugation (for 3 min at 3000 rpm) and were washed several times with nanopure water until a neutral pH was achieved. All nanowire solutions were stored at room temperature. The diameters of the individual segments of the new nanostructures were measured from calibrated SEM images. The diameter ratio reflects the ratio of the porous gold to the solid gold segments (the latter used as 100%). For each potential (-0.9, -1.0, and -1.1 V), the data were collected from 20 step-cone wires of five segments each, where five measurements were performed on each segment for a total of 1500 measurements.