

Functionalized Metallic Carbon Nanotube Devices for pH Sensing

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Single-wall carbon nanotubes (SWNTs) are attractive for sensor applications especially due to their large surface-to-volume ratio^[1]. Pristine semiconducting SWNTs have been successfully used to detect gas molecules such as NH₃, NO₂, oxygen^[2,3] as well as humidity^[4], via changes in electrical conductivity. Furthermore, the possibility to use water with or without an electrolyte as a gating medium^[5,6] has sparked interest in the realization of SWNT-field effect transistors (FETs) for detecting molecules such as ammonia in solution.^[7] Towards the aim of sensing specific molecules in solution, SWNTs have been chemically modified, in most cases through non-covalent functionalization.^[8] Most of the devices demonstrated until now, rely in one way or another on the analyte-dependent gating mechanism of semiconducting SWNTs. While this imparts good sensitivity to the devices, they have the disadvantage that parasitic charges on the substrate have a strong influence on sensor stability and selectivity. Here, we present a novel route to chemical sensors which uses metallic SWNT as the starting basis. Our strategy comprises the covalent attachment of analyte-sensitive functional groups in controlled density to individual contacted metallic SWNTs. The attached moieties function as scattering sites, whose effect on charge transport through the tubes is modulated by the analyte concentration.

In this study, we demonstrate a pH sensor using this principle, where the sensitivity to pH is attained by covalent attachment of amino-substituted phenyl radicals to individual metallic SWNTs via gentle electrochemical modification (ECM). The low functionalization degree allows for minimal destruction of the π -conjugated framework, ensuring that the tubes show sufficient conductivity after modification. Electrochemistry represents an excellent tool for nanotube functionalization, which enables for instance exclusive modification of the metallic tube fraction of a mixture of metallic and semiconducting SWNTs.^[9] Moreover, preferential decoration of defect sites along the tubes with metal clusters has been achieved by application of a low overpotential within metal salt solutions.^[10] Here, we demonstrate that the density of moieties covalently attached

to a SWNT can be effectively controlled by a series of electrochemical couplings.

Metallic SWNTs were identified by their weak (< 2) back-gate dependence ratio (bGDR), defined as the ratio of the maximum resistance at a back-gate voltage of $V_{bg} = +5$ V to the minimum resistance at $V_{bg} = -5$ V. Figure 1 displays the back gate-

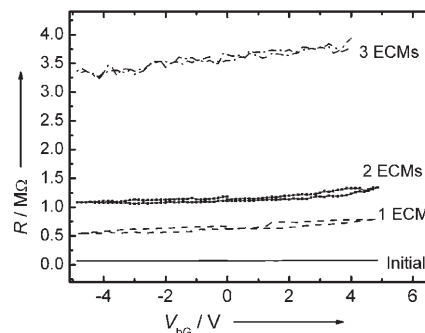


Figure 1. Back-gate dependence of resistance for a pristine metallic SWNT (solid line) and for the same tube after 1, 2 and 3 electrochemical modifications (ECMs). All measurements were performed in air. The parameters of the ECM were: -450 mV versus platinum for 30 s in a 0.1 mM solution of 4-diazo-*N,N*-diethylaniline tetrafluoroborate in DMF with 0.1 M LiClO₄ as supporting electrolyte.

dependent resistance of a metallic SWNT measured in air after a series of three ECMs. With every modification, the resistance of the tube increases, signifying a higher density of covalently attached *N,N*-diethylaniline moieties along the tube^[11]. This aspect is consistent with the observation that bGDR also increases^[12,13] with every subsequent ECM. At the same time, the absence of large GDR values (> 100) makes it unlikely that the gate dependence originates from the opening of a gap in the electronic band structure of the metallic tube. This assertion is supported by theoretical studies on various types of covalently functionalized SWNTs, according to which the main effect of the attached groups is to induce impurity states near the Fermi level that act as scattering centers.^[14] Gap opening in such tubes may also occur; however, this usually requires the presence of a high density of covalently bonded moieties in an ordered pattern^[15,16]. By performing separate control experiments in the absence of the diazonium salt, we have ensured that the resistance increase of the modified SWNT exclusively results from the covalently coupled *N,N*-diethylaniline moieties and not from unwanted modifications during the electrochemical step.^[11]

For an evaluation of the pH dependence of the devices, we first consider the minimum resistances obtained from the back-gating characteristics. Besides providing reproducibility, the use of the minimum resistance value ensures that the interpretation of the measurements is not obscured by hysteresis effects.^[4,9,17] In Figure 2, this quantity is plotted versus solution pH for a pristine metallic SWNT and the same tube with two different degrees of ECM. It is apparent that while the minimum resistance of the unmodified tube remains constant, it shows a notable increase with pH after the first and second ECM. Furthermore, the slope of the calibration curve and corre-

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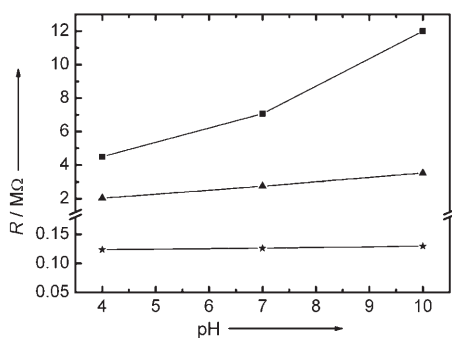


Figure 2. Resistance versus pH for a pristine metallic SWNT (stars, bGDR = 1.4) and for the same tube after 2 ECMs (triangles, bGDR = 2) and 4 ECMs (squares, bGDR = 4). The resistance values plotted correspond to the minimum resistance of the sample in solution at $V_{BG} = -3$ V. The connecting lines serve as guide to the eye.

spondingly the pH-sensitivity of the device are found to increase with the extent of ECM.

The pH sensitivity of the modified metallic SWNTs can be understood by considering that in chemically functionalized nanotubes, the sp^3 -bonded carbon centers introduced by the covalently attached groups act as scattering sites which determine the resistance of the tube^[12,13,15]. Figure 2 indicates that the scattering strength of the sp^3 -centers decreases with increasing protonation degree of the appended *N,N*-diethylaniline groups. This trend provides a hint that the scattering strength is proportional to the local charge density, as schematically illustrated by Figure 3. At sufficiently high pH, the *N,N*-diethylaniline groups are not protonated, allowing for partial delocalization of the lone electron pair on the nitrogen atom towards the nanotube through the intermediate benzene ring. By contrast, such electron donation is prevented at

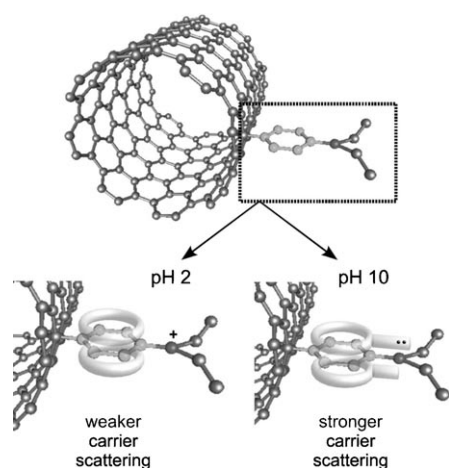


Figure 3. Schematic depiction of the sensing mechanism involving the *N,N*-diethylaniline moiety attached to a (8,8) metallic SWNT. At high pH, the lone pair of electrons on the nitrogen atom enhances the electron density on the aromatic ring due to resonance delocalization. This results in a stronger scattering for electron transport through the tube leading to a high resistance. On the contrary at low pH, the nitrogen atom is protonated and thus the electron density at the benzene ring is relatively lower. Correspondingly, the samples exhibit a lower resistance at acidic pH. Note that the atomic coordinates are not computed by any theoretical model.

low pH by the prevailing protonation of the nitrogen atom. With every subsequent modification, the number of attached *N,N*-diethylaniline groups increases and thereby the average strength of pH-dependent scattering increases. Hence, the pH sensitivity of the modified tube is expected to increase with every ECM, consistent with the results in Figure 2. The persistence of the substituted amino groups on the nanotube side-walls is supported by spectroscopic measurements on glassy carbon electrodes modified by electro-reduction of a 4-diazo-*N,N*-diethylaniline salt.^[18] Furthermore, in separate experiments we have observed that the resistance of metallic SWNTs electrochemically modified with 4-bromobenzene diazonium salt (where the diethylamino group was absent) did not show any remarkable pH dependence. Moreover, control experiments with pH buffers of different ionic strengths have shown that the ionic strength has a negligible influence on the device resistance at a certain pH (see Supporting Information).

Figure 4 depicts the pH-dependent electrical characteristics of three different metallic SWNTs after the first ECM was per-

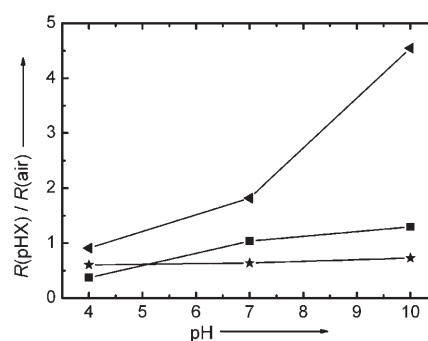


Figure 4. Normalized resistance versus pH for three different metallic SWNTs electrochemically modified once under the same conditions as in Figures 1 and 2. The bGDR values for the three SWNTs after modification are 1.7 (stars), 3 (squares) and 20 (triangles).

formed with identical parameters as for the sample in Figure 2. In this plot, the resistance in solution was normalized with respect to their corresponding resistance in air, to enable comparison of the responses from different devices with varying starting resistance. None of the nanotubes exhibit measurable pH dependence prior to modification. The bGDR of the three unmodified tubes is 1.0, 1.2 and 2.6, respectively, which increased to 1.7, 3 and 20 after ECM. The bGDR represents a qualitative measure for the defect density, with bGDR ≈ 1 indicative of a close-to-perfect metallic nanotube^[12,13]. Based upon the data in Figure 4, two conclusions can be drawn. First, the modification extent of the nanotubes increases with the amount of contained defects, which is in agreement with the well-documented enhancement of chemical reactivity at tube defects.^[15,19] Secondly, the pH sensitivity of the modified nanotubes is correlated with the magnitude of the bGDR after tube modification.

In addition to the back-gated configuration, the device characteristics were also measured by liquid-gating in a manner similar to previous studies.^[5,6] The complete gate dependence

of resistance curves are imprinted with a slight hysteresis both for the back-gated and liquid-gated configurations. In order to avoid ambiguities, we focus on a reproducible portion of the curve, that is the gate voltage scan from positive to negative voltages. Figure 5a shows this portion of the back-gate de-

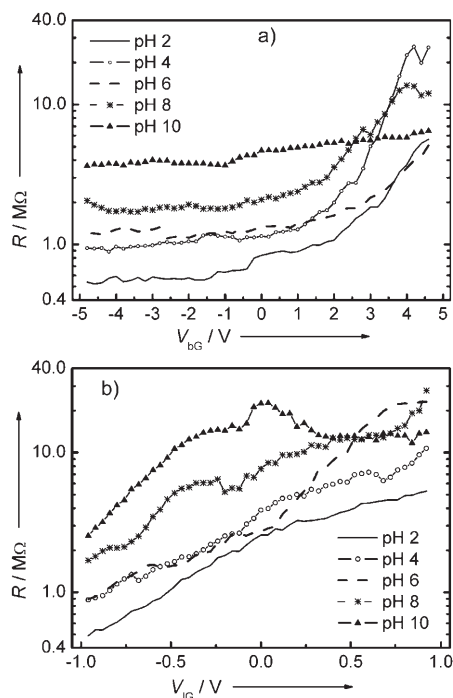


Figure 5. pH dependent transport measurements on a metallic SWNT after two ECMs (0.1 mM 4-diazo-*N,N*-diethylaniline tetrafluoroborate, 0.1 M LiClO₄ in DMF, -0.45 V, 30 s). a) Back-gate and b) liquid-gate dependence of resistance in various buffer solutions.

pendence for a metallic SWNT after two ECMs. It is apparent that at each pH value, the tube resistance is relatively constant for values of $V_{BG} < -1$ V. Furthermore, the minimum resistance increases with increasing pH, consistent with the data in the previous Figures. Similar curves for the liquid-gate dependence of the same sample are presented in Figure 5b. In this case, the resistance increase with pH is discernable for all values of liquid-gate voltages ($V_{LG} < 0$ V). The values of the minimum re-

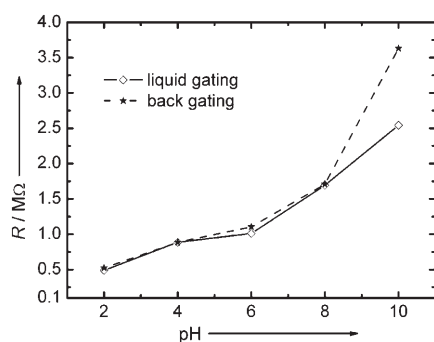


Figure 6. Minimum resistance (at $V_{BG} = -5$ V or at $V_{LG} = -1$ V) as a function of solution pH for back-gated and liquid-gated configurations for the sample in Figure 5.

sistance obtained from both sets of measurements are plotted as a function of pH to obtain the calibration curves in Figure 6.

The gate dependence curves in Figures 5a and b provide additional support for the pH-dependent carrier scattering model. In both gating configurations, a resistance increase with rising pH is clearly observable within the negative gate voltage regime. The possibility of a shift of the characteristics (comparable to the threshold voltage shift in semiconducting tubes) can be excluded by observing that the resistance upon back-gating saturates for $V_{BG} < -2$ V. This observation is contradictory to the possibility of band-gap opening being the origin of the pH-dependent sensitivity, which complements the argument given above in connection with Figure 1.

Finally, the quasi-linear shape of the calibration curve in Figure 6 deserves further attention. Since the resistance of the tube is associated with the protonation degree of the attached *N,N*-diethylaniline groups, one would expect a sigmoidal calibration curve similar to an acid-base titration curve^[20]. The absence of such a behaviour could be due to the covalent bonding of the diethylaniline group to the nanotube, which might shift the pK_a to values higher than ≈ 6.6 , the value reported for *N,N*-diethylaniline in solution. Alternatively, the groups could be attached to various sites along the tube where they exert different scattering strengths. Interactions between closely spaced attachment sites may lead to more complex behaviour^[21] than the classical Henderson-Hasselbach relationship^[20].

In conclusion, we have presented a novel approach to pH sensors based on the gentle covalent modification of metallic SWNTs with electrochemically generated amino-substituted phenyl radicals. The attached organic moieties function as pH-dependent carrier scattering sites, as a result of which the resistance of the modified tube varies as a function of pH. The degree of functionalization and hence the pH-sensitivity can be controlled by varying the parameters of ECM. Defective tubes attain a high functionalization degree even after the first modification due to the higher reactivity at defect sites. Utilizing this principle, functionalized SWNTs can be designed for various chemical- and bio-sensing applications, offering new perspectives for the development of sensitive nanoscale (bio-) chemical sensors. In future work, it could be extended to dense networks of nanotubes, where the transport is predominantly through the metallic fraction.

Experimental Section

SWNTs produced by the arc-discharge process (MER, Tucson, AZ) were deposited from an aqueous dispersion on a n^+ -doped silicon substrate with thermally grown SiO₂ (thickness 200 nm). Individual tubes were contacted by 15 nm thick AuPd electrodes with 0.3 nm titanium as adhesion promoter. The separation between the electrodes was ≈ 1.5 μ m. Electrochemical modification (ECM) of metallic SWNTs was carried out in an electrochemical cell by applying -450 mV versus a platinum pseudo-reference electrode for 30 s in *N,N*-dimethylformamide (DMF) containing 0.1 mM 4-diazo-*N,N*-diethylaniline tetrafluoroborate and 0.1 M LiClO₄ as supporting electrolyte. After each ECM, the samples were heated at 100 °C for one hour to remove solvent molecules.

The sensor experiments were performed by measuring the complete back-gate characteristics in a ≈ 20 nL droplet (≈ 50 μm diameter) of the test solution before and after ECM of the tubes. Ready-to-use standard pH buffers (Hydrion™ -total ionic strength ca. 0.05 M) from Aldrich were used as test solutions. In addition to the back-gated configuration, the device characteristics were also measured through liquid-gating in a manner similar to previous studies^[5,6]. In our experiments, an adjacent AuPd electrode (≈ 0.6 mm away, see Supporting Information) that was in contact with the test solution droplet was used as the gate, whose voltage was swept in the range of $V_{\text{IG}} = -1$ V to $+1$ V, within which the leakage current was well below 1 nA. To prevent evaporation of the droplet, the sample with the aqueous test solution was covered by a non-volatile organic liquid (squalane) during the measurements.

Keywords: carbon nanotubes · electrochemistry · functionalization · sensors · surface chemistry

- [1] G. Cuniberti, G. Fagas, K. Richter, *Introducing Molecular Electronics, (Lecture Notes in Physics Vol. 680)*, Springer Verlag, Berlin-Heidelberg, **2005**.
- [2] P. G. Collins, K. Bradley, M. Ishigami, A. Zettl, *Science* **2000**, *287*, 1801.
- [3] J. Kong, N. R. Franklin, C. Zhou, M. G. Chapline, S. Peng, K. Cho, H. Dai, *Science* **2000**, *287*, 622.
- [4] W. Kim, A. Javey, O. Vermesh, Q. Wang, Y. Li, H. Dai, *Nano Lett.* **2003**, *3*, 193.
- [5] M. Krueger, M. R. Buitelaar, T. Nussbaumer and C. Schoenenberger, *Appl. Phys. Lett.* **2001**, *78*, 1291.
- [6] S. Rosenblatt, Y. Yaish, J. Park, J. Gore, V. Sazonova, P. L. McEuen, *Nano Lett.* **2002**, *2*, 869.
- [7] K. Bradley, J. C. P. Gabriel, M. Briman, A. Star, G. Gruner, *Phys. Rev. Lett.* **2003**, *91*, 218301.
- [8] K. Besteman, J. Lee, F. G. M. Wiertz, H. A. Heering, C. Dekker, *Nano Lett.* **2003**, *3*, 727; E. Katz, *ChemPhysChem* **2004**, *5*, 1085; M. Trojanowicz, *Trends Anal. Chem.* **2006**, *25*, 480; G. Gruner, *Anal. Bioanal. Chem.* **2006**, *384*, 322.
- [9] K. Balasubramanian, R. Sordan, M. Burghard, K. Kern, *Nano Lett.* **2004**, *4*, 827.
- [10] Y. Fan, B. R. Goldsmith, P. G. Collins, *Nature Mater.* **2005**, *4*, 906.
- [11] K. Balasubramanian, M. Friedrich, C. Jiang, Y. Fan, A. Mews, M. Burghard, K. Kern, *Adv. Mater.* **2003**, *15*, 1515.
- [12] K. Balasubramanian, M. Burghard, K. Kern, M. Scolari, A. Mews, *Nano Lett.* **2005**, *5*, 507.
- [13] M. Bockrath, W. Liang, D. Bozovic, J. H. Hafner, C. M. Lieber, M. Tinkham, H. Park, *Science* **2001**, *291*, 283.
- [14] H. Park, J. Zhao, J. P. Lu, *Nano Letters* **2006**, *6*, 916.
- [15] M. Burghard, *Surf. Sci. Reports* **2005**, *58*, 1.
- [16] H. Hu, B. Zhao, M. A. Hamon, K. Kamaras, M. E. Itkis, R. C. Haddon, *J. Am. Chem. Soc.* **2003**, *125*, 14893; K. N. Kudin, H. F. Bettinger, G. E. Scuseria, *Phys. Rev. B* **2001**, *63*, 045413.
- [17] M. Radosavljevic, M. Freitag, K. V. Thadani, A. T. Johnson, *Nano Lett.* **2002**, *2*, 761.
- [18] J. K. Kariuki, M. T. McDermott, *Langmuir* **2001**, *17*, 5947.
- [19] M. W. Zhao, Y. Xia, J. P. Lewis, L. Mei, *J. Phys. Chem. B* **2004**, *108*, 9599.
- [20] D. A. Skoog, D. M. West, *Fundamentals of Analytical Chemistry 8th Ed.* Thomson Brooks/Cole, CA, 2003.
- [21] A. Onufriev, D. A. Case, G. M. Ullmann, *Biochem.* **2001**, *40*, 3413.

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