

Effects of Water and Different Solutes on Carbon-Nanotube Low-Voltage Field-Effect Transistors

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Semiconducting single-walled carbon nanotubes (swCNTs) are a promising class of materials for emerging applications. In particular, they are demonstrated to possess excellent biosensing capabilities, and are poised to address existing challenges in sensor reliability, sensitivity, and selectivity. This work focuses on swCNT field-effect transistors (FETs) employing rubbery double-layer capacitive dielectric poly(vinylidene fluoride-co-hexafluoropropylene). These devices exhibit small device-to-device variation as well as high current output at low voltages (<0.5 V), making them compatible with most physiological liquids. Using this platform, the swCNT devices are directly exposed to aqueous solutions containing different solutes to characterize their effects on FET current–voltage (FET I – V) characteristics. Clear deviation from ideal characteristics is observed when swCNTs are directly contacted by water. Such changes are attributed to strong interactions between water molecules and sp^2 -hybridized carbon structures. Selective response to Hg^{2+} is discussed along with reversible pH effect using two distinct device geometries. Additionally, the influence of aqueous ammonium/ammonia in direct contact with the swCNTs is investigated. Understanding the FET I – V characteristics of low-voltage swCNT FETs may provide insights for future development of stable, reliable, and selective biosensor systems.

applications in novel high performance electronics^[4,5] as well as in the emerging field of biosensors.^[6–9] However, as highlighted in a recent review on carbon nanotube chemical sensors, selectivity in such sensors remains poorly understood, and thus presents an important challenge.^[10]

Functionalized and pristine individual CNTs have shown high sensitivity and selectivity down to the single molecule level.^[11–14] However, single CNT devices are challenging to make and characterize compared to CNT networks which add further complexity due to inter-CNT contacts. Such systems may not be as sensitive or selective compared to single CNT devices, but may be a cost-effective alternative for particular environments.^[15,16] One roadblock to the development of reliable biosensors is the complex behavior of water confined to small volumes or surfaces. The high dielectric permittivity of water molecules ($\epsilon_r \approx 80$) is typically measured in bulk, i.e., water molecules are able to rotate freely in 3D. Once water is

confined to a small volume or on surface, the rotational degree of freedom is reduced, resulting in a dramatic decrease of its permittivity to a value of about $\epsilon_r \approx 2$.^[17,18] Milli-Q (MQ) water, ultrapure water purified employing well established protocols (ISO: 3696), exhibits a resistivity of about $\rho = 18.2$ M Ω cm under strictly controlled conditions (i.e., without exposure to ambient atmosphere).^[19,20] On the other hand, once exposed to ambient conditions, which typically has a CO_2 concentration of

1. Introduction

Carbon nanotubes (CNTs) possess robust mechanical properties, thermal conductivity, and extraordinary electrical performance due to their unique structure and bonding.^[1,2] In particular, their sp^2 -hybridization allows for considerable electronic delocalization, resulting in excellent charge transport.^[3] In recent years, semiconducting carbon nanotubes have found

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about 414 ppm,^[21] the room temperature conductivity and pH of MQ water eventually stabilize at $\sigma = 1 \pm 0.5 \mu\text{S cm}^{-1}$ and 5.5, respectively.^[22,23] In addition to its complex behavior, water also possesses a low electrochemical window (i.e., as narrow as 1.23 V).^[24] Practical aqueous-based biosensors must therefore operate in low-voltage conditions. This further demonstrates that water and its solutes constitutes a complex medium and its impact on device characteristics must be understood in greater detail due to the fact that most physiological fluids contain a high degree of water indispensable for many vital processes.

Here, we report on the characteristics of single-walled carbon nanotube (swCNT) networks exposed directly to aqueous solutions containing different solutes. This is made possible by employing a solid-state dielectric poly(vinylidene fluoride-co-hexafluoropropylene) (ePVDF-HFP), which has been demonstrated to be compatible with swCNTs and also enables low-voltage field-effect transistor (FET) operation.^[25,26] We show that upon exposure to pure water or water containing different electrolytes, a change in on-current, threshold voltage, and apparent device mobility can be observed. Clear deviations from ideality are observed when swCNTs are directly contacted by water. Selective response to Hg^{2+} is discussed along with reversible pH response using two distinct device geometries. Additionally, the influence of aqueous ammonium/ammonia in direct contact with the swCNTs is investigated. These results demonstrate that carefully analyzing the FET current–voltage (I – V) characteristics can offer insight into the sensing mechanisms of CNT-based biosensors^[10,27] crucial for the development of stable, reliable, and selective biosensor systems.

2. Results and Discussion

The device structure used for this study is shown schematically in **Figure 1a**. These devices are bottom-gate, top-contact and utilize ePVDF-HFP as the dielectric as mentioned above.^[25,26] Device preparation is discussed in detail in the Experimental Section. To confirm that swCNTs can be deposited on the hydrophobic ePVDF-HFP layer, we utilized atomic force microscopy (AFM). A network composed of interconnected swCNTs with uniform thickness is clearly visible on top of the ePVDF-HFP layer in both the topography and phase images, with a surface roughness of about $R_{\text{RMS}} = 0.72 \text{ nm}$, and the maximum peak values in topography of $R_{\text{PV}} = 6.5 \text{ nm}$ (**Figure 1b,c**). An average tube thickness of about $1.2 \pm 0.6 \text{ nm}$ was extracted, which is consistent with the diameter of arc-discharged swCNTs (see Section S1 in the Supporting Information).

The dielectric properties of ePVDF-HFP were studied in detail in previous works.^[25,26] Stability of the dielectric layer was addressed by comparing the as-prepared capacitors, with vacuum annealed (four days), immersed in MQ water (24 h) and in artificial perspiration (24 h) exhibiting high stability and negligible changes with a constant capacitance value of about $C_i = 300 \pm 50 \text{ nF cm}^{-2}$ in agreement with previous data (see also **Figure S2** in the Supporting Information).

To benchmark our swCNT-FET devices in the absence of aqueous media, electrical characterization was carried out under ambient conditions ($T = 25^\circ\text{C}$ and relative humidity (RH) = 38–43%). **Figure 1d,e** shows the threshold voltages and

mobility extracted for a total of 95 devices. FET mobility and threshold voltages were extracted in both the linear and saturation regimes by employing different drain–source voltages ($V_{\text{D}} = -0.1 \text{ V}$ for linear and $V_{\text{D}} = -1 \text{ V}$ for saturation). All devices exhibited clear p-channel behavior, which is expected for CNT-based FETs in ambient conditions due to oxygen p-doping (see also **Figures S6 and S7** in the Supporting Information).^[10]

Threshold voltage (V_{TH}) was extracted by taking the x -axis intercept of the linear regression in linearized drain currents. As clearly seen in **Figure 1d**, operation in both linear and saturation regimes lead to a Gaussian distribution of V_{TH} values centered close to zero. In the linear regime, we found that $V_{\text{TH,lin}} = 49 \pm 200 \text{ mV}$, while in the saturation regime, $V_{\text{TH,sat}} = 93 \pm 180 \text{ mV}$.

Mobility values were extracted by taking the slope of the linear regression of linearized drain currents, and therefore represents an average value over a range of gate voltages. Values as high as $\mu_{\text{lin}} = 22 \pm 5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $\mu_{\text{sat}} = 27 \pm 7 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ were extracted for the linear and saturation regimes, respectively (**Figure 1e**). We note that a slightly higher value for saturation mobility, along with a higher standard deviation compared to values extracted in the linear regime are in agreement with previous publications;^[26] this is often attributed to the lower contact resistance at higher drain bias. Although charge carrier transport in individual swCNTs is described best with the ballistic transport, swCNT networks are usually composed by multiple swCNT junctions in the transport pathways. Such junctions often limit the mean free path of charge carriers, thus resulting in much lower charge carrier mobility, i.e., diffusive mobility. In this context, it is interesting to note, that even for high performance CNT thin-film FETs and very short channels ($L = 200 \text{ nm}$) operating in gigahertz integrated circuits, a strong gate-voltage-dependent transconductance was still reported.^[28] To characterize the ideality of our devices, we use the recently introduced reliability factor (r), defined as the ratio of the maximum channel conductivity experimentally achieved in a FET at the maximum gate voltage to the maximum channel conductivity expected in a correctly functioning ideal FET.^[29] For an ideal device, this factor is close to $r = 1$ and reflects a gate-voltage-independent mobility with the same value in both linear and saturation regimes (see also Section S3 in the Supporting Information). Although high values of r (i.e., typically $r > 96\%$) were extracted for our devices, some deviations from ideal metal–oxide–semiconductor field-effect transistor (MOSFET) theory were noted in the linear regime (vide infra). Despite these deviations, however, both mobility values as well as the drain currents are high even at voltages below 0.5 V, the voltage threshold for full compatibility with most physiological media. Additionally, high reproducibility and low device-to-device variation for samples prepared from the same batch of swCNTs ink were observed. Thus, the combination of swCNTs and ePVDF-HFP represents an ideal platform to study the effect of aqueous media on the electrical characteristics of swCNT FETs in low-voltage conditions.

2.1. Bias Stress and Stability under Different Environments

It is known that swCNT FETs measured under inert conditions exhibit ambipolar device (i.e., both electron and hole transport)

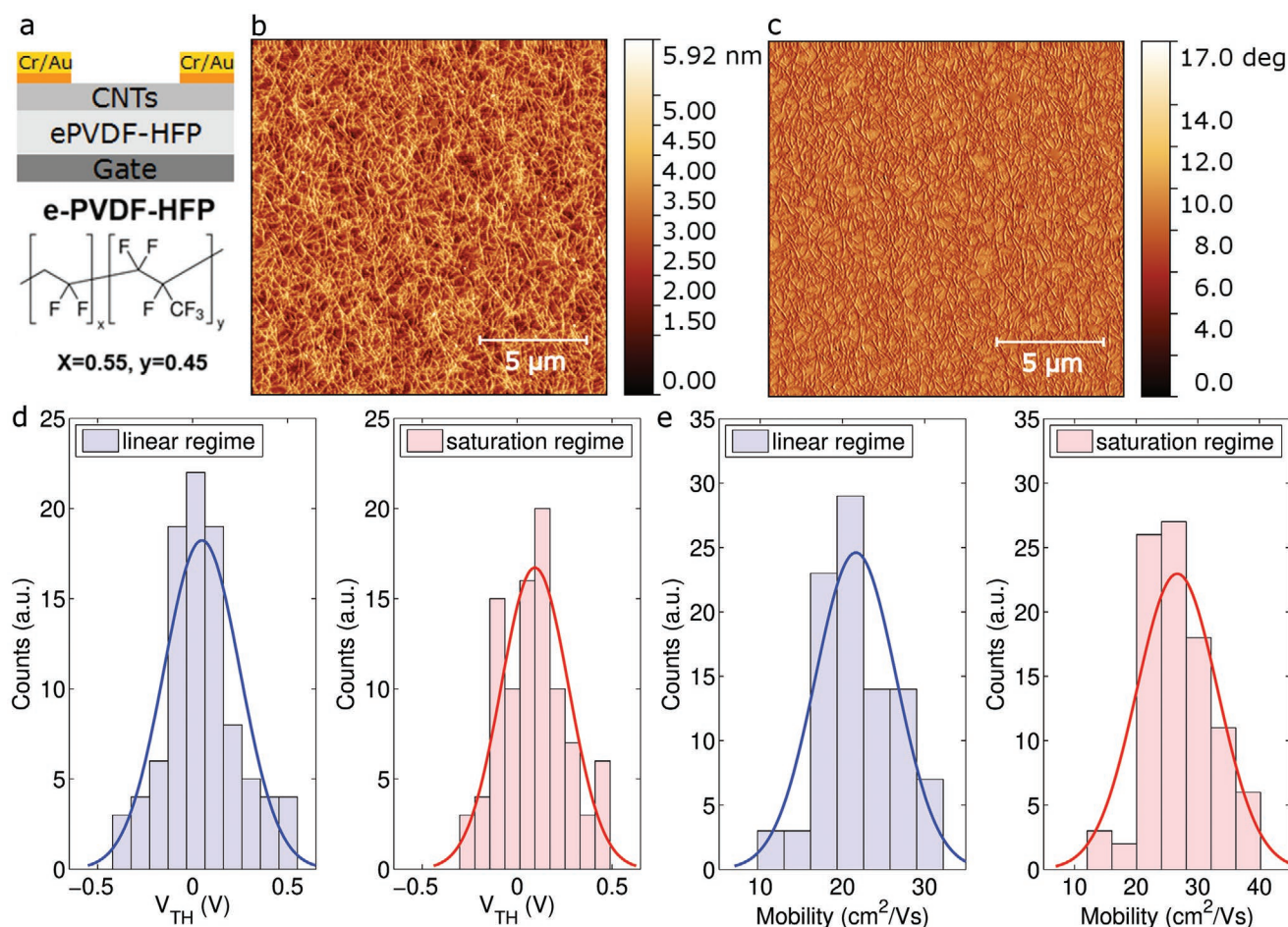


Figure 1. Electrical characteristics of low-voltage, single-walled carbon nanotube (swCNT) network field-effect transistors. a) FET device structure consisting of bottom-gate, top-contact geometry comprising a $d = 1.4 \mu\text{m}$ thick dielectric layer; thermally evaporated 5/50 nm thick chromium/gold source and drain electrodes. Channel widths of $W = 4 \text{ mm}$ and varying channel lengths $L = 50, 100, \text{ and } 200 \mu\text{m}$ were used in this work. Chemical structure of the double-layer dielectric ePVDF-HFP is shown below. b,c) AFM images of solution-processed swCNT networks on top of ePVDF-HFP, topography and phase, respectively. d) Threshold voltage histogram for 95 devices. The average threshold voltages calculated in the linear ($V_D = -0.1 \text{ V}$) and saturation regime ($V_D = -1.0 \text{ V}$) are $V_{\text{TH,lin}} = 49 \pm 200 \text{ mV}$ and $V_{\text{TH,sat}} = 93 \pm 180 \text{ mV}$, respectively. e) Field-effect mobility histograms for the same 95 devices; the corresponding average values in the linear and saturation regimes are: $\mu_{\text{lin}} = 22 \pm 5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $\mu_{\text{sat}} = 27 \pm 7 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively.

characteristics. On the other hand, when measured under ambient conditions, swCNTs are typically p-doped due to physisorption of oxygen on surface.^[10] In this context, possible effects leading to a change in the swCNT network conductance upon interaction with an analyte in the channel region are as follows:

- Increase (decrease) in swCNTs conductance (σ) caused by p-doping (n-doping) is typically reflected by a shift of threshold voltage toward more positive (negative) values;
- Decrease in charge carrier mobility (μ) can be caused by introduction of electrical defects due to reorganization of swCNT network or charge carrier traps in both p- and n-channel operations;
- Increase in swCNT network conductance (σ) caused by introduction of nonpercolating high-conducting sites in both p- and n-channel operations.

The phenomena listed above can occur both along a single swCNT and/or between CNT tube-to-tube connections. Device

characteristics may also change due to contact effects between electrode metal and swCNTs, such as Schottky barrier modulation. Top-contact architectures may reduce such variations since the swCNT network is fully covered by the electrode material. With the aim of gaining information on bias stability, we operated the FETs under continuous bias and carried out electrical measurements under ambient conditions. **Figure 2a** shows the typical output characteristics of swCNT-based low-voltage FET measured as-prepared, compared to the same device after about 45 min of applied bias, shown in **Figure 2b**. More information regarding bias stress measurements and the employed protocol is reported in the Experimental Section as well as in Section S3 (Supporting Information). Very low hysteresis effects were found in the output characteristics both in curves before and after bias stress. Importantly, the on-current remained almost unchanged, exhibiting only a slight decrease at low gate voltages. Once the same device was measured directly exposed to phosphate-buffered saline (PBS), diluted to 20 times (PBS 0.05×), it again exhibits low hysteresis effects

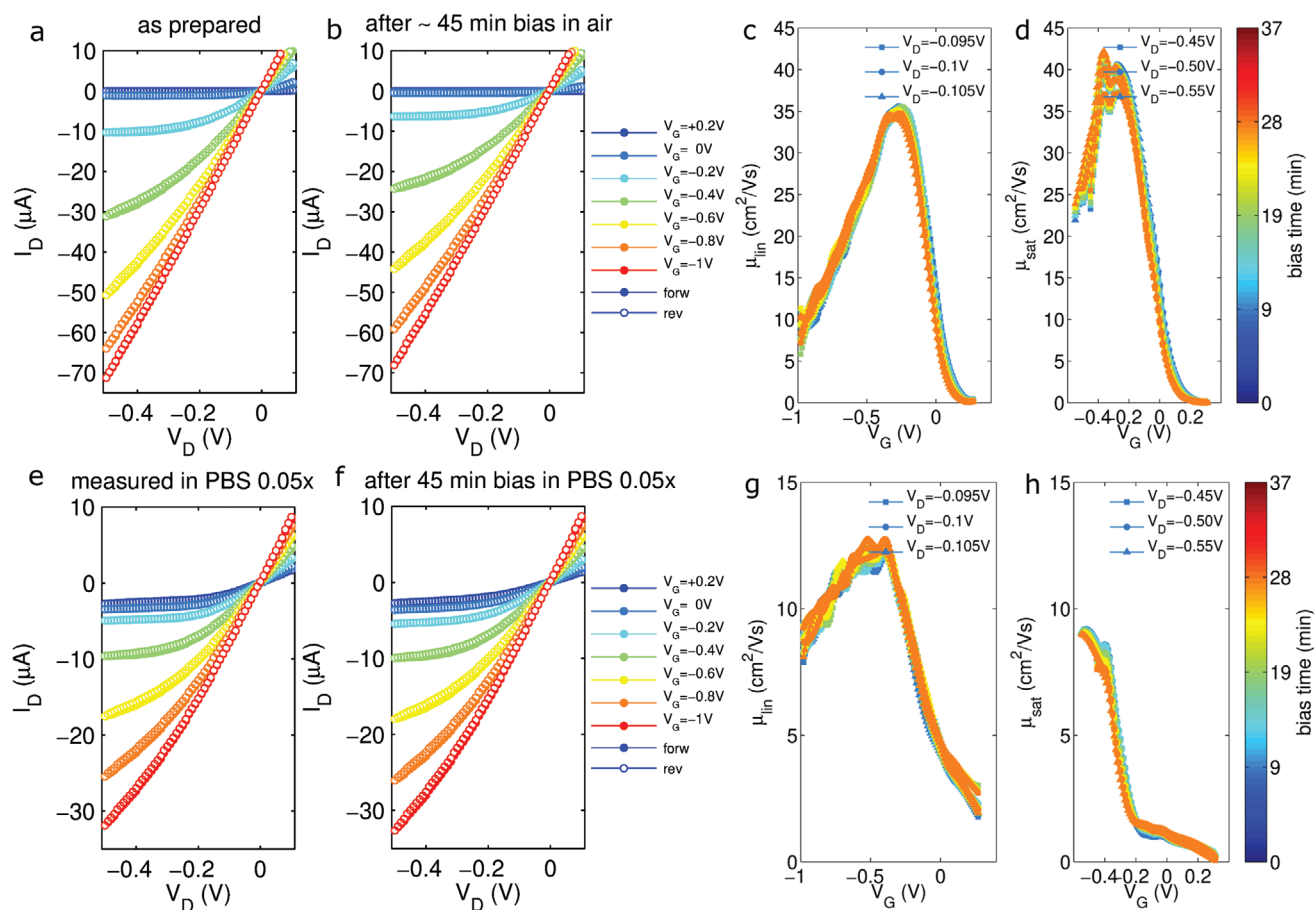


Figure 2. Low-voltage CNT-based field-effect transistors. a, b) swCNT FET output characteristics measured under ambient conditions ($T = 25 \pm 3^\circ\text{C}$, $\text{RH} = 38\text{--}43\%$) before and after bias stress experiments of about 45 min. e, f) Output characteristics of the same device before and after bias stress in PBS 0.05x. c, d) Evolution of gate-voltage-dependent apparent mobility under ambient conditions, and g, h) under PBS 0.05x.

and good bias stability. PBS is often used to emulate physiological liquids and constitutes an easily accessible medium to study the influence of different solutes on device characteristics (see also Figure S19 in the Supporting Information). This demonstrates that the swCNT-based network has high electrical stability and robustness to bias stress. However, a clear decrease in on-current at high gate voltage was observed in PBS 0.05x (Figure 2e, f).

The mobility in ideal MOSFETs measured in the linear regime (at low $|V_D|$) is inversely proportional to the drain voltage, while it gets independent from drain voltage in the saturation regime (at high $|V_D|$). Thus, three different drain voltages for both regimes were used to monitor device ideality. The mobility profile, on the other hand, contrary to conventional MOSFET theory, exhibits strong gate voltage dependence in both the linear and saturation regimes, shown in Figure 2c, d. Average mobility values extracted by the linear-fit method represented in Figure 1e are probably closer to the real swCNT network mobility, while the strongly gate-voltage-dependent values in Figure 2c, d represent apparent field-effect mobility. Mobility extraction by MOSFET theory assumes constant charge carrier mobility and voltage-independent gate capacitance. This, however, might not be the case for CNT networks under humid environments, and multiple polarization mechanisms

(vide infra) might be involved, leading to an apparent charge carrier mobility.

For polymer-based FETs, similar effects have been attributed to the presence of water.^[30,31] Recently, for polymer and small-molecule-based diodes, the presence of water pockets inside the electrically active material was shown to exhibit localized trap states measured at about $E_{\text{trap}} = 0.3\text{--}0.4\text{ eV}$ above (below) the highest occupied molecular orbital (lowest unoccupied molecular orbital) of the active material.^[32] Water clusters were proposed to be the source of hole trapping limiting hole transport when the ionization energy of a material surpasses 6 eV.^[33] Similarly, we believe that the presence of water or humidity at the surface of swCNTs has a strong influence on the local electric field, and thus on the charge transport in the FET.^[34,35]

Next, we investigated the influence of stabilized Milli-Q water (stabilized under ambient conditions: i.e., $\sigma = 1 \pm 0.5\ \mu\text{S cm}^{-1}$ and pH of about 5.5 ± 0.5 for 24 h) in direct contact with the CNT network. Immediately after injection of stabilized MQ water into the polydimethylsiloxane (PDMS) reservoir, output characteristics were measured (Section S3, Supporting Information). We observed that the drain current started to decrease at high gate values, but interestingly the output characteristics exhibited a strong “p-doped” like behavior indicated by a change in threshold voltage to more positive values as well as less-effective

bottom-gating (i.e., devices cannot be switched off even at elevated positive V_G). This can be observed in the relatively high and positive threshold voltage $V_{TH} = 1.5 \pm 0.1$ V, for both linear and saturation regimes extracted from transfer characteristics compared to values for the same device of $V_{TH} = 0.3 \pm 0.2$ V in ambient conditions. Threshold voltages in all media (air, MQ water, and PBS 0.05×, vide infra) were extracted in the following voltage ranges: linear regime with $V_D = -0.1$ V: $-1 < V_G < -0.5$; saturation regime with $V_D = -0.5$ V: $-0.55 < V_G < -0.3$. Hysteresis effects in transfer characteristics are a powerful tool to study polarization mechanisms, however, as reported in previous works,^[25,26] due to the double layer formation in ePVDF-HFP at low frequency, fast changes are masked. Transfer characteristics, with a constant sweep speed of $v_{\text{sweep}} = 173 \pm 0.2$ mV s⁻¹, both in linear and saturation regimes shown in **Figure 3**, appeared to exhibit two regions of gate-voltage-dependent drain current as evidenced by the change in slope, when measured in MQ water. This suggests that there may be other additional polarization mechanisms such as orientated water molecules in a thin water layer on the CNT surface.

After 45 min of bias stress, the bottom-gate effect was partially recovered, exhibiting a threshold voltage closer to zero with a value of about $V_{TH} = 0.5 \pm 0.1$ V. The maximum drain current in the output characteristics at high gate voltage, however, decreased from a value of $I_D = 72$ μ A measured under ambient conditions to a value of about $I_D = 32$ μ A measured in stabilized MQ water.

Judging from the abrupt increase of V_{TH} and almost unchanged on-current at high gate values, as well as reversibility upon water removal, we attribute the drastic change to a variation of the effective gate-field, rather than desorption of CNTs from the surface. Reversibility upon water removal is a very important aspect specially for targeting durable biosensors. In this context, the importance of water molecules and their electrostatic interaction in proximity to sp²-hybridized carbon atoms was recently reported.^[36–41]

FET mobility, on the other hand, shows a significant decrease to about $40 \pm 5\%$ of the initial value measured under ambient

conditions. This was found to be the case for both gate-voltage-dependent apparent mobility as well as for mobility values extracted employing the linear fit method in both linear and saturation regimes. This further supports our hypothesis that the changes in the electrical behavior of the swCNT network is due to the presence of water changing the effective electric gate-field close to the CNT network.

Figure 2e shows exposure of the same device to PBS 0.05× with the corresponding electrical bias stress in Figure 2f. The electrical properties of PBS 0.05× have been measured by four-probe-AC techniques and exhibit a much higher conductivity than pure water of about $\sigma = 0.94 \pm 0.05$ mS cm⁻¹ at $T = 25 \pm 3$ °C. Similar to our earlier result, negligible changes were observed under 45 min of electrical bias even when the swCNT network is exposed to PBS 0.05×. This highlights high bias stability, but importantly, also high sensitivity of swCNTs networks in aqueous environments and its potential for biosensors operating in biological liquids.

2.2. Selective Response of Carbon Nanotube FETs to Mercury Ions

To study the influence of different solutes on the performance and device characteristics of low-voltage swCNT FETs, we investigated exposure of our CNT FET to several previously reported analytes in aqueous conditions. We started with Hg²⁺ ions in water. Previously, it has been shown that by dissolving HgCl₂ in water, Hg²⁺ can be selectively detected by CNTs.^[42] Solutions containing Hg²⁺ in different concentrations ranging from 1×10^{-9} to 100×10^{-6} M were prepared and allowed to stabilize at room temperature $T = 25 \pm 3$ °C. Two sets of samples were studied and compared: a first batch with CNTs as-prepared and a second batch with CNTs activated by oxygen plasma treatment (5 s, 150 W).

Figure 4a shows drain current (I_D) and gate leakage current (I_G) measured in low-voltage CNT FETs applying constant $V_D = -0.1$ V and $V_G = -0.3$ V at increasing concentrations of HgCl₂ in MQ water. These voltage parameters, i.e., linear regime, were chosen in agreement with very stable on-current and negligible leakage current. Our measurement setup allows us to investigate the dependence of I_D on different solute concentrations while applying low voltages compatible with most electrolytes in water. **Figure 4b** shows the results from a similar experiment done with plasma-treated CNTs. Drain currents measured in stabilized MQ water were extracted to be $I_{0,\text{ap}} = 115 \pm 5$ nA and $I_{0,\text{plasma}} = 24 \pm 5$ nA, for the as-prepared and plasma-treated samples, respectively. This is in agreement with literature values, wherein plasma treatment resulted in drain current decreases for swCNT FETs driven in p-channel operation due to the introduction of electrical defects (C–O, C=O, O–C=O).^[43,44]

A clear increase of drain current at higher levels of HgCl₂ in water was observed in both cases, reaching a comparable maximum drain current of $I_{D,\text{ap}} = 2.1 \pm 0.1$ μ A and $I_{D,\text{plasma}} = 3.0 \pm 0.1$ μ A, for the as-prepared (ap) and plasma-treated samples (plasma) ($c_{\text{HgCl}_2} = 100 \times 10^{-6}$ M), respectively. Although very different initial drain currents in stabilized MQ water were measured for both the as-prepared and plasma-treated samples ($I_{0,\text{ap}} = 115 \pm 5$ nA and $I_{0,\text{plasma}} = 24 \pm 5$ nA), the maximum

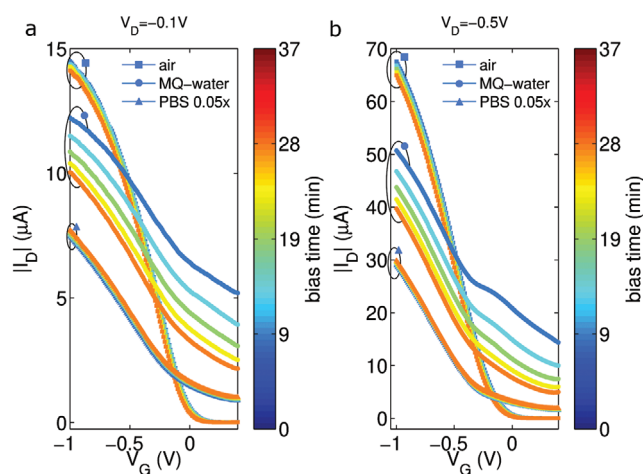


Figure 3. Low-voltage CNT-based field-effect transistors. swCNT FET transfer characteristics measured in a) linear and b) saturation regimes. Drain current (I_D) measured under ambient conditions ($T = 25 \pm 3$ °C, RH = 38–43%) shown in square symbols, MQ water shown in circular symbols, and PBS 0.05× shown in triangular symbols, respectively.

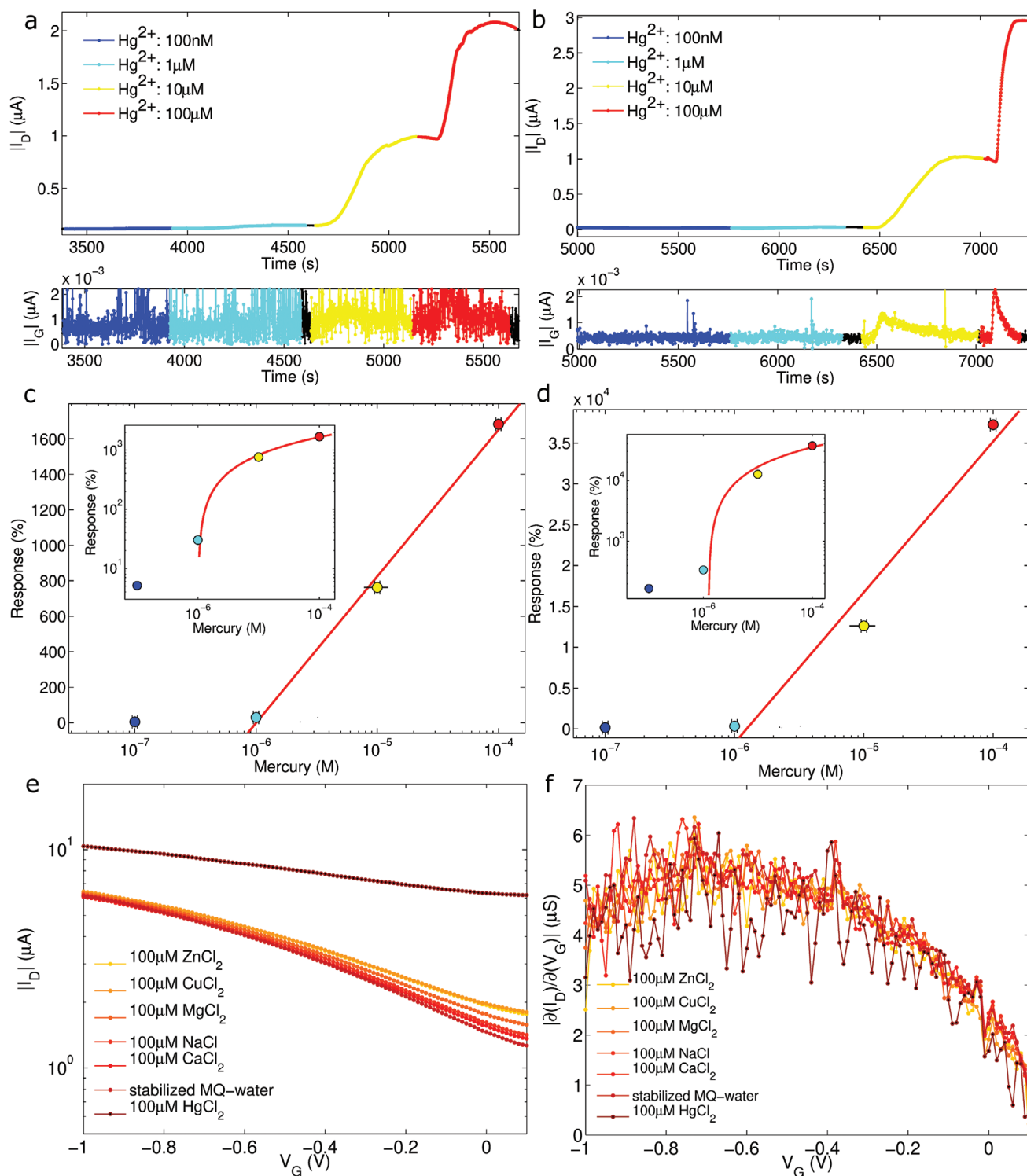


Figure 4. Selective response to mercury (Hg^{2+}). a) Drain current (I_D) and gate leakage current (I_G) measured in low-voltage CNT FETs applying constant $V_D = -0.1$ V and $V_G = -0.3$ V at different concentrations of HgCl_2 in MQ water. c) Response ($\Delta I/I_0$) to different concentrations of Hg^{2+} ions with log-log plot in the inset. b) I_D and I_G measured at constant $V_D = -0.1$ V and $V_G = -0.3$ V of plasma-activated low-voltage CNT FETs with d) the corresponding response and log-log plot in the inset. e) Semilogarithmic I_D -transfer characteristics at $V_D = -95$ mV measured in water with different ions for selective detection of HgCl_2 . f) The corresponding transconductance ($\partial I_D / \partial V_G$) at different ion concentrations.

current at 100×10^{-6} M of HgCl_2 was surprisingly similar. To quantitatively understand the relationship between HgCl_2 concentration and drain current, we plotted $\Delta I/I_0$ (response) as a function of Hg^{2+} concentration, shown in Figure 4c,d. Both device types exhibit a clear increase in drain current at higher Hg^{2+} concentration. Interestingly, similar for both the as-prepared and plasma-activated CNTs, the response started to increase at concentrations Hg^{2+} higher than 1×10^{-6} M. At 1×10^{-6} M HgCl_2 , the electrical conductivity was found to be very close to that of stabilized MQ water ($\sigma = 1 \pm 0.5 \mu\text{S cm}^{-1}$). In both cases, response increases fairly linearly with concentrations of HgCl_2 . Performing a linear regression of the response reveals that the plasma-treated swCNTs show higher sensitivity to Hg^{2+} with $S_{\text{ap}} = 359\% \text{ dec}^{-1}$ and $S_{\text{pa}} = 8013\% \text{ dec}^{-1}$, for the as-prepared and plasma-activated CNTs, respectively. Interestingly, the insets shown in Figure 4c,d exhibit a typical behavior one would expect for a material in transition from nonpercolating charge transport toward percolation.^[45] According to classical percolation theory, an insulator–conductor transition takes place when the volume fraction of the conductive phase approaches the percolation threshold. This is consistent with our observation of a solute-concentration-dependent drain current, and suggests that 1×10^{-6} M HgCl_2 is the threshold for the insulator–conductor transition.

The selectivity of mercury detection was further tested in the as-prepared devices by exposing them to a set of solutions, including both mono- and bivalent ionic solutions: ZnCl_2 , CuCl_2 , MgCl_2 , NaCl , CaCl_2 , MQ water, HgCl_2 . High selectivity of the swCNT network toward HgCl_2 was observed and is clearly visible, reflecting in a shift of the transfer curve toward higher values of I_D (Figure 4e). Detection results in terms of sensitivity and selectivity are comparable to literature data.^[42] This may be due to two separate reasons: 1) the creation of an alternative conduction path through elements connected electrically in parallel to the semiconducting swCNT network or 2) p-type doping by HgCl_2 . To confirm that the solutes themselves did not contribute to the measured conductivity of the device, the conductivity of all solutions was measured and found to be at least 2 orders lower compared to the estimated swCNT conductivity in the on state at $V_D = -0.1$ V and $V_G = -0.3$ V.

Previously, swCNT conductance increase upon exposure to Hg^{2+} was attributed to the favorable and irreversible reduction of Hg^{2+} to Hg^0 by swCNTs at less negative reaction potentials than needed for other ions. The same study noted the formation of Hg^0 clusters adjacent to swCNTs, which may also be present in our samples.^[42]

Moreover, for all tested metal ions, including recent literature reports,^[42,46,47] mercury is the only metal existing in liquid form at ambient conditions (i.e., $p = 1013$ mbar, $T = 25$ °C). Due to its high surface tension, mercury does not wet, and tends to form liquid droplets. Liquid metals such as mercury possess no periodic structure and tend to have conductivities slightly lower than solid metals, on the order of $\sigma = 1 \times 10^4 \text{ S cm}^{-1}$.^[48]

Therefore, we believe that probably the origin for Hg^{2+} sensitivity in swCNTs may be twofold. i) Strong redox reaction between Hg^{2+} and swCNTs resulting in swCNTs^{2+} . This would cause p-type doping of the swCNTs, resulting in a positive threshold voltage shift and I_D current increase in p-channel FETs, both of which we observed. ii) Formation of Hg^0 clusters,

adjacent to the swCNTs (electrical healing of defects) and/or at tube-to-tube junctions (reducing intertube contact resistances) which act as resistive element with good conductivity, electrically connected in parallel to pristine semiconducting swCNTs network. Such a resistive element would not be affected by the gate voltage. In fact, the same transconductance ($\partial I_D / \partial V_G$, which is proportional to mobility) was found for all tested species of ions including HgCl_2 (Figure 4f). Similarly, gate leakage current was also found to be the same for all measured conditions (see also Figure S12 in the Supporting Information). This hypothesis would also explain the irreversibility of Hg^{2+} detection, normally seen in such sensors with electrical readout. It is, however, difficult to unambiguously decouple the extent to which either mechanism dominates.

Reversible electrical Hg^{2+} detection on the other hand has been recently shown in swCNT FETs employing functionalization, using a 33-base thiolated-DNA probe, which demonstrated selective binding due to a conformational change, while mercury remains in the oxidation state Hg^{2+} .^[47,49,50] This approach was found to work even in very complex aqueous media, such as the marine environment. This further highlights the high sensitivity and selectivity of electrically driven networks of swCNTs in aqueous solutions, but shows on the other hand also that in such systems, multiple working mechanisms are often superimposed.

2.3. Reversible pH Response and Ammonium/Ammonia Detection of swCNT FETs

It is known that pH has an important influence on the electrical I – V characteristics of devices with active layer materials based on conjugated carbon (i.e., swCNTs, graphene). In graphene-based devices, for instance, the Dirac voltage ($V_{\text{Dirac}} = \text{gate voltage with balanced electron and hole transport}$) is highly sensitive to pH variations. V_{Dirac} has been observed to shift toward more positive values with increasing pH, which was attributed to accumulation of holes and an increase in the hydroxide ion concentration (OH^-) near the graphene layer (p-type doping).^[51]

In order to investigate the pH response of our swCNT FET, a set of solutions employing PBS 0.05× with adjusted pH were prepared. The measurement setup was modified to include a PDMS flow cell on top of the swCNT FET that contained a Pt electrode connected to source (GND) to electrically stabilize the electrolyte solution. Figure 5a shows changes of I_D as well as I_G with pH for the swCNT FETs. Contrary to what expected for a p-channel material and electrostatic or capacitive coupling, I_D current clearly decreases at higher pH levels.

Recently, plasma-activated aligned swCNTs have been used as a pH sensing element in extended gate architectures, coupled to a commercial n-MOSFET.^[43,52] Highly aligned swCNTs were connected in series between a n-MOSFET-gate, electrolyte solution, and reference electrode, and exhibited a clear current decrease at higher pH levels. This is in agreement with the decreasing current observed in our swCNT FETs at high pH levels. A similar response has also been observed in graphene-based pH sensors with the active layer directly exposed to the electrolyte solution and buffer concentrations of 0.05 M. Importantly, by changing the buffer composition, both positive and

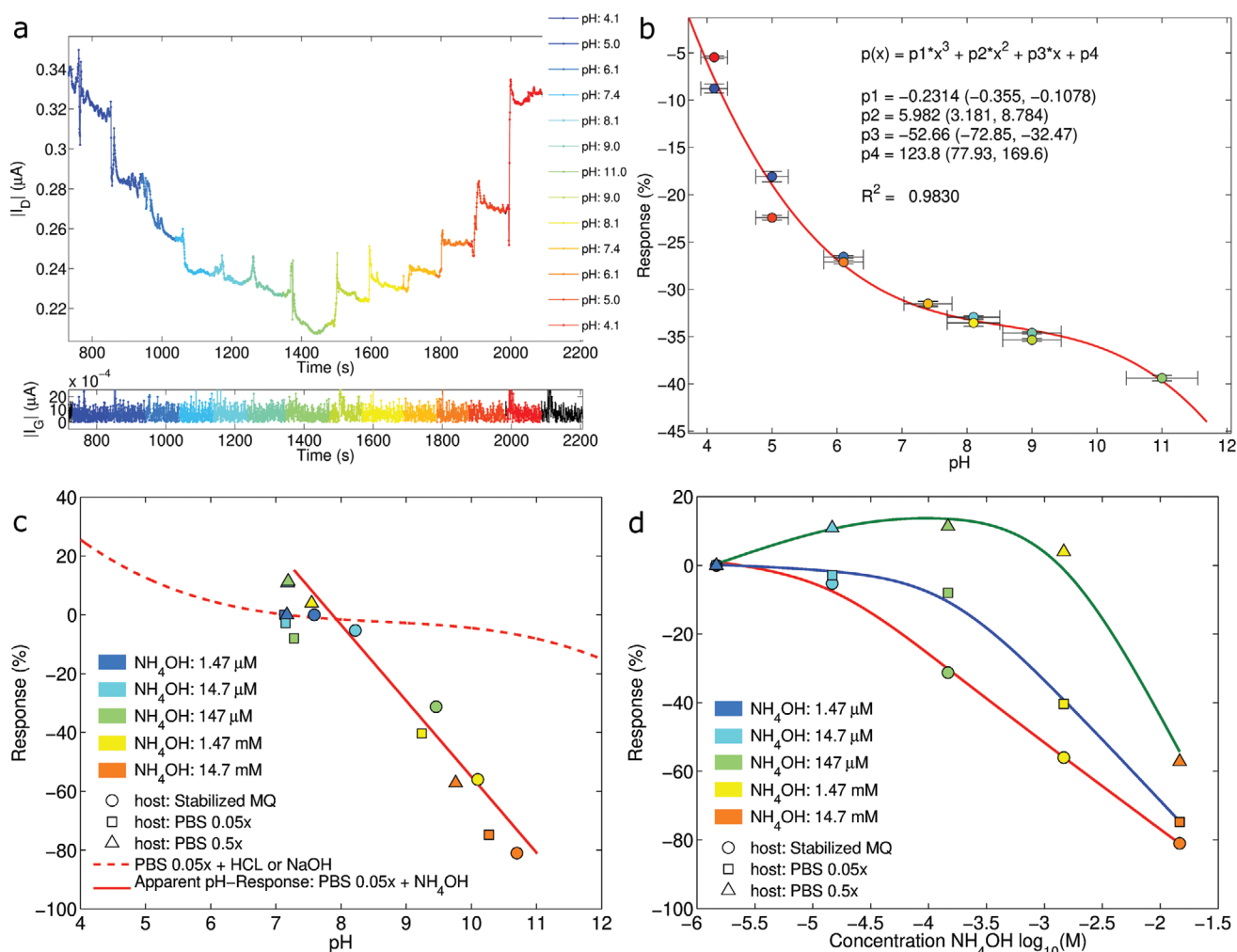


Figure 5. Low-voltage swCNT FET response to pH and NH_4OH . a) Drain current (I_D) and gate-leakage current (I_G) measured at $V_D = -0.1$ V and $V_G = -0.3$ V with the swCNT network exposed to PBS 0.05x at different pH. b) Reversible pH response of the swCNT FET with 3rd order polynomial fit. c) pH response of the swCNT FET with different concentrations of NH_4OH (shown in different colors) in host solutions of different ionic strengths (shown in different symbols: MQ water (○), PBS 0.05x (□), and PBS 0.5x (Δ)). d) swCNT FET response to NH_4OH concentration in host solutions with different ionic strengths.

negative shifts of V_{Dirac} were observed, thus leading to a buffer-dependent or apparent pH sensitivity.^[51]

Figure 5b shows the reversible pH response ($\Delta I/I_0$) extracted from Figure 5a, which clearly follows a 3rd order polynomial behavior. This further implies that the sensitivity ($S = \partial[\Delta I/I_0]/\partial \text{pH}$) would be described best by a quadratic expression. Common pH sensors typically show a linear response to pH, as reflected in a constant sensitivity. This means that multiple sensing mechanisms toward pH may be superimposed in our swCNT FETs, thus leading to this higher order dependence. Once the CNT network is exposed to aqueous environments, a thin water layer on top of CNT surface may enable doping/dedoping along with other electrostatic interactions, which can become even more complex by adding electrolytes.

To investigate if better-defined electrical response can be observed, we deposit an insulating layer on the CNT surface that can potentially allow electrostatic modulation of CNT I – V characteristics. Previously, we have shown that by evaporating

50 nm of SiO_x as a topmost encapsulation and pH sensitive layer in FET structures allows for reversible pH sensing with constant sensitivity.^[53] Therefore, as a proof of concept, we deposited on top of the swCNT network 50 nm of thermally evaporated SiO_x covering both the FET channel and source-drain electrodes. By employing a Pt electrode connected to source (GND) to electrically stabilize the electrolyte solution, we studied the response of our device to different solutions of PBS 0.1x at different pH. Figure S13 (Supporting Information) shows a typical pH response of such a transistor driven at $V_D = -50$ mV and $V_G = -300$ mV. The current clearly increased at higher pH values, showing good reversibility and exhibited a sensitivity of about $S_{\text{pH}} = 8 \pm 1\% \text{ pH}^{-1}$. At a lower gate voltage ($V_G = -150$ mV), a higher sensitivity of $S_{\text{pH}} = 11 \pm 1\% \text{ pH}^{-1}$ was extracted for the same device (Figure S15, Supporting Information). This is consistent with electrostatic sensing theory, the site binding model,^[54] and capacitive coupling of the pH sensitive SiO_x topmost layer.

As anticipated earlier, devices fabricated using swCNTs grown by chemical vapor deposition on silicon substrates on top of silicon dioxide exhibited clear p-channel behavior when measured in air, while n-channel characteristics could only be measured in vacuum. It was further reported that ammonia (NH_3) treatment in air resulted in a clear decrease of p-channel drain current, while a similar treatment in vacuum resulted in an increase of n-channel drain current, which was ascribed to charge transfer from ammonia physisorbed on nanotubes.^[55] The influence of ammonia and nitrogen dioxide (NO_2) on the electrical performance of CNTs was studied previously, exhibiting a clear decrease of drain current for NH_3 while exposure to NO_2 exhibited a clear increase.^[56] Similar experiments have also been carried out for CNTs exposed to the same chemicals in aqueous environments.^[57] From an applications point of view, the detection of ammonium concentrations in urine is highly interesting and allows for monitoring of the progression of chronic kidney diseases.^[58]

In order to study the response of our swCNT network to ammonium, we exposed our devices to different concentrations of NH_4OH in water (Figures S16–S18, Supporting Information). Figure 5c shows the fitted 3rd order pH response of the swCNT network (data set from Figure 5b offset by 32%) compared to the measured device response to different NH_4OH concentrations. Interestingly, all NH_4OH solutions exhibited very similar linear responses but at greater magnitudes compared to the pH response extracted in Figure 5b. Figure 5d on the other hand shows the same data set plotted as function of NH_4OH concentration. With increasing ionic strength of the solution, the drain current decrease appears to be shifted toward higher concentrations of NH_4OH . This can be attributed to a decrease of the Debye length with increasing salt concentration.^[59] Literature consistently points to the fact that aqueous solutions of $\text{NH}_3/\text{NH}_4\text{OH}$ contain neutral ammonia (and water) molecules at a much higher concentration compared to ammonium and hydroxide ions.^[60–62] These findings suggest that at the measured solution pH, NH_3 appears to have a strong effect on the electrical conductivity of swCNTs and that our sensor response cannot be attributed to changes in pH only.

To summarize, the pH response of our swCNT network has been tested employing different architectures, exhibiting distinct current changes attributed to different operation mechanisms. For swCNTs directly exposed to aqueous solutions, a current decrease at higher pH was observed, leading to a 3rd order pH response. This might indicate the superposition of multiple sensing mechanisms. Employing SiO_x as the topmost layer for pH response, on the other hand, leads to an increased drain current at higher pH. This is consistent with previous observations of capacitive coupling of SiO_x and swCNT channel, exhibiting a linear, gate-voltage-dependent pH response. With NH_4OH , our devices exhibited a clear decrease of drain current with increasing concentration, an opposite trend compared to our observations with HgCl_2 plotted in Figure 4. This is in agreement with previous literature.^[57]

3. Conclusion

Semiconducting swCNTs are promising for emerging biomedical applications. In particular, they have demonstrated excellent

biosensing capabilities, and are poised to address existing challenges in sensor reliability, sensitivity, and selectivity. In this work, we focused on swCNT FETs employing rubbery double-layer dielectric poly(vinylidene fluoride-co-hexafluoropropylene). These devices exhibit high reproducibility and small device-to-device variation as well as high current output at low voltages (<0.5 V), making them compatible with most physiological liquids. Using these devices, we monitored the FET I – V characteristics as a way of understanding the active layer's response to different aqueous environments. We showed that direct contact with aqueous environments including different solutes induced considerable changes in the electrical response of swCNT network and suggesting the coexistence of multiple sensing mechanisms. When operated in water, our device characteristics change significantly and do not exhibit ideal MOSFET behavior, possibly due to multiple superimposed polarization effects (i.e., polarization of water and different solutes in aqueous environments). This reflects the high sensitivity of such networks, but the responsiveness toward more than one stimulus complicates the design of selective sensors in complex environments. Different strategies toward the achievement of fully selective sensors, decoupling, and enhancing sensing mechanisms have been pointed out. The present work will contribute to understanding and unraveling the electrical response of swCNT networks for the development of more reliable and fully selective biosensors in complex aqueous environments.

4. Experimental Section

Material and Device Preparation: Highly doped n-type Si (100 , $\rho < 0.004\ \Omega\ \text{cm}$) substrates were used to fabricate common-gate rigid devices. ePVDF-HFP was purchased from 3M Co (3M Dyneon Fluoroelastomer FE) and dissolved in 2-butanone in a concentration of $c = 120\ \text{mg mL}^{-1}$. The obtained solutions were filtered through a $0.2\ \mu\text{m}$ polytetrafluoroethylene filter and spin-coated at $1000\ \text{rpm}$ for $1\ \text{min}$. After $10\ \text{min}$ of baking at $T = 80\ ^\circ\text{C}$ in ambient conditions, all samples were vacuum annealed at $T = 150\ ^\circ\text{C}$ for $2\ \text{h}$ in a vacuum of $p = 50\ \text{mbar}$. Dielectric thickness was measured to be about $d = 1.40 \pm 0.01\ \mu\text{m}$ on the Si-wafer pieces using FILMETRICS F20-EXR Thin-Film Analyzer. Cr, Au source and drain electrodes with a thickness of about $d = 5/50\ \text{nm}$, respectively, were thermally evaporated using a shadow mask. On top, $50\ \text{nm}$ SiO_x was thermally evaporated for the second pH sensor architecture. PBS 1 $\times$ was prepared by using deionized water, Milli-Q quality with $\rho = 18.2\ \text{M}\ \Omega\ \text{cm}$, and phosphate-buffered saline tablets purchased from Sigma-Aldrich. pH levels of the electrolyte solutions were changed by adding hydrochloric acid (HCl) 37% or solid sodium hydroxide (NaOH), both purchased from Sigma-Aldrich and used as obtained. PBS 0.1 $\times$ and PBS 0.05 $\times$ were obtained by dilution of PBS 1 $\times$. Solutions of mercury and other ions were made by dissolving chloride salts in MQ or diluted PBS solutions as follows: ZnCl_2 , CuCl_2 , MgCl_2 , NaCl , CaCl_2 , HgCl_2 . In case of ammonium solutions, NH_4OH was used. The polymer sorted swCNTs^[63] were deposited by drop casting on the ePVDF-HFP layer for $5\ \text{min}$. This was followed by soaking the sample in toluene for 1 , 2 , and $2\ \text{min}$ to remove the wrapping polymers. Between each soaking steps, the samples were dried with nitrogen. After swCNT deposition, the substrate was annealed at $150\ ^\circ\text{C}$ for $25\ \text{min}$. In order to etch the swCNTs in case of mercury response, $5\ \text{s}$ plasma with power of $150\ \text{W}$ was used.

The electrical conductivity of all solutions was measured by using a handheld Ohaus ST10C conductivity Meter (AC), range 0.00 – $19.99\ \text{mS cm}^{-1}$. The pH level of all solutions was measured by using a handheld Ohaus ST20 waterproofed pH meter, range 0.00 – $14\ \text{pH}$, $T = 0.0$ – $99.0\ ^\circ\text{C}$, and measurement resolution $0.01\ \text{pH}$ (see also Figure S19 in the Supporting Information).

Electrical Characterization and Data Analysis: Electrical device characteristics were recorded using a setup including Keithley Source Meter, Model 2635 and Model 2400. Field-effect mobilities were calculated using the standard MOSFET model with a gate capacitance for ePVDF-HFP of $C_i = 300 \text{ nF cm}^{-2}$ (see also the Supporting Information).^[25] Measurements under ambient conditions ($T = 25 \pm 3 \text{ }^\circ\text{C}$ and $\text{RH} = 38\text{--}43\%$) as well as exposed to different environments were measured in a homemade flow cell system, allowing for continuous solution supply at a constant flow rate of about 0.5 mL min^{-1} .

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

biosensors, low-voltage field-effect transistors, response mechanisms, single-walled carbon nanotubes, water and electrolyte solutions

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