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High-Performance Lithium-ion Battery Anode Based on Core-Shell Heterostructure of Silicon-Coated Vertically Aligned Carbon Nanofibers

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Method of Mass Calculation:

Mass of Si shell: The mass of the Si shell was directly measured by two independent methods. **First**, in situ quartz crystal microbalance (QCM) was used to measure the Si mass during Si deposition with magnetron sputtering and to control the
10 desired deposition thickness. Magnetron sputtering is a reliable process that can uniformly deposit Si (and other materials) over a large area of 16" in diameter. Our samples (~17.5 mm dia. Cu disks) and the QCM are placed within this area and should have received the same amount of Si deposition. This is a well-established fabrication technique and a gold standard in controlling the deposition in microelectronics fabrication. It is much more reliable than measuring the Si mass before and after deposition (as what people normally do using slurry casting or chemical vapor deposition, where deposition cannot be
15 precisely measured with in-situ techniques). The only error may be due to the small variation of the tooling factor.

Second, more precise Si mass was determined by examining the thickness of the sputtered silicon on a flat Si(100) wafer which was placed next to the Cu disks. As an example, the SEM image (see Fig. S1) shows the cross-section of a layer of sputtered amorphous silicon with an average thickness of 456 nm on top the Si(100) wafer. This value is close to the reading from QCM (~500 nm). Due to the uniform deposition, the area-specific amount of Si sputtered onto the VACNFs on Cu disks
20 should be the same as in the area next to them. Thus we use the ***nominal thickness*** (i.e. the thickness equivalent to that on a flat Si wafer) to represent the area-specific amount of Si deposition on VACNFs on Cu. The nanostructure only affects how the Si is distributed within an area but does not alter the total quantity in this area. For a Si layer with 456 nm nominal thickness and density of 2.33 g/cm^3, the mass per electrode (~17.5 mm in dia.) can be calculated as:

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$$\text{Si Mass} = (4.56 \times 10^{-5}\text{cm}) * 3.14 * (1.75/2 \text{ cm})^2 * 2.33 \text{ g/cm}^3 = 2.55 \times 10^{-4} \text{ g}$$

The mass-specific capacity is thus:

$$\frac{\text{Current(mA)} \times \text{ChrageTime(h)}}{\text{Si Mass}} = \frac{\text{Current(mA)} \times \text{ChrageTime(h)}}{2.55 \times 10^{-4} \text{ g}}$$

Mass of VACNFs: The mass of carbon in the VACNFs could not be reliably measured by weighing the sample before and after PECVD (due to many factors such as thermal history, oxidation of Cu, moisture adsorption, etc.). There is no reliable
30 in-situ measuring technique (such QCM) as well. Hence it has to be estimated from the average structure observed by TEM and SEM, giving ~2.64×10^{-4} g per sample (or ~1.1x10^{-4} g/cm^2) for a 3 μm long VACNF array, comparable to the mass of Si (at 500 nm nominal thickness). It needs to be noted that this method is quite conservative and likely overestimated the carbon mass. The real carbon mass should be less, not more.
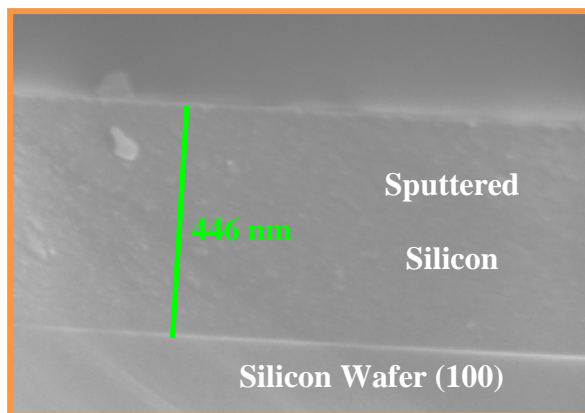
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40 **Figure S1.** A SEM image of the cross section of a Si wafer after sputter-coating ~500 nm Si to confirm the thickness read by in-situ quartz-crystal microbalance (QCM).
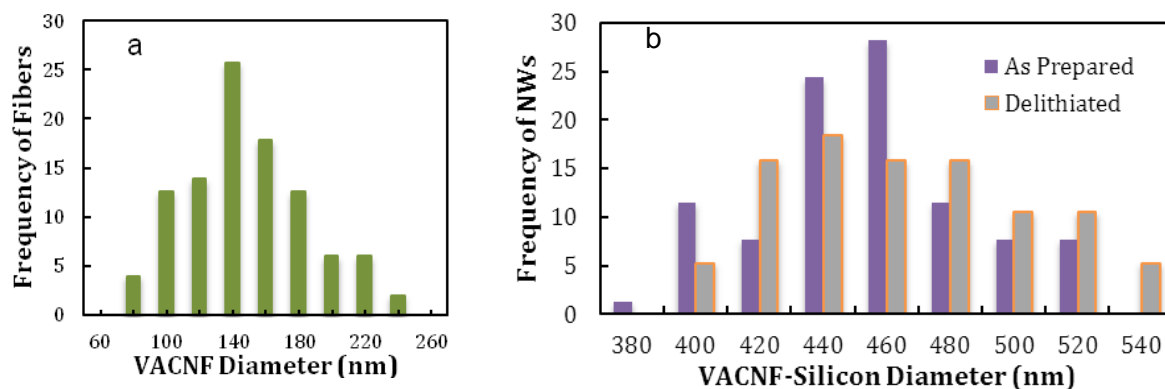
Figure S2. Histograms of the diameter distribution of (a) a 3.0 μm long "as-grown" VACNF array and (b) the similar VACNF array coated with 0.50 μm nominal Si thickness in the " as-prepared" state (purple) and in the delithiated (discharged) state after 100 charge-discharge cycles (grey). The vertical axis is the percentage of appearance within the discrete diameter ranges.
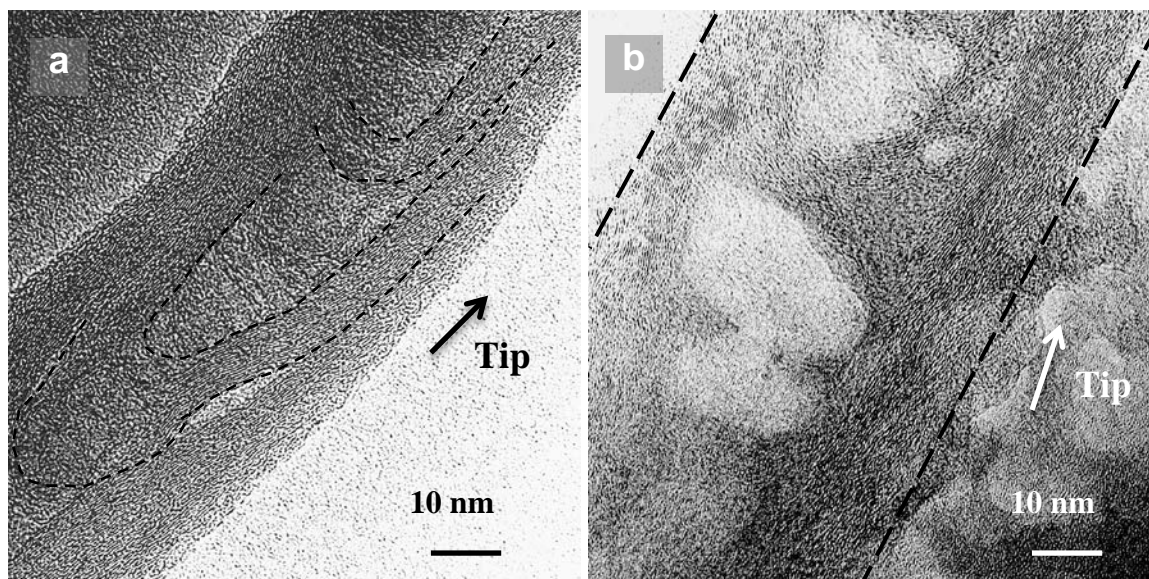

Figure S3. Transmission electron microscopy images of "as-grown" VACNFs before (a) and after (b) lithium intercalation/extraction cycles. The sample in (b) was in the delithiated (discharged) state when it was taken out from the electrochemical cell. The thin dashed lines in panel (a) are visual guidance of the stack of cup-like graphitic layers inside the VACNFs. The arrows in panel (a) and (b) indicate the direction toward the CNF tip. The long dashed lines represent the sidewall surface of the CNF. The CNF in each TEM measurement is a different one. They were randomly picked from the samples through different treatments for representing the physical effects of the processes.
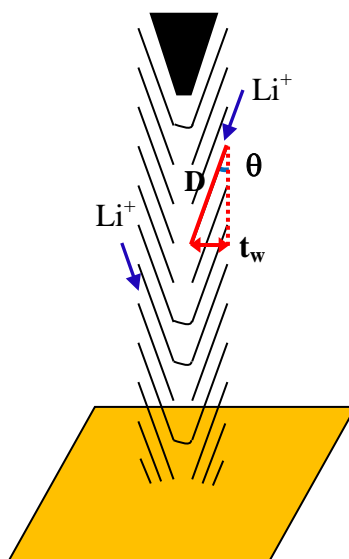
Figure S4. Schematic of the "cup-stacking" graphitic microstructure of the PECVD-grown VACNFs. The average values of the parameters are: CNF radius r_{CNF} = 74 nm, the CNF wall thickness t_w = ~50 nm, graphitic cone angle θ = 10°, and the graphitic cone length $D = t_w/\sin\theta$ = 290 nm.
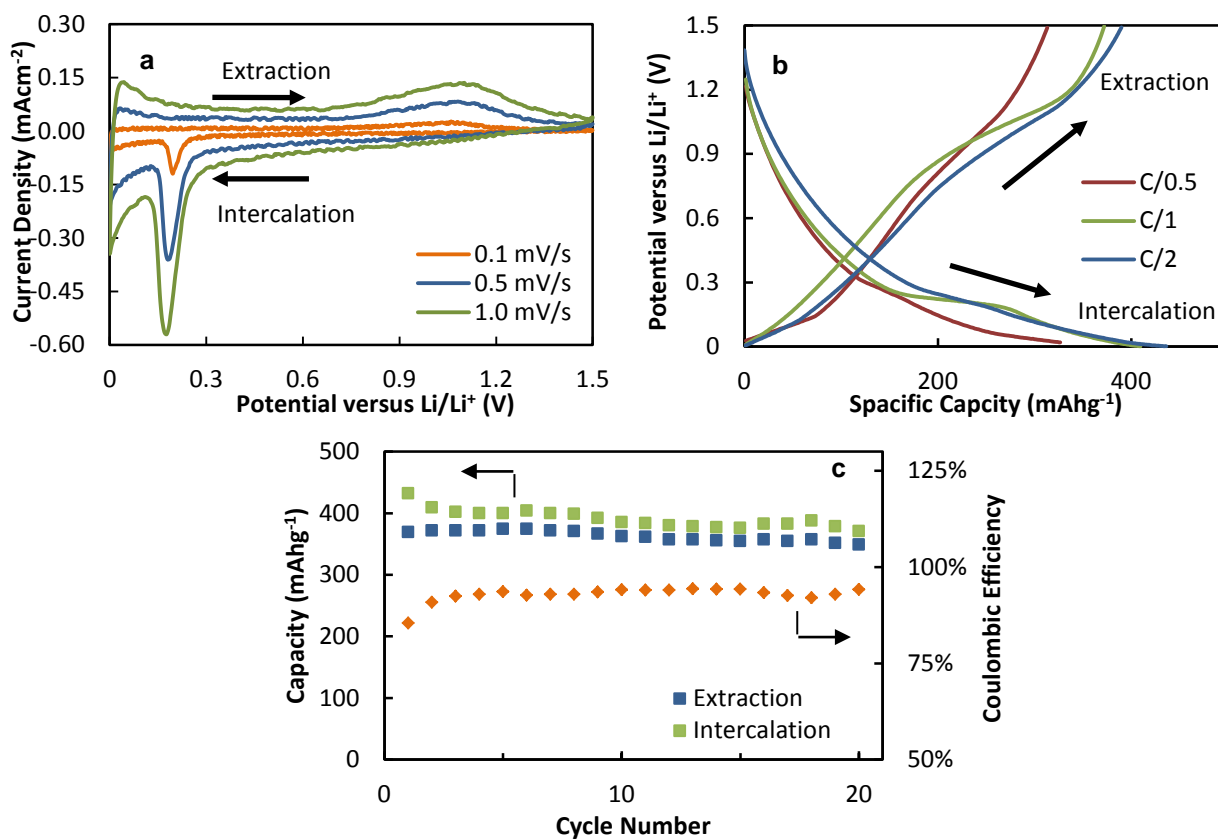

Figure S5. Characterization of lithium intercalation and extraction of "as-grown" 3.0-µm long VACNFs. (a) Cyclic voltammograms from 1.5 V to 0.001 V versus a Li/Li$^+$ reference electrode at 0.1, 0.5 and 1.0 mV/s scan rates. A lithium disk was used as the counter electrode. All data were taken from the second cycle and normalized to the exposed geometric surface area. (b) The galvanostatic charge-discharge profiles at C/0.5, C/1 and C/2 power rates, corresponding to current densities of 647, 323, and 162 mA/g (normalized to estimated carbon mass) or 71.0, 35.5, and 17.8 µA/cm^2 (normalized to the geometric surface area), respectively. (c) Intercalation and extraction capacities (to left vertical axis) and Coulombic efficiency (to right vertical axis) versus the cycle number at C/1 charge-discharge rate.
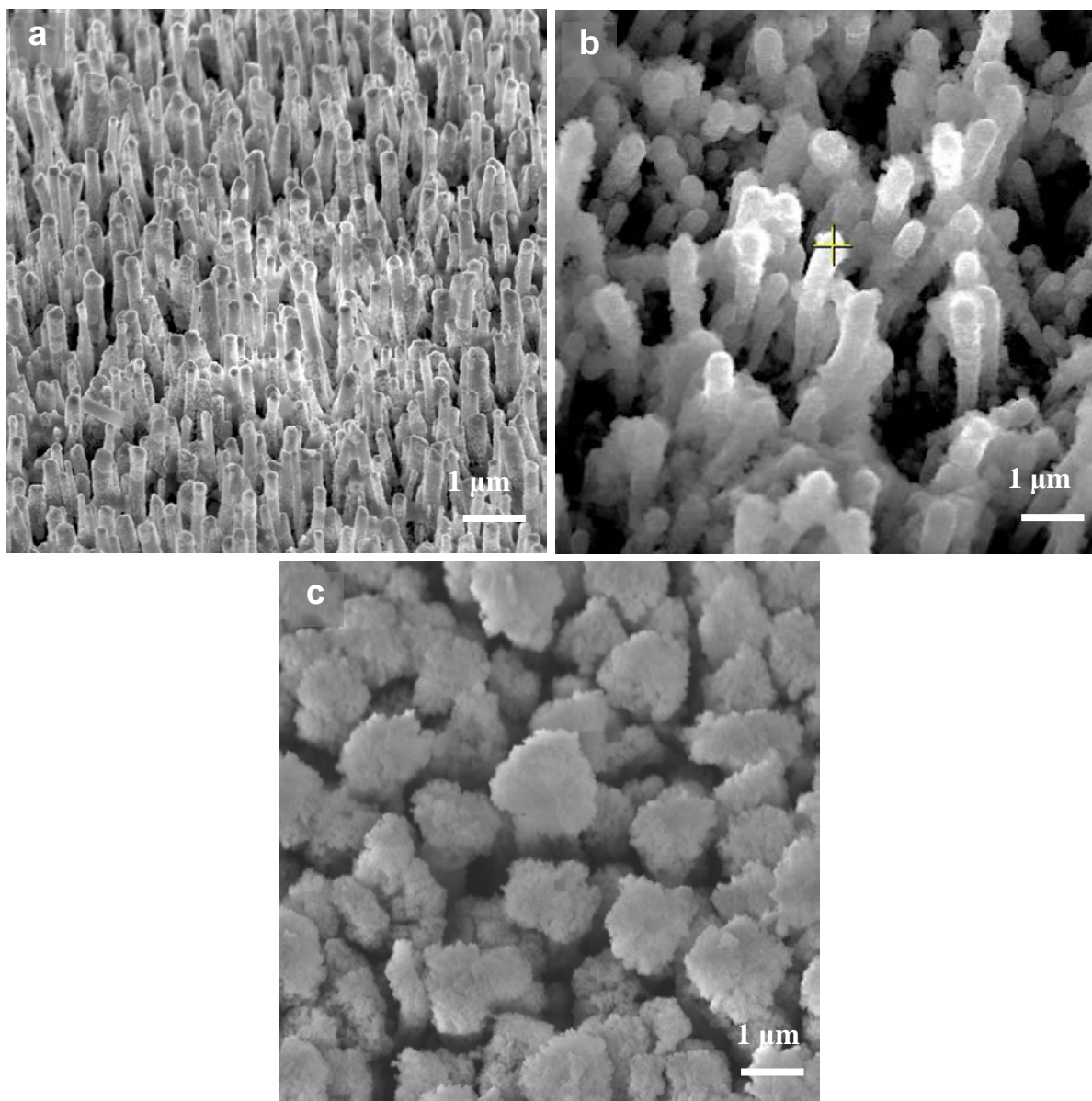
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Figure S6. Scanning electron microscopy images of (a) 3.0 μm long VACNFs in the delithiated (discharged) state after lithium intercalation/extraction cycles; and Si-coated VACNF core-shell nanowire arrays after 100 cycles in the delithiated state (b) and in the lithiated (charged) state (c) when they were taken out from the electrochemical cells. All images are 45° perspective views.

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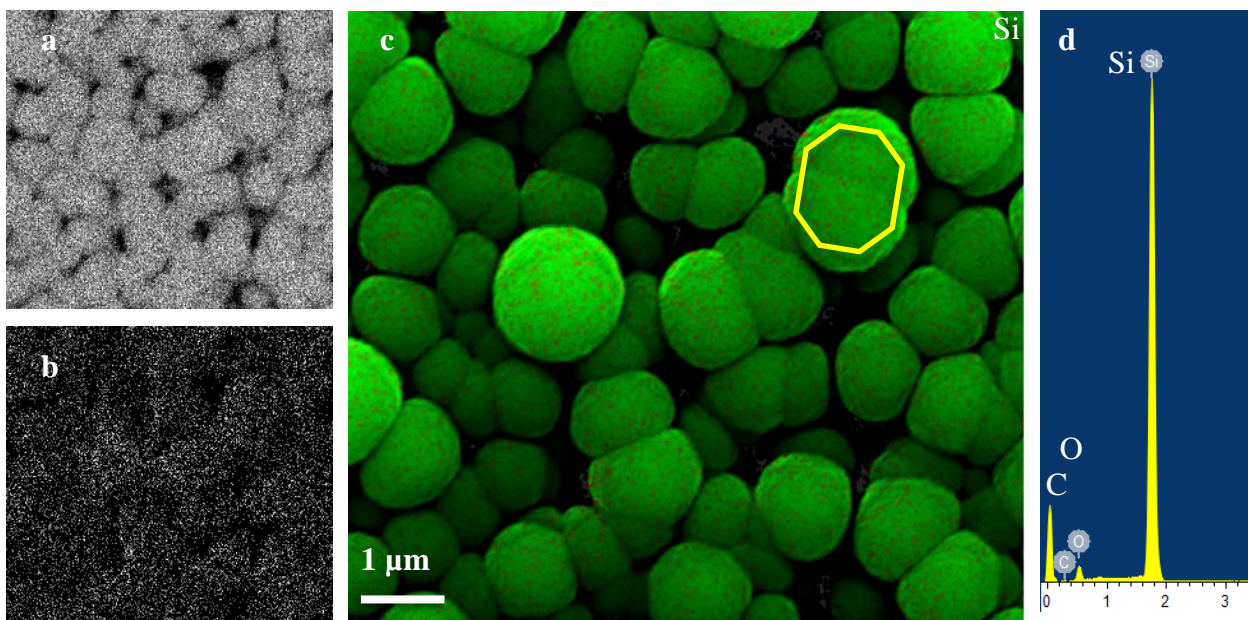
Figure S7. Energy Dispersive X-ray Spectroscopy (EDS) showing composition mapping of (a) silicon, (b) oxygen, and (c) both silicon (green) and oxygen (red), on a 3.0 µm long VACNF array coated with Si of 1.5 µm nominal thickness. The sample was transported and stored in ambient conditions for about one month before the EDS measurements. (d) The EDS spectrum of the area circled by the yellow octagon in (c) indicates the oxygen to silicon atomic ratio of ~0.22:1. Some carbon signal was also observed from the beneath carbon nanofiber core.
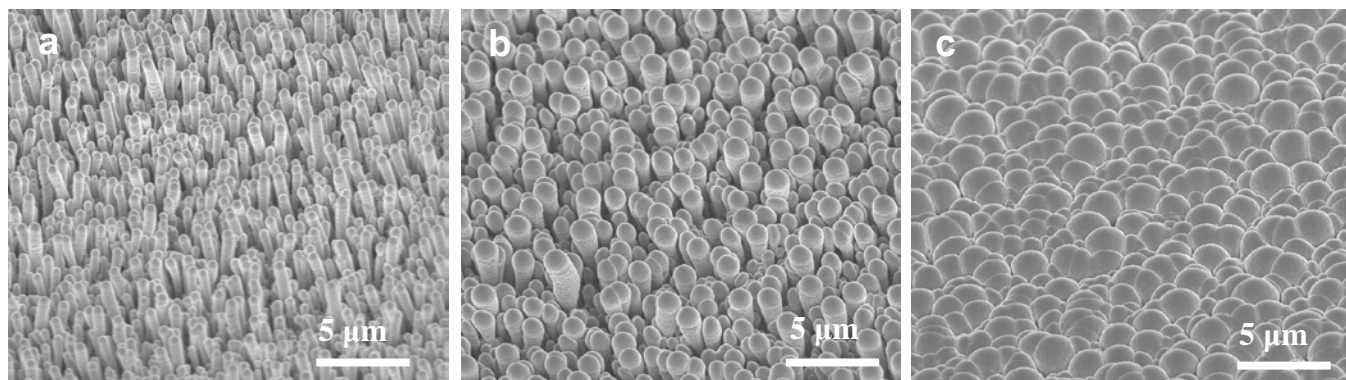
Figure S8. Scanning electron microscopy images of the freshly prepared VACNF-Si core-shell nanowire arrays (on ~10 µm long VACNF arrays). The nominal Si thickness is (a) 0.50 µm, (b) 1.5 µm, and c) 4.0 um, which were measured in-situ using a quartz crystal microbalance during deposition. All images are 45° perspective views.
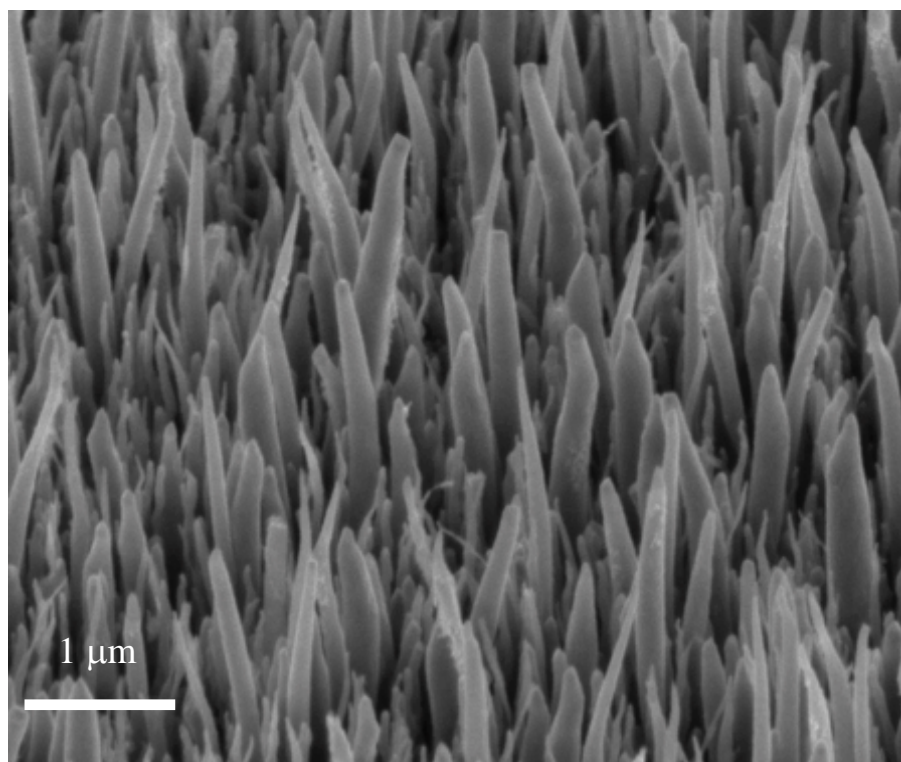
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Figure S9. A scanning electron microscopy image of an "as-grown" 10-µm long VACNF array at the 45° perspective view.