SUPPORTING INFORMATION FOR

Detection beyond the Debye screening length in a high frequency nanoelectronic biosensor

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SWNT FET mixing current

The current-voltage characteristics for SWNT FET is modeled similar to conventional Si FETs and represented as[1]

$$I_{sd} = \frac{\mu C_g'}{L}(V_g + \frac{V_{sd}}{2})V_{sd} \qquad \text{(S1)}$$

, where μ is the hole mobility, C_g' is the gate capacitance per unit length, L is the nanotube length, V_g is the gate voltage, and V_{sd} is the drain-source voltage. Amplitude modulated (AM) small signal is applied at the source,

$$V_{sd} = v_{ac}(1 + m\cos\omega_m t)\cos\omega_c t = v_{ac}(\cos\omega_c t + \frac{m}{2}\cos(\omega_c - \omega_m)t + \frac{m}{2}\cos(\omega_c + \omega_m)t \qquad \text{(S2)}$$

, where v_{ac} is the small signal AC driving voltage (20 mV from Agilent 8648B), *m = 0.78* is the modulation depth, ω_m is the modulation frequency (1.43 kHz), and ω_c the carrier frequency. We monitor the output response using a lock-in amplifier (Stanford Research SR830) which measures AC current at the modulated frequency. Using equations (S2) in (S1), and

trigonometric relations, we find that the nonlinear I_{sd}-V_g relation of the transistor in equation (S1) mixes the ω_c and $\omega_c \pm \omega_m$ terms in equation (S2) to yield a mixing current term,

$$I_{mix}^{\omega_m} = \frac{1}{4}\frac{\mu C_g^{'}}{L} m v_{ac}^2 .$$

From equation (S1) we can also derive[1] $\frac{\mu C_g^{'}}{L} = -\frac{\partial G}{\partial V_g}$, where G is the conductance of the device. Therefore,

$$I_{mix}^{\omega_m} = -\frac{1}{4}\frac{\partial G}{\partial V_g} m v_{ac}^2 \qquad \text{(S3)}$$

To evaluate the mixing current measurement scheme for solution-based sensing, we characterize pristine SWNT FET device in 100 mM NaCl solution. Figure S1 shows I_{mix} measured as a function of V_g for a typical device (red). Theoretical mixing current (▲, solid triangle) is also calculated using the measured DC transfer curve of nanotube FET (black). To the first order, the measured I_{mix} agrees well with the theory.

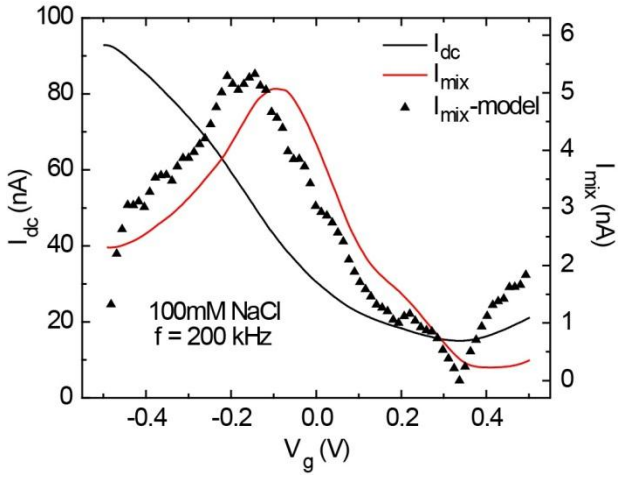

Figure S1. Mixing current of pristine SWNT FET in 100mM NaCl solution. DC current, I_{dc} (black, V_{sd} = 10 mV) and mixing current, I_{mix} (red, modulation f = 200 kHz) as a function of V_g for the device in 100 mM NaCl solution. Theoretical I_{mix} obtained using the model in equation S3 is also shown (▲) for comparison.

SWNT sidewall functionalization

The SWNT devices were incubated in 6 mM 1-Pyrenebutanoic Acid, succinimidyl ester- PBSE (Molecular Probes, Inc., USA) in DMF for 1 hr at room temperature. The devices were then left in 20 mg/ml solution of Biotin-PEO Amine (Pierce Chemicals, USA) for 18 hr at room temperature so that the Biotin-PEO Amine attaches to PBSE through nucleophilic substitution of the amines. The devices were exposed to 1mg/ml streptavidin (Invitrogen, USA) in 7.2 pH PBS buffer solution to achieve the final streptavidin-biotin binding. After each step the die was thoroughly rinsed to remove any residual molecules.

To evaluate the nanotube sidewall functionalization, we monitor the FET transfer curves **in air** after each functionalization step (Fig. S2a). We observed that the transfer curve shift to the right after biotinylation (red) and streptavidin binding (blue). This can be attributed to the electrostatic gating by the electronegative amine groups present on biotin PEO-amine and streptavidin. The transfer curve shift is consistently observed among 10 devices, showing successful sidewall functionalization. A histogram of these devices is shown in Figure S2b for change in surface charge density after streptavidin binds to biotin. The device studied in Fig S2a is marked in Fig S2b (*).

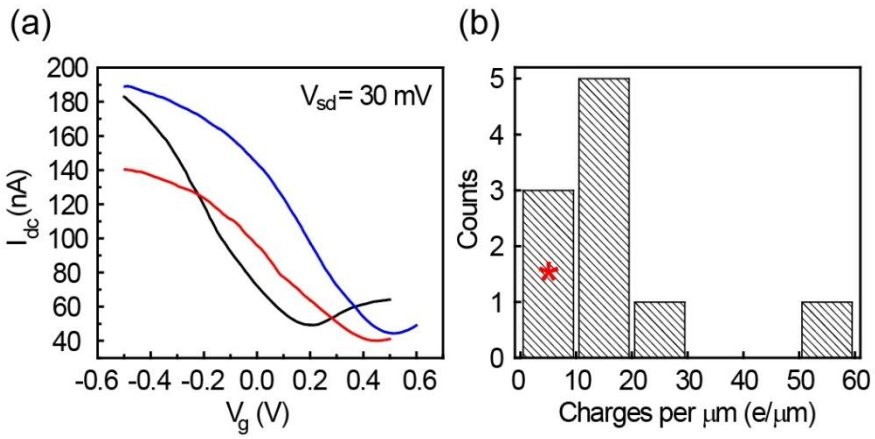

Figure S2. Threshold voltage shift of SWNT FET confirms successful nanotube sidewall functionalization. (a), I_{dc}-V_g curve for pristine nanotube FET (black), after biotinylation (red) and after streptavidin binding (blue). Measurements are done in air. (b), Histogram of 10 devices for surface charge density induced after streptavidin binds to biotin.

From the shift in the Dirac point voltage (voltage with minimum conductance) we can roughly estimate the changes in 1D surface charge density of the nanotube after streptavidin binds to biotin. Using a wire on infinite plane model for the suspended gate, capacitance per unit length is $C' = \frac{2\pi\varepsilon_0}{\cosh^{-1}(\frac{d}{r})}$, d is the distance of suspended gate electrode from the nanotube (500nm) and r is the radius of nanotube (~1nm). Therefore, the 1D charge density of nanotube can be estimated from the capacitance and the voltage shift, $Q' = C' \times \Delta V$. For this device, we obtain a Q' ~ -3 e / μm. Measurements from 10 devices reveal that protein binding induces a surface charge density on the order of 10s of e / μm.

Control experiment on a fully passivated device

Figure S3 shows the mixing current signal change before and after streptavidin binding step on a fully passivated device. Here, the SWNT and the metal electrodes are passivated by SiO_2. We can clearly see that there is no significant change between the two steps even in DI water. For an unpassivated device as in Fig 2b of main text, we should see significant signal change in DI water where the Debye screening length is also large.

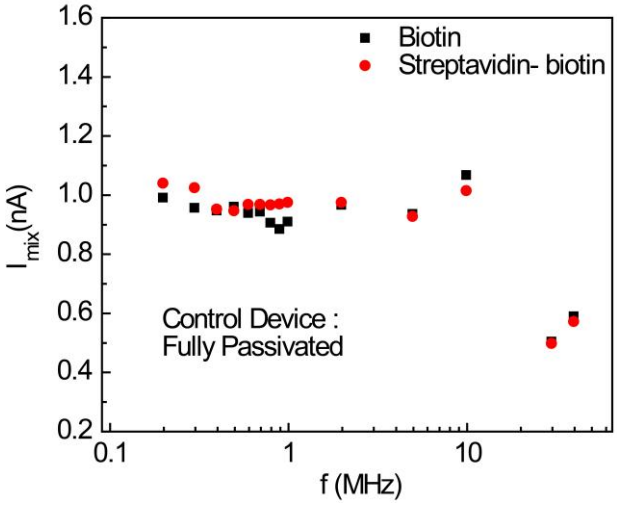

Figure S3. Mixing current signal before (■) and after (●) streptavidin binding on a control device with passivated SWNT channel and metal electrodes in DI water.

Gate potential due to 1D array of dipoles

We consider a 1D array of dipoles at distance of *h* nm above the nanotube as shown in Figure S4. For simplicity, we assume all dipoles point up in the unperturbed state.

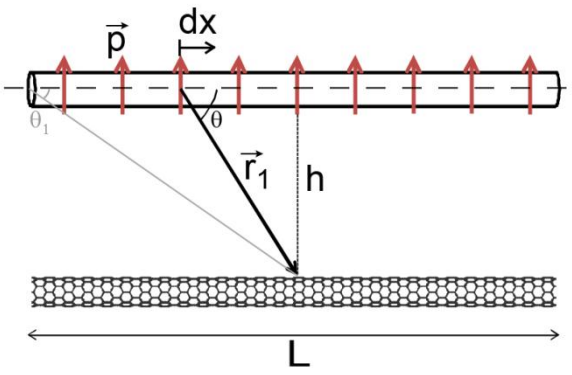

Figure S4. Modeling the mixing current using 1D array of molecular dipoles. 1D array of biomolecular dipoles located *h* nm above a nanotube of length *L*.

Let *n* be the 1D dipole density per unit length, then the potential due to the dipole element *dx* can be written as

$$d\phi = \frac{n\hat{r_1} \cdot \vec{p}dx}{4\pi\varepsilon \cdot h} = -\frac{np\sin\theta \cdot dx}{4\pi\varepsilon \cdot r_1^{\,2}} \ .$$

Using $dx\cos\theta = dr_1$; $\sin\theta = \frac{h}{r_1}$ and therefore $\cos\theta d\theta = -\frac{hdr_1}{r_1^{\,2}}$, we have

$$d\phi = \frac{np\sin\theta d\theta}{4\pi\varepsilon \cdot h}. \qquad \text{(S4)}$$

To obtain the surface potential induced by the 1D dipole array, we can integrate equation S4 over the length of the nanotube,

$$\phi = \int_{\theta_1}^{\pi-\theta_1} \frac{np\sin\theta d\theta}{4\pi\varepsilon \cdot h} = \frac{2np\cos\theta_1}{4\pi\varepsilon \cdot h} = \frac{2np}{4\pi\varepsilon \cdot h} \cdot \frac{L/2}{\sqrt{\left(L/2\right)^2 + h^2}} .$$

Since, L/2 (μm) >> h (nm), we have $\phi = \frac{2np}{4\pi\varepsilon \cdot h}$

Mixing Current Due to 1D Array of Dipoles

A potential δV_{sd} at the source affects the nanotube charge distribution in the same way as a potential δV_g (but with opposite sign) of same magnitude applied to the gate[1]. Therefore, the oscillatory signal applied at the source also acts as a signal across the gate. This sinusoidal potential at source can drive the biomolecular dipoles located above the nanotube when we increase the probing frequencies because the double layer weakens. The fluctuating dipoles now act as local gating potential. We assume that the molecular dipoles are flipping at the same frequency as the driving AC voltage, ω_c.

The dipoles in the target biomolecules, even though driven by source voltage, experience a force which is frequency dependent[2]. When the ionic strength of the solution is high, e.g. 100 mM NaCl (λ_D~1 nm), we can assume that the biomolecules are within the bulk solution and experience the bulk electric driving force. The bulk field can be related to the actual source voltage through an attenuation and phase factor, γ and θ respectively[2].

From here, we can estimate the local gating potential of the dipole array to be,

$$\Delta V_g = \gamma\phi\cos(\omega_c t + \theta)$$

γ (always ≤ 1) represents the strength of the dielectric screening and θ represents the phase lag in the dipole response and dependent of bulk liquid parameters. The theoretical model in ref 2 for phase lag and attenuation treats a case of bulk liquid between two parallel plate electrodes. Assuming that the bulk liquid in our case is formed by the top gate electrode and the nanotube (separation d = 500nm), attenuation and phase factor can be accounted for, to a decent approximation, by the same equations derived for two parallel plate electrodes,

$$\gamma = \frac{\Omega}{\sqrt{\Omega^2 + 4}},$$

$$\theta = \tan^{-1}\frac{2}{\Omega},$$

where $\Omega = \frac{\omega d}{D\kappa}$. ω is the applied carrier frequency, d is the separation between top gate electrode and nanotube (500nm), D is the ion diffusion coefficient (of the same order ~10^{-9} m^2 s^{-1} for Na^+ and Cl^-, from CRC handbook) and κ is the inverse Debye length. Clearly, if we go to very high frequencies, we have γ =1 and θ=0°.

From equation S1, we observe that the frequency dependent dipole gate voltage also induces a mixing current component,

$$I_{sd} = \frac{\mu C_g^{'}}{L}\Delta V_g V_{sd}$$

$$I_{sd} = \frac{\mu C_g^{'}}{L}\Delta V_g v_{ac}[\cos\omega_c t + \frac{m}{2}\cos(\omega_c - \omega_m)t + \frac{m}{2}\cos(\omega_c + \omega_m)t]$$

$$= \frac{\mu C_g^{'}}{L}\gamma\phi\cos(\omega_c t + \theta)\cdot v_{ac}[\cos\omega_c t + \frac{m}{2}\cos(\omega_c - \omega_m)t + \frac{m}{2}\cos(\omega_c + \omega_m)t]$$

Now, a similar analysis to find mixing current by lock-in at ω_m yields

$$I_{mix}^{\omega_m} = \gamma\frac{m}{2}\frac{\mu C_g^{'}}{L}v_{ac}\phi\cos\theta \qquad \text{(S5)}$$

Here, the capacitance per unit length $C_g^{'}$ is between the 1D array of dipoles and the carbon nanotube. The capacitance between two cylinders of radius *a* and *b* which are separated by

distance *h*, is $C_g^{'} = \frac{2\pi\varepsilon}{\log(x + \sqrt{x^2 - 1})}$ where $x = abs(\frac{D^2 - a^2 - b^2}{2ab})$ and $D = h + a + b$.

Here, $a=r$ (nanotube radius) and is 1 nm; b (streptavidin radius) is 2.5 nm and h is 5 nm. For the model, we assume a nanotube mobility μ = 1 $m^2V^{-1}s^{-1}$, which is acceptable for a good SWNT device.

References

1 Rosenblatt, S. *Pushing the limits of carbon nanotube transistor* Thesis, PhD thesis, Cornell University, (2006).

2 Kang, K. & Dhont, J. K. G. Electric-field induced transitions in suspensions of charged colloidal rods. *Soft Matter* **6**, 273-286, doi:10.1039/b910046f (2010).