Supporting Information

Fabrication and Size Dependent Properties of Porous Silicon Nanotube Arrays

*Xuezhen Huang, Roberto Gonzalez-Rodriguez, Ryan Rich, Zygmunt Gryczynski and Jeffery L. Coffer**

Xuezhen Huang, Roberto Gonzalez-Rodriguez, Jeffery L. Coffer
Department of Chemistry
Texas Christian University, Fort Worth, TX 76129 USA
E-mail: j.coffer@tcu.edu

Ryan Rich, Zygmunt Gryczynski
Department of Physics
Texas Christian University, Fort Worth, TX 76129 USA

Experimental Details

ZnO NWA fabrication. ZnO NWA templates were prepared on FTO glass (1.5 cm x 1.5 cm, TEC-15, MTI Co.) seeded prelimarily in a mixture solution (1:1 v:v) 0.03 M $Zn(NO_3)_2$ and 0.03 M hexamethylenetetramine at 92 ºC for 10-40 h. Polyethylenimine (100 μl, branched, low molecular weight, Aldrich) was added into 100 ml of ZnO growth solution to adjust the ratio of L/D of ZnO NWs when desired. A ZnO seed layer was formed by spin-coating a mixture of 0.01 M zinc acetate (in methanol) and 0.03M NaOH (also in methanol) (4:1 V:V) onto FTO substrates (without heating and stirring), followed by an oxidative treatment in air at 250 ºC for 20 min.

Si NTA Fabrication. A ZnO NWA sample was inserted into a quartz tube reactor and Si depostion on the ZnO NWA was achieved through the use of silane (15 sccm, 0.5% in He) mixed with He carrier gas (150 sccm) that was passed through a furnace operating at 500 ºC for 8 min. These Si-coated ZnO NW samples were then placed in another quartz reactor and heated to 450ºC; NH_4Cl was loaded in an alumina boat located upstream and heated to 350ºC. The gaseous etchant was transported via He gas downstream (100 sccm) to the furnace for 1 hr for removal of the ZnO NWA substrate.

Confocal Microscopy/Spectroscopy. Fluorescence lifetime microscopy and associated imaging measurements were conducted on a Microtime 200 system from PicoQuant, GmbH (Berlin, Germany). Excitation was provided by a 470 nm pulsed laser diode operating at 20 MHz, which was directed into the sample by a 60x 1.2 NA water immersion objective, part of an Olympus IX71 microscope. Scattered light was removed by a 473 and 500 long pass filters, and the light passed through a 30 μm pinhole. The signal was detected by a single photon avalanche diode from Perkin Elmer (SPCM-AQR-14). All data processing was performed by SymPhoTime software, version 5.3.2, also from PicoQuant.

Supporting Figures

Supporting Figure 1. Cross sectional SEM image of a ZnO NWA film achieving 14 μm in length with an average diameter of ~120 nm.

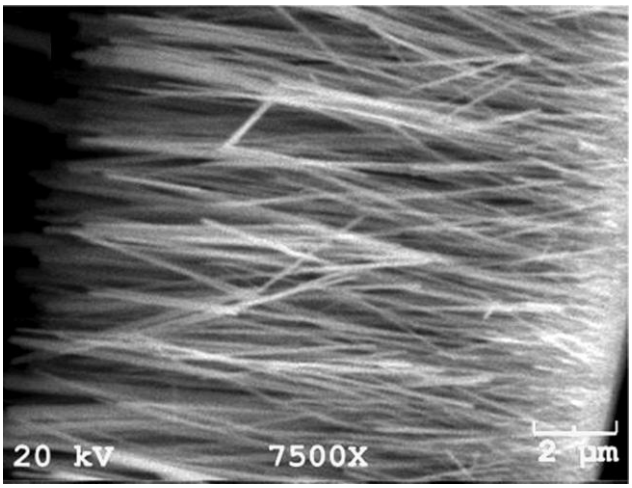
Supporting Figure 2. (a) TEM image of Si NT (top) and Si/ZnO NW (bottom); EDX linescans of (b) Si NT (produced by etching of ZnO core) and (c) Si/ZnO NW.

Supporting Figure 3. TEM image of Si NT sample with relatively thick sidewalls of 70 nm on 100 nm ID hollow structure; scale bar = 50 nm.

Supporting Figure 4. (a) TEM image of densely-packed Si NTA film; NT lengths reach values of 3 μm in such films (scale =200 nm); (b) HREM image of an annealed Si NT.

Supporting Figure 5. (c) Porous Si NTs (after annealing at 600 ºC for 30 min). Inset: HRTEM lattice image of Si NTs. (d) Amorphous Si NTs with large thickness (after annealing at 600 ºC for 30 min). Scale bars are 200 nm and 20 nm for (a) and (b), respectively.

Supporting Figure 6. Dissolution of Si NTs possessing a 10 nm thick shell in phosphate-buffered saline at 37^{o}C as a function of time (in hours).



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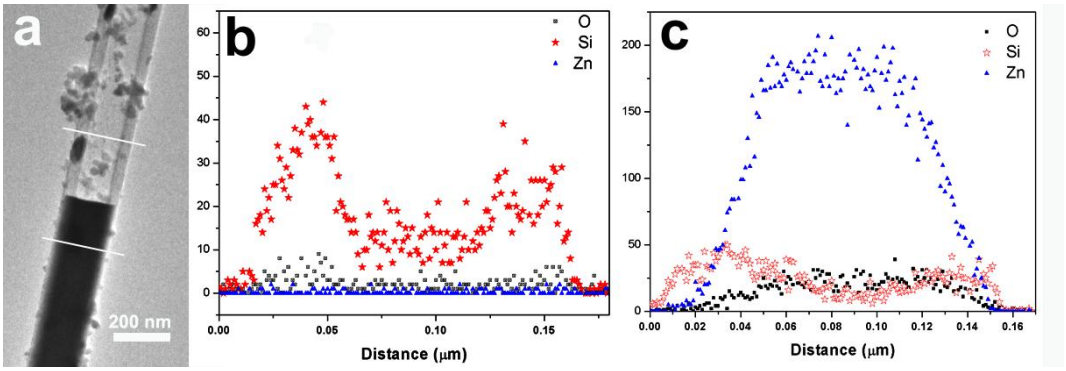
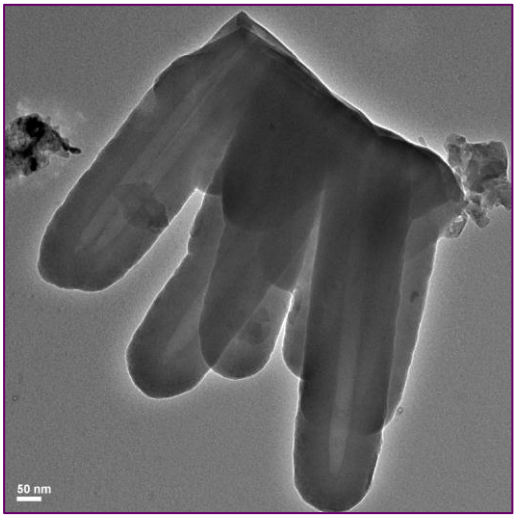
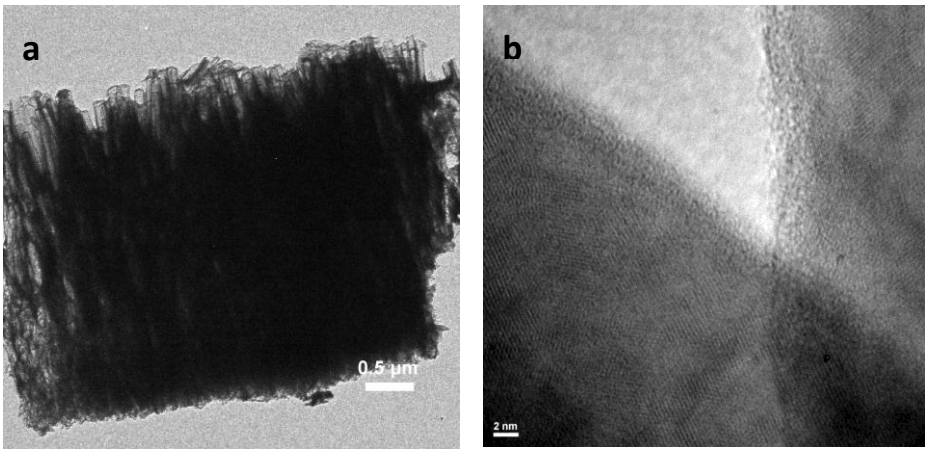


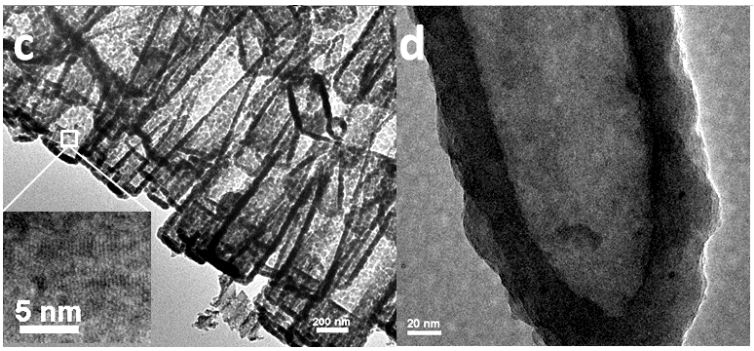
Supporting Figure 2. (a) TEM image of Si NT (top) and Si/ZnO NW (bottom); EDX linescans of (b) Si NT (produced by etching of ZnO core) and (c) Si/ZnO NW.



Supporting Figure 3. TEM image of Si NT sample with relatively thick sidewalls of 70 nm on 100 nm ID hollow structure; scale bar = 50 nm.



Supporting Figure 4. (a) TEM image of densely-packed Si NTA film; NT lengths reach values of 3 µm in such films (scale =200 nm); (b) HREM image of an annealed Si NT showing lattice spacings associated with the <111> orientation (inset: corresponding FFT image); scale bar = 2 nm



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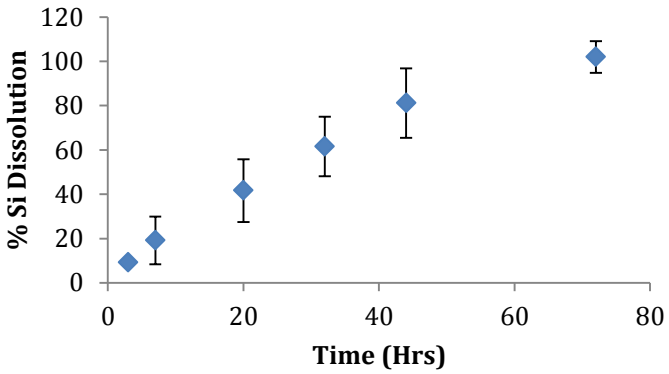

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