Supplementary Information

3D nanoporous nanowire current collectors for thin film microbatteries

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Materials and Methods

Fabrication of Au nanotubes: WHATMAN alumina membranes (pore diameter = 200 nm) were used for the electrodeposition of Au-Ag alloy nanorods. Before electrodeposition the alumina membranes were cleaned by sonicating them in deionized water for 30 minutes and dried in a vacuum oven at 80^{o}C for 4 hours. A 200 nm film of gold was sputtered onto the branched side of the alumina membrane which served as the electrical contact for the electrodeposition process. Polyaniline nanowires were first grown using a cyclic voltammetry three electrode electrodeposition method with Aniline (0.1M) and Sulfuric acid (0.5M) electrolyte. The electrodeposition was conducted between -0.2V to 1.2V for 80 cycles with an Ag/AgCl (in 3M NaCl) reference electrode. The PANI nanowires were contracted in diameter by annealing the PANI/Alumina membrane in vacuum at 80 ^{o}C. Then, gold was electroplated around the PANI nanowires using a TECHNIC Inc Orotemp gold plating solution as electrolyte at a voltage of -0.9 V w.r.t Ag/AgCl in 3M NaCl reference electrode. This was followed by etching of the PANI nanowire using concentrated nitric acid and then the alumina membrane was stuck onto a stainless steel foil using a thin layer of silver paste. The alumina membrane was etched using 3M solution of NaOH and then the Au nanotube film was cleaned thoroughly using DI water and dried in a vacuum oven for 4 hrs at 80 ^{o}C.

Fabrication of Au Nanoporous Nanorods: WHATMAN alumina membranes (pore diameter = 200 nm) were used for the electrodeposition of Au-Ag alloy nanorods. Before electrodeposition the alumina memebranes were cleaned by sonicating them in Deionized water for 30 minutes and dried in a vacuum oven at 80^{o}C for 4 hours. A 200 nm film of gold was sputtered onto the branched side of the alumina membrane which served as the electrical contact for the electrodeposition process. Au-Ag alloy nanowires were electrodeposited by a potentiostatic method at -0.9 V (w.r.t Ag/AgCl in 3M NaCl reference electrode) using a 3:1 (v: v) mixture of

gold (TECHNIC Inc Orotemp) and silver (TECHNIC Inc RTU) precursor solutions respectively as the electrolyte. A platinum wire served as the counter electrode and the gold coating on the alumina membrane served as the working electrode for this three electrode electrodeposition setup. Electrodeposition of Au-Ag nanorods was conducted for 4 minutes in order to obtain nanorods of height ~500 nm. The alumina membrane was treated with concentrated nitric acid for 10 minutes to remove the silver component in each individual nanorod followed by thorough rinsing with DI water to remove any traces of nitric acid. The alumina membrane was then stuck onto a stainless steel substrate using a thin layer of silver paste and the alumina was dissolved using 3M NaOH. The vertically aligned Au-Ag nanorod array was rinsed again with DI water and dried in a vacuum oven for 4 hrs at 80 ^{o}C.

Fabrication of PANI coated Au substrate: PANI was electrodeposited onto the planar and nanostructured substrates using a three electrode galvanostatic electrodeposition setup using the gold substrate as the working electrode, a platinum wire as the counter electrode and the Ag/AgCl in 3M NaCl as the reference electrode. A current density of 1 mA/cm^2 for 2 minutes was applied using an aniline (0.15M) + Sulfuric acid (0.5M) + Sodium Sulfate (0.5M) electrolyte solution to obtain a film of PANI around each of the three gold based current collectors – i) planar thin film of gold sputtered onto stainless steel foil, ii) vertically aligned array of Au nanotubes on a stainless steel foil, iii) vertically aligned array of gold nanoporous nanorod on a stainless steel foil.

Electrochemical Measurements. All galvanostatic charge/discharge measurements were conducted using an ARBIN BT 2000 Battery Analyzer. The electrochemical measurements for all the three configurations, – i) planar thin film of gold sputtered onto stainless steel foil, ii) vertically aligned array of Au nanotubes on a stainless steel foil, iii) vertically aligned array of gold nanoporous nanorod on a stainless steel foil were performed in a Swagelok-type cell using Ni-Sn thin film as the working electrode, Li metal foil as a counter/reference electrode and 1M

solution of $LiClO_4$ in 1:1 (v/v) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) as an electrolyte. A glass microfiber filter was used as the separator. The cells were charged and discharged between 3.6 V and 2 V vs Li/Li^+ at current rates 0.04 mA/cm^2. The rate capability study for the nanoporous nanorod coated with PANI electrode was conducted at current rates of 0.04, 0.2, 0.4 and 0.8 mA/cm^2 and the cells were charged and discharged between 3.6 V and 2 V vs Li/Li^+.

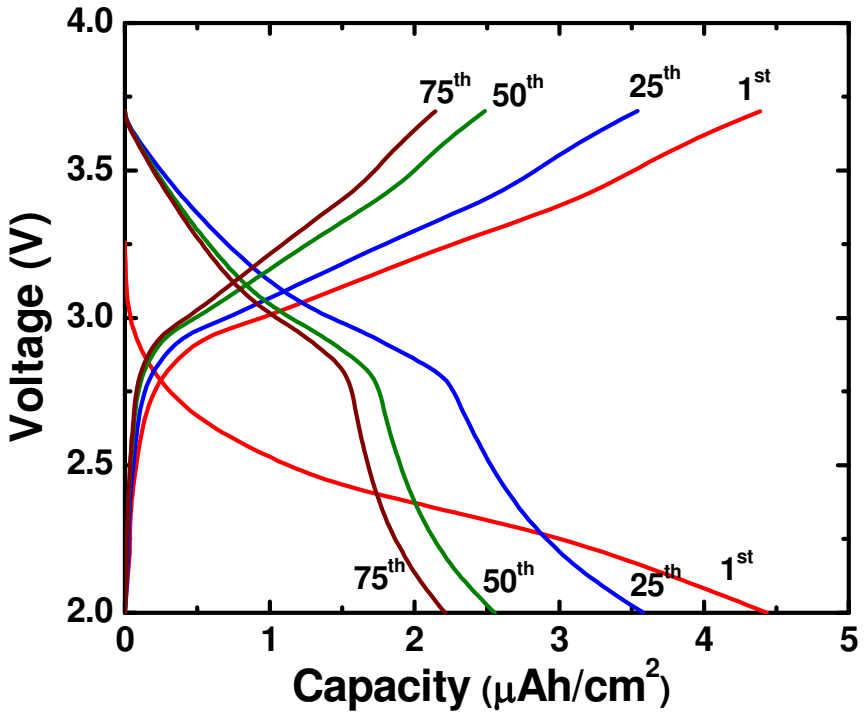

Figure S1: Voltage vs discharge capacity profile for the planar PANI configuration

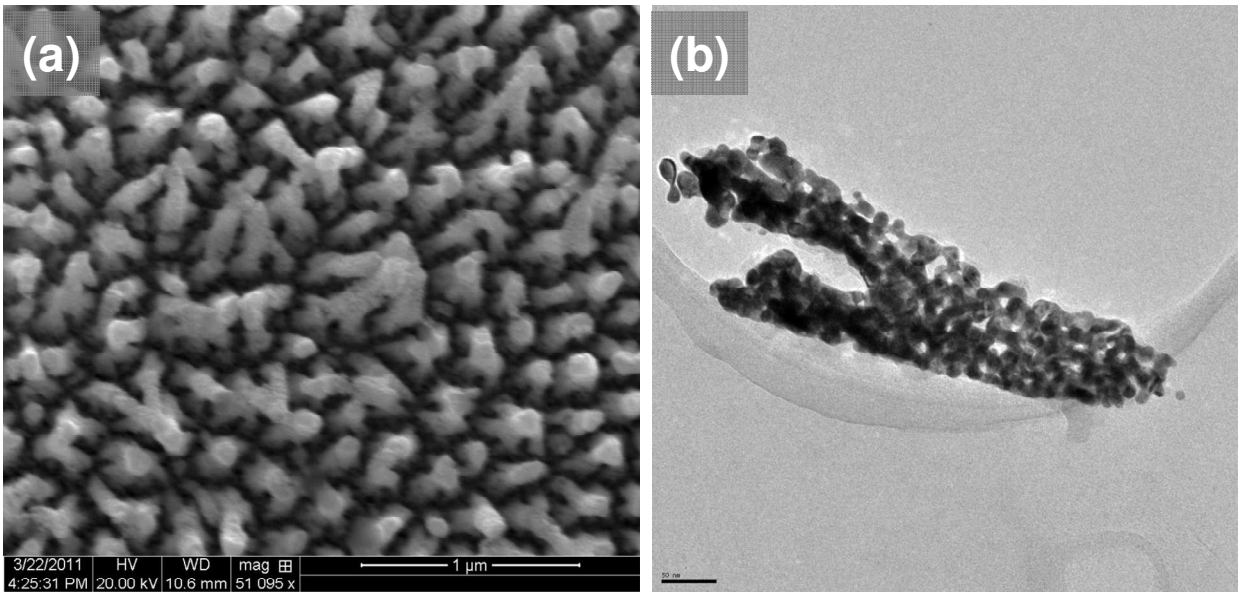

Figure S2: (a) SEM and (b)TEM images of porous Au nanorods

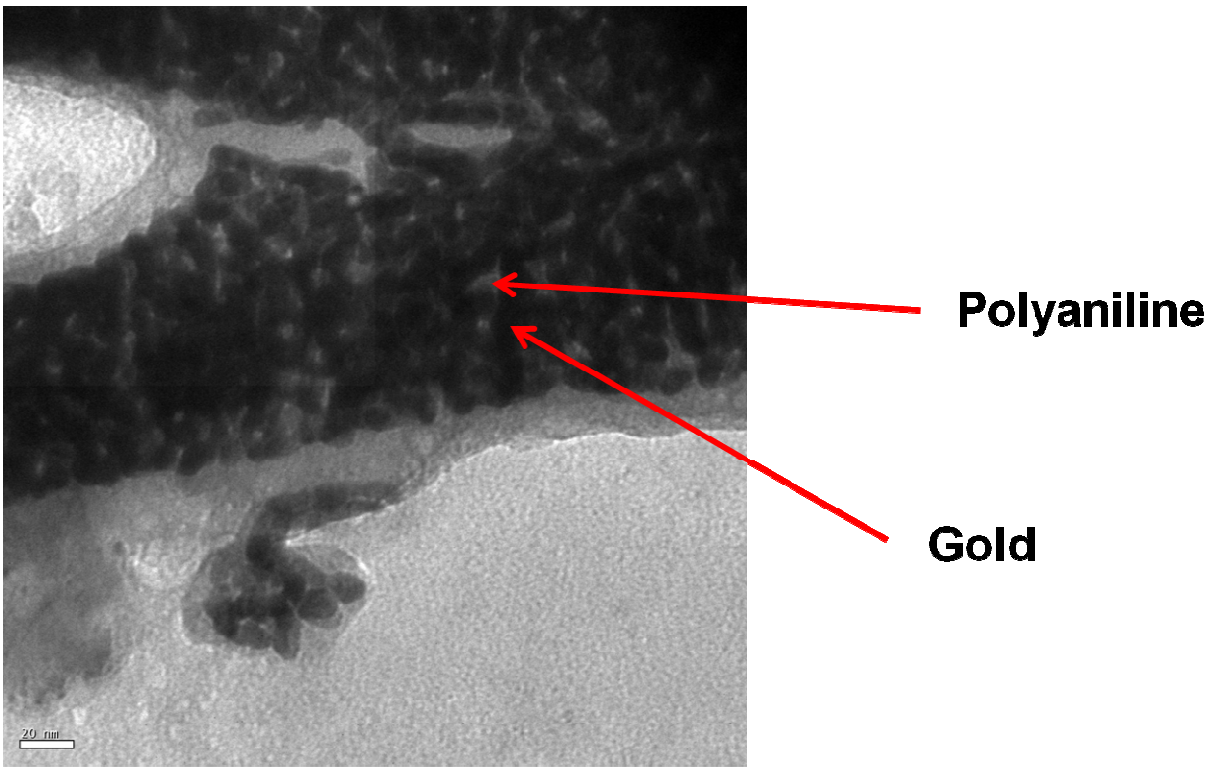

Figure S3: TEM image of PANI coated nanoporous gold nanorod clearly showing the both the gold (darker sections) and PANI (lighter sections) segments within the nanorod. Polyaniline can be seen within the pores of the nanoporous gold nanorod as shown. PANI layer thickness ~20 nm.

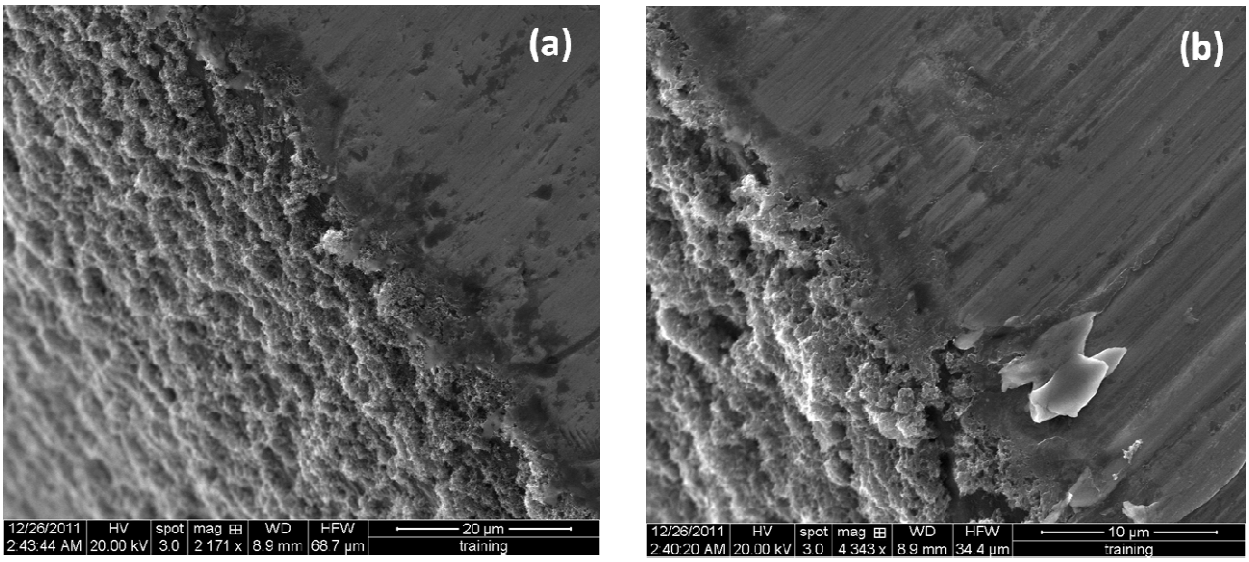

Figure S4: a) Low magnification and b) high magnification cross sectional SEM image of PANI coated on planar substrate showing an average PANI thickness of ~2µm.