

## Electrical Detection of *Hepatitis C* Virus RNA on Single Wall Carbon Nanotube-Field Effect Transistors

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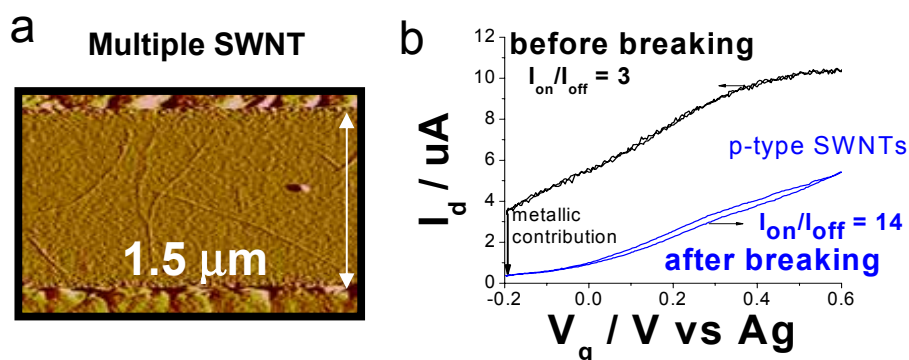
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### Electronic Supplementary Information:

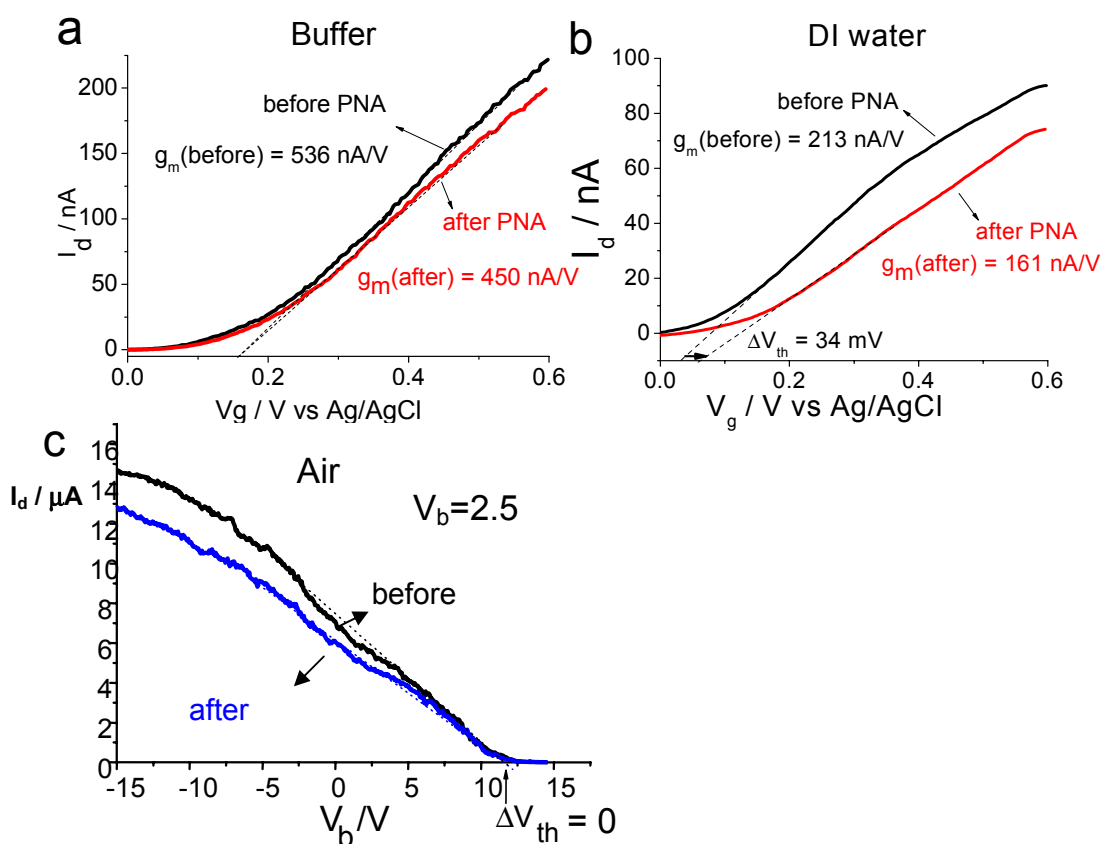
**Fabrication of SWNT devices.** The SWNT-FET devices used here were fabricated using a chemical vapor deposition (CVD) technique catalyzed by a thin Al/Ni stack. The catalysts were deposited on a heavily doped Si wafer with a 200 nm oxide layer. An array of gold electrodes (~ 300 nm thick) separated by  $\mu$ m-sized gaps and aligned to overlap the catalyst pads was thermally evaporated. The devices were annealed (~600 °C) in a hydrogen-rich environment to ensure better contact between the nanotubes and the metallic electrodes. The catalyst island density and pattern controlled the density of carbon nanotubes grown. Higher density of catalyst seeds allowed multiple SWNTs to be obtained in a single gap (Fig. 1a). We used low and high density SWNT devices. Low density SWNT devices consisted of few (1 to 4) SWNTs between a pair of gold electrodes (1-2  $\mu$ m gap, 2- $\mu$ m width, 250-nm thick) while high density devices comprised multiple SWNTs bridging interdigitated electrodes (finger width: 1.5  $\mu$ m) with gap from 1 to 10  $\mu$ m.

**Electrochemical breaking down of metallic tubes.** Before starting the SWNT modification, we characterized each device by measuring the  $I_d$ - $V_g$  properties at various gate voltages applied to the back of the chips. The characterization showed pure p-type semiconducting, pure metallic and mixed p-type/metallic devices. Devices with pure p-type features were used in our experiments. In the case of mixed p-type/metallic devices we broke down the metallic tubes as many as possible to get pure p-type semiconducting devices. Many approaches has been used for breaking down carbon nanotubes.<sup>1,2</sup> We used over-oxidation potentials to destroy the metallic tubes while p-type behavior tubes are turned off through the gate potential. Carbon nanotubes have strong carbon-carbon bonds able to withstand very high current densities, exceeding  $10^9$  A/cm<sup>2</sup>.<sup>1,2</sup> However, at high enough currents, nanotubes ultimately fail due to the rapid oxidation of the carbon shell. Our approach used a combination of fixed electrochemical gate potential ( $V_g$ ) and a variable bias potential ( $V_b$ ). Electrochemical gate potential was fixed to -0.2 V vs Ag/AgCl at WE1 to turn off the p-type tubes of our devices. High potential was then applied at WE2. A  $V_b$  swept from 0.5 to 1.5V in phosphate buffer solution (PBS) with pH > 7 was applied to induce carbon oxidation. Fig. 1b shows the  $I_d$ - $V_g$  curves before and after the breakdown. Before and after breakdown, the  $I_{on}/I_{off}$  ratio value was ~3 and ~14, respectively. In general,  $I_{on}/I_{off}$  values resulting from breaking down were variable and depended on the gap size between gold electrodes. Better  $I_{on}/I_{off}$  ratio was found on devices with larger gap size.



**Fig. 1.** (a) AFM images of devices with high density of SWNTs between interdigitated electrodes. (b)  $I_d$ - $V_g$  curves obtained on a multiple SWNT device in PBS pH = 7.4 before and after electrochemical breaking down of metallic tubes.  $V_b = -10$  mV.

**Conductance behavior of PNA-modified SWNT devices.** Fig. 2a-b show the  $I_d$ - $V_g$  curves before and after PNA adsorption on bare SWNT-FET device in buffer and DI, respectively. The curves marked as “before” shows the p-type behavior of bare SWNT devices. According to IUPAC electrochemical sign convention, p-type behavior of the SWNT devices was defined by increasing drain current values with increasing electrochemical gate positive potentials values. So, for the convention used in this communication, more positive  $V_g$  values increase the concentration of positively charged holes (p-type carriers). As it is stated in the communication, incubation of the device with PNA capture probe on the device resulted, with equal probability, either in a decrease in the transconductance,  $g_m = (\partial I_d / \partial V_g)|_{V_b = -10 \text{ mV}}$ , or in a decrease of  $g_m$  associated with a small positive shift in threshold potential ( $V_{th}$ ) (Fig. 2a-b). Since p-type conductance features obtained in water were similar to those found in buffer it is likely that impurities (in water or from the chip) as well as dissolution of  $\text{CO}_2$  from air, which renders an equilibrium pH  $\sim 5.5$ , were responsible for ionic conduction and provided enough ionic strength in solution to allow electrochemical gate control. A possible source of the decrease of  $g_m$  could be a change of the capacitance due to the PNA adsorption on SWNT wall, SWNT/Au contacts or on gold electrodes. To rule out the last two possibilities, which would preclude the use of a SWNT-FET for channel conductance sensing applications, we performed backgate conductance measurements ( $I_d$ - $V_{bg}$  curves) in air on contact passivated devices where the applied gate voltage is not affected by the area of the electrodes (Fig. 2c). We found that the  $I_d$ - $V_{bg}$  curves obtained after PNA adsorption showed similar changes to those observed in the  $I_d$ - $V_g$  (electrochemical gate potential) curves, suggesting a  $g_m$  change induced by PNA adsorption on SWNT walls.



**Fig. 2.** p-type branches of  $I_d$  vs electrochemical ( $V_g$ ) and backgate ( $V_{bg}$ ) potential before and after PNA adsorption on SWNT-FET device in: buffer (a), DI water (b), air (c). (a and c)  $g_m$  decrease after PNA adsorption without changing threshold voltage ( $V_{th}$ ). (b) Both  $V_{th}$  and  $g_m$  change after PNA adsorption. Forward and backward currents were averaged.

**Estimation of PNA surface coverage on SWNT devices.** We explored the possibility of estimating PNA surface coverage ( $\theta_{PNA}$ ) by assuming capacitance changes due to PNA adsorption taken place only on SWNT walls. To simplify, we considered only those cases with pure  $g_m$  changes. Under these conditions and far from saturation  $I_d$ , the electrochemically-gated transconductance for bare ( $g_m(\text{bare})$ ) and PNA-modified ( $g_m(\text{PNA})$ ) SWNT can be expressed as:<sup>3</sup>

$$g_m(\text{bare}) = \mu C_g' V_d / L \quad (1)$$

$$g_m(\text{PNA}) = \mu C_g'(\text{PNA}) V_d / L \quad (2)$$

where  $\mu$  is the mobility of SWNT,  $V_d$  is source-drain voltage,  $L$  is the length of SWNT,  $C_g'$  is the capacitance of a bare SWNT determined by quantum capacitance ( $C_q$ ) and liquid gate capacitance ( $C_{lg}$ ) in series:<sup>4</sup>

$$1/C_g' = 1/C_q + 1/C_{lg} \quad (3)$$

and  $C_g'(\text{PNA})$  is the capacitance after PNA adsorption with contributions from  $C_q$  in series with two capacitors  $C_{lg}$  and PNA capacitance ( $C_{PNA}$ ) in parallel according to:

$$1/C_g'(\text{PNA}) = 1/C_q + 1/[\theta_{PNA} C_{PNA} + (1-\theta_{PNA}) C_{lg}] \quad (4)$$

The values of each capacitance component were estimated as follows:

-  $C_{lg}$  from  $\epsilon_0 \kappa A_{SWNT} / \lambda_D$  where  $\epsilon_0$  is permittivity of free space,  $\kappa$  is the dielectric constant of the liquid (80 for buffer),  $A_{SWNT}$  is the area of the SWNT ( $2 \pi r L$ ,  $L = 1$  or  $1.5 \mu\text{m}$  and  $r = 1$  nm) and  $\lambda_D$  is the Debye length (2.6 nm for buffer solution of ionic strength of 14 mM). The resulting value is  $1.7 \times 10^{-9} \text{ F}/(\text{m} \times \text{tube})$ .

-  $C_q$  from literature data  $4 \times 10^{-10} \text{ F}/(\text{m} \times \text{tube})$ .<sup>5</sup>

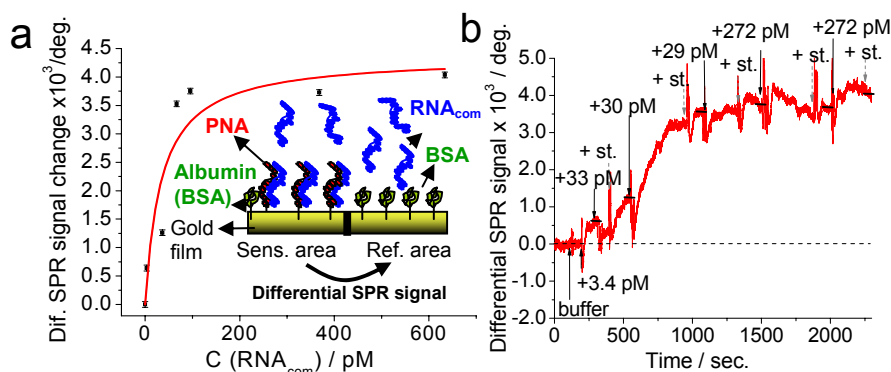
-  $C_{PNA}$  from  $\epsilon_0 \kappa_{org} A_{SWNT} / d_{PNA}$  where  $\kappa_{org}$  is the dielectric constant of an organic layer (assumed  $\sim 3$  for PNA),  $d_{PNA}$  is the averaged thickness of a PNA layer (1 nm). The estimated  $C_{PNA}$  value is  $1.67 \times 10^{-10} \text{ F}/(\text{m} \times \text{tube})$ . For 4 SWNT of 1.5- $\mu\text{m}$  length, a value of  $\sim 1 \times 10^{-15} \text{ F}$  is assessed.

The  $C_g'(PNA)$  value was obtained from eqs.(1)-(2):

$$C_g'(PNA) = [g_m(PNA) / g_m(\text{bare})] \times C_g'(\text{bare}) \quad (5)$$

using experimental values of  $g_m(\text{bare})$  and  $g_m(PNA)$  as well as the estimated  $C_g'(\text{bare})$  from eq.(3). The  $C_g'(\text{bare})$  values used in the calculation of  $C_g'(PNA)$  were validated by comparing mobility values of bare SWNT ( $1000 \text{ cm}^2/\text{V}\cdot\text{s}$  in buffer) calculated from eq.(1) which were of same order of those obtained from backgate experiments ( $\sim 4000 \text{ cm}^2/\text{V}\cdot\text{s}$ ) using geometric dimensions of the FET. The agreement between these values assessed from different ways indicates that reasonable values of  $C_{lg}$  and  $C_q$  were used for  $C_g'(PNA)$  calculation. The assessed mobilities were within the range of those reported previously CVD-grown SWNTs.<sup>5</sup>  $C_g'(PNA)$  values in the range of  $\sim 1.1 \times 10^{-15} \text{ F}$  in buffer were obtained and  $\theta_{PNA}$  values of 0.8-0.9 were estimated from eq.(4). This surface coverage indicates that a high percentage of the SWNT area is covered by PNA. It also indicates that we could effectively adsorb PNA in the sidewall of the SWNTs using our experimental procedure.

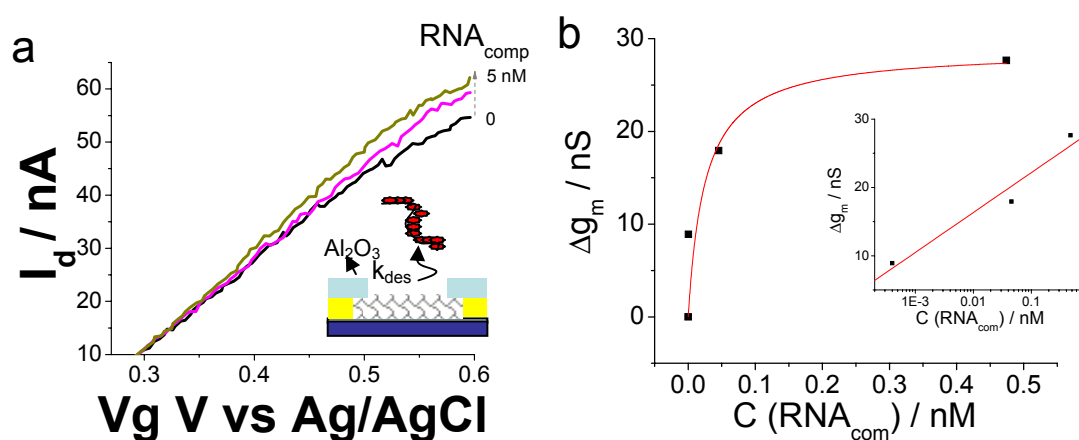
**Determination of PNA-RNA<sub>com</sub> affinity constant.** The affinity constant of PNA-RNA<sub>com</sub> was assessed by High Resolution Differential-Surface Plasmon Resonance (HRD-SPR) (Fig. 3). Differential SPR Angle changes between a sensing area modified with covalently attached PNA + Bovine Serum Albumin (BSA) and a reference area modified with BSA were monitored upon increasing concentrations of RNA<sub>com</sub> and accounted for RNA<sub>com</sub>-PNA hybridization. Quasi-stationary responses of SPR signal stabilized after solution stirring were obtained as a function of RNA<sub>com</sub> concentration and the PNA-RNA<sub>com</sub> affinity constant was estimated from fitting to Langmuir equation. A value of  $K_{aff} = (3 \pm 1) \times 10^{10} \text{ M}^{-1}$  was obtained.



**Fig. 3.** (a) Inset: Schematic representation of the HRD-SPR sensor used to measure the affinity constant of PNA-RNA<sub>com</sub> hybrids. PNA was covalently attached to the sensing area of the sensor while an inert layer of BSA was used to modified the reference area. The RNA<sub>com</sub> binding on the sensing area was simultaneously measured with respect to the reference area to subtract non-specific binding events on the sensor surface. (a)

SPR differential response vs RNA<sub>com</sub> concentration (from b). Full line corresponds to a fitting of experimental results to Langmuir isotherm ( $K_{\text{aff}} = (3 \pm 1) \times 10^{10} \text{ M}^{-1}$ ). (b) Real-time response of RNA<sub>com</sub> binding on PNA-modified SPR sensor upon increasing RNA<sub>com</sub> concentrations and stirring (+st.) steps. Tris buffer pH 7.4 (ionic strength = 14 mM).

**Response of RNA<sub>com</sub> on PNA-modified SWNT devices with Al<sub>2</sub>O<sub>3</sub> passivated contacts.** Interpretation about transduction mechanism of biomolecules detection on SWNT devices requires special care on controlling the nature of electronic contacts.<sup>6,7</sup> For this reason, we study the incidence of different type of passivation on our SWNT- devices. We consistently found increasing transconductances ( $g_m$ ) changes when RNA<sub>com</sub> sequence was injected on PNA-modified SWNT devices previously passivated with dodecanethiol or with a microfabricated layer of Al<sub>2</sub>O<sub>3</sub> on the contacts. Fig. 4 shows an example of the last case.



**Fig. 4.** (a)  $I_d$ - $V_g$  curves resulting from exposure of a PNA modified SWNT-FET device towards increasing RNA<sub>com</sub> concentrations. The device contacts were passivated with a microfabricated layer of Al<sub>2</sub>O<sub>3</sub> (inset). (b) Calibration plots of  $g_m$  changes vs. RNA<sub>com</sub> concentration. The full line shows the fitting with Langmuir isotherm ( $K_{\text{aff}} = 2 \times 10^9 \text{ M}^{-1}$ ).

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