Supporting Information

Chemical Gating of a Synthetic Tube-in-a-Tube Semiconductor

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1. Preparation of Tube$^2$ thin films

Double-walled carbon nanotubes (DWCNTs; Unidym DW411UA) were dispersed in 1% wt/vol sodium cholate and sorted by density gradient ultracentrifugation.$^1$ DWCNT thin films (50 mm diameter) were created using a vacuum filtration method$^2,3$ where 0.4 μg of DWCNTs were filtered over nitrocellulose membranes with 50 nm pore size. DWCNTs were transferred to silicon wafers with 300 nm thermal oxide coating (Silicon Quest International) through application of heat and pressure. Nitrocellulose membranes were dissolved using an acetone vapor bath and the DWCNT film was rinsed copiously with isopropyl alcohol, ethanol, and water, followed by an annealing step at 200 °C in vacuum.

On-chip devices of 15 and 20 μm channel length were patterned using photolithography with Cr/Au contacts of 10 and 75 nm thickness respectively using electron beam deposition. Additional steps of photolithography were used to remove residual DWCNTs between transistor arrays and passivate the electrodes from any reaction.

Devices were characterized for conductance and transport properties using a Keithley 4200 semiconductor characterization system followed by an electrical breakdown step to remove metallic DWCNTs. Outertube selective functionalization was performed using 3-fluoro-4-carboxybenzenediazonium tetrafluoroborate using electrochemical acceleration with a $V_{SD}$ of 1 V for 30-60 minutes. Further verification of the functionalization was accomplished with FT-IR spectroscopy (Figure S1) and further corroborated through Raman scattering (see Figure 2b, in main text).

![IR spectra of a thin film of Tube$^2$](image.png)

**Figure S1.** IR spectra of a thin film of Tube$^2$ with 2-fluorobenzoic acid terminating groups in comparison with its precursor, DWCNT.

Further covalent linking of oligonucleotides to Tube$^2$ was performed by linking amino-modified single stranded DNA sequences using 20 mM 1-ethyl-3-(3-
dimethylaminopropyl)carbodiimide and 20 mM N-hydroxysuccinimide with 1 μM of the oligonucleotide sequence to the carboxylic acid groups attached to the outertube.

2. Electrical response of on-chip Tube^2 films

2.1. pH dependence

It was observed that pH can greatly affect the sensor response of Tube^2 thin film transistors at zero gate voltage. At higher pHs, there was a higher conductance change indicative of higher affinity towards ammonium ions. This effect is resultant on the deprotonation of the carboxylic acid terminal groups and their higher affinity with the ammonium ion moiety due to electrostatic interactions.

![Figure S2. pH sensing dependence of Tube^2 TFTs. Current change as a function of ammonium ion concentration at different pHs. The data was obtained through single point measurements (not ISD-Vg sweep) only at V_g = 0 V (without applying a gate voltage) and V_SD = -1 V.](image-url)
2.2. Nonspecific Interferents

Transport characteristics of Tube^2 with carboxylic acid terminating groups were characterized in a thin film transistor configuration before and after the addition of 10 μM of ammonium ions and 10 μM of sodium dodecyl sulfate (SDS), a well-known surfactant for carbon nanotubes. At a neutral pH of 7, in which SDS should be nearly completely deprotonated, addition of SDS generates minimal change in the transport properties indicative of minimal to no interaction between SDS and Tube^2, whereas the ammonium ion generates changes in the transport properties. We hypothesize this effect to be a result of electrostatic repulsion between the deprotonated carboxylic acid groups that are attached to the Tube^2 surface and SDS.

Figure S3. Transport curves of Tube^2 TFTs to specific and nonspecific binding. Current versus gate voltage for a p-type Tube^2 TFT when exposed to target (ammonium, black) and interferent (sodium dodecyl sulfate, red).
2.3. Oligonucleotide base length

The signal response, measured in threshold voltage shift, as an effect of oligonucleotide base length of the probe and target sequence were evaluated for Tube\textsuperscript{2} sensors. Shorter probe and target sequences (10 and 23 bases) resulted in lower overall threshold voltage shifts at the same concentration and a lower analytical sensitivity compared with longer sequences.

Even at ionic strengths of 10 mM, 23-base oligonucleotide sequences show higher response compared with 10-base sequences, indicating that Debye screening is not a dominant factor for detection of oligonucleotide as long as 23 bases. This feature is likely due to a major advantage of Tube\textsuperscript{2} where the separation between circuit and receptor layer is fundamentally small.

![Figure S4. Base pair dependence. Threshold voltage shifts in response to oligonucleotide concentration for ssDNA modified Tube\textsuperscript{2} TFTs.](image-url)
2.4. IS6110 Detection

Tube\(^2\) point sensors (see the main text) showed a similar level of signal response and current change as photolithography patterned Tube\(^2\) sensors (Figure S5). Evaluation of the transport properties of Tube\(^2\) thin films confirms that electrostatic gating remains the primarily sensing mechanism for the detection of IS6110 with a detection limit of 15 nM that is only 3 times lower in detection limit than with the self-assembled point sensors.

**Figure S5.** Detection of IS6110 tuberculosis biomarker with Tube\(^2\) TFT at zero gate voltage. (a) Transport properties of a Tube\(^2\) TFT with 15 base oligonucleotide probe before and after addition of 15 nM (red), 30 nM (green), and 100 nM (yellow) IS6110. (b) Current values as a function of IS6110 concentration. Note that data in (b) were obtained through single point measurements (not Isd-Vg sweep) only at V\(_g\) = 0 V (without applying a gate voltage) and V\(_sd\) = -0.1 V.
3. Tube$^2$ point sensors

3.1. Protocol

Tube$^2$ point sensors were fabricated by directly dicing a metal-silicon-metal wafer into 3.5 x 0.5 mm$^2$ pieces (Figure S6). The metal (10 nm Cr, which serves as an adhesion layer, and 150 nm Au) was deposited using electron beam deposition on both sides of a 20 µm thick, undoped silicon wafer (Virginia Semiconductor Inc.). The two metal layers serve as the source and drain electrodes. The nanostructure network is self-assembled from an aqueous suspension on the freshly cleaved surface to bridge the two electrodes. The channel length of this two-terminal device is defined by the thickness of the silicon wafer. After self-assembly, residual surfactant are removed as mentioned in the Experiment Section.

Figure S6. A lithography-free approach to the fabrication of Tube$^2$ field effect point sensor by a straightforward dice-and-dip procedure.
3.2. 23-base oligonucleotide detection

Sensitivity curve of the Tube\(^2\) point sensor in response to the 23-base oligonucleotide remain linear down to 50 nM and is capable of signal response above noise levels at 30 nM, which is a rather small drop in sensitivity compared with the photolithography patterned devices.

![Figure S7](image)

**Figure S7.** Sensitivity curve of 23-base oligonucleotide-modified Tube\(^2\) point sensors to various cDNA concentrations.

4. References

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