Supporting Information for:

Core-Shell and Segmented Polymer-Metal Composite Nanostructures

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Electrochemical Procedures. Anodized aluminum oxide (AAO) membranes (Whatman, pore size = $0.2 \mu m$, thickness = $\sim 60 \mu m$, area = 2.3 cm^2 , density = $\sim 10^8 \text{ pores per membrane}$) were purchased from VWR.

Galvanostatic Deposition of Metal. All electroplating solutions—Oromerse BR Gold, pH ~ 10.2 (gold); Orotemp 24 "C", pH ~ 7.4 (gold); nickel sulfamate RTU (Techni nickel "S"), pH ~ 5.5 (nickel); Techni-silver E-2 (silver), pH ~ 12.5; and Techni Copper PC 75 (copper), pH ~ 3.5—were purchased from Technic, Inc., Cranston RI. All metals were plated at a current density of 0.5 mA/cm² using a potentiostat/galvanostat (Princeton Applied Research 273A). Platinum foil served as the counter electrode.

Potentiostatic Deposition of Polyaniline. Aniline (puriss >99.5%, Fluka) was purchased from Aldrich and distilled at 90°C/30 mmHg before use. Electropolymerization using a bipotentiostat (Pine, AFCBP1) was carried out at +0.8 V vs. Ag/AgCl from a solution of 0.1 M aniline in 0.5 M Na₂SO₄, 0.1 M H₂SO₄ (aq, pH ~ 1). Platinum foil served as the counter electrode.

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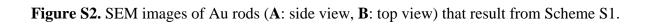
Plasma Etching. To make the gold nanotubes (Figures 3, S1), the PANI-Au core-shell sample was exposed to oxygen plasma (300 mTorr, 18 W) for 5 min using an SPI Plasma Prep II (West Chester, PA).

Scanning Electron Microscopy (SEM) and Electron Backscattered Diffraction (EBSD). For imaging, a small portion of each membrane containing the PANI-metal composite was cut out and placed on an SEM stub (held by conductive carbon tape). The membrane was then dissolved by covering it with a drop of 1 M NaOH for 90 minutes, washing with copious amounts of de-ionized water, and drying in air. The samples were imaged with a Leo SEM (Model 982, resolution: 4 nm at 1 keV) under high vacuum (10 ⁻⁷ torr) using a 2-3 keV electron beam. The SEM was equipped with an EBSD system. The EBSD measurements were performed at a working distance of 13 mm, and an electron beam energy of 15 keV.

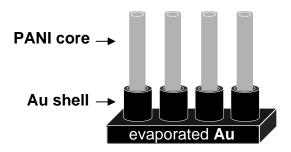
Scheme S1: Alternate procedure for preparation of the segmented polymer-metal nanostructures (without forming the SAM of thioaniline on the Au rods): 1) electrodeposition of Au; 2) electropolymerization of PANI; 3) dissolution of the AAO membrane. (This method leads to detachment of the PANI tubes from the gold upon dissolution of the membrane.)

Figure S1. A) Large-area SEM image of the gold nanotubes pictured in Figure 2.

B) The EBSD spectrum of the boxed region in Figure S1A (the fibrous material that is tethered to the inside of the gold nanotubes) from 0-6 keV and 7.5-15 keV (inset). This spectrum identifies the fibrous material as gold.



Structure 1: core-shell



Structure 2: segmented

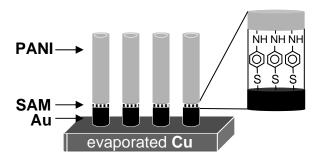
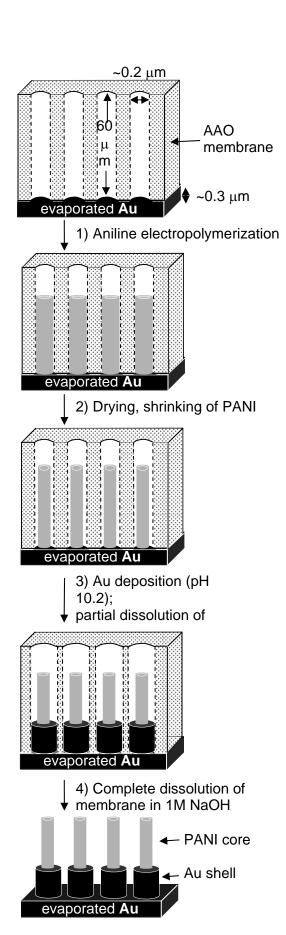


Figure 1.



Scheme 1.

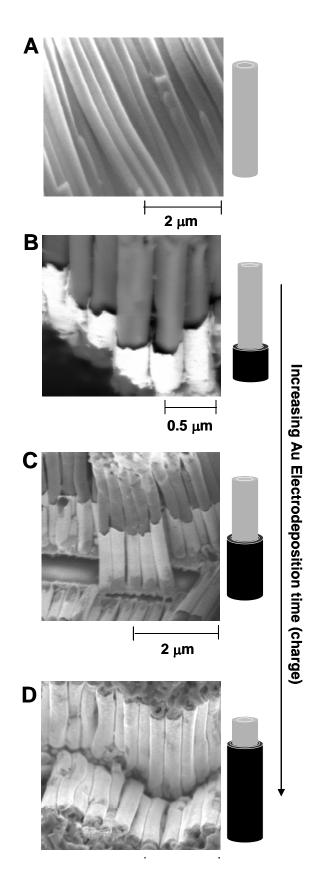


Figure 2.

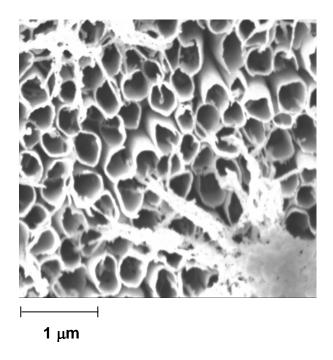
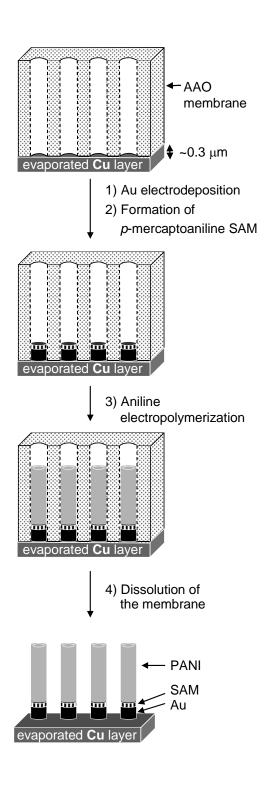


Figure 3.



Scheme 2.

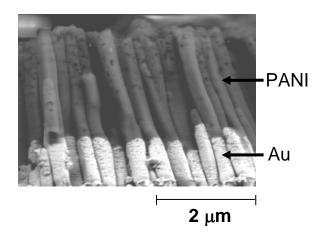
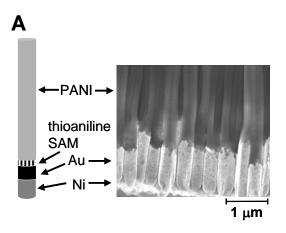


Figure 4.



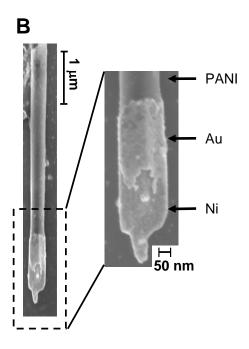
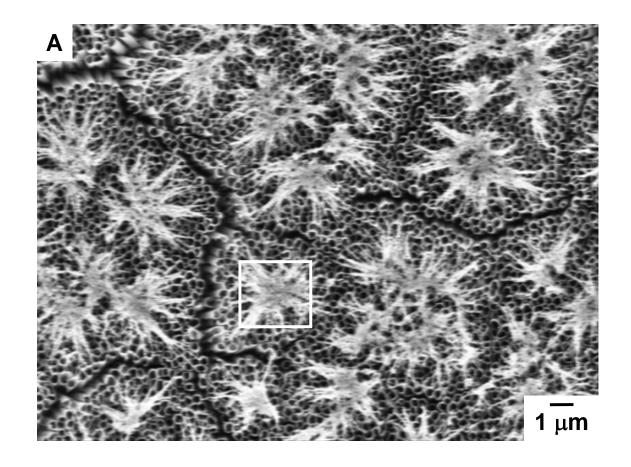


Figure 5.



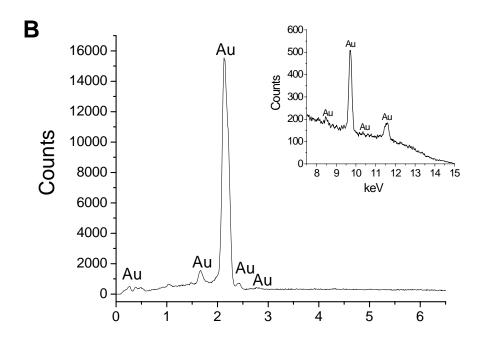
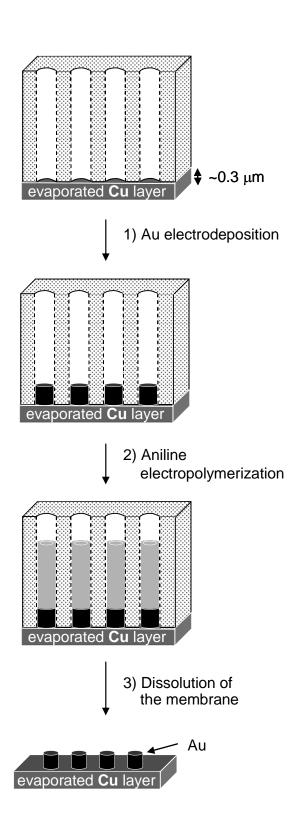


Figure S1.



Scheme S1.

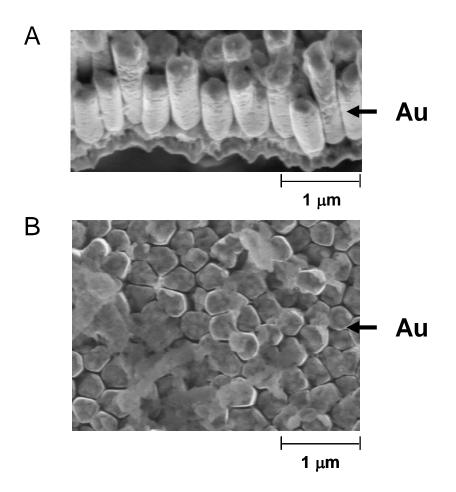


Figure S2.