Supporting Information

# High-performance 3D tubular nanomembrane sensor for DNA detection

*Mariana Medina-Sánchez[1*], Bergoi Ibarlucea[2*], Nicolás Pérez [1], Dmitriy D. Karnaushenko [1], Sonja M. Weiz [1], Larysa Baraban[2], Gianaurelio Cuniberti[2], Oliver G. Schmidt[1,3]*

*[1]Institute for Integrative Nanosciences, IFW Dresden, Helmholtzstraße 20, 01069 Dresden, Germany*

*[2] Institute of Materials Science and Max Bergmann Center for Biomaterials, Center for Advancing Electronics Dresden (CfAED), Dresden University of Technology, 01062 Dresden, Germany*

*[3]Material Systems for Nanoelectronics, Chemnitz University of Technology, Reichenhainer Straße 70, 09107 Chemnitz, Germany*

**Characterization of the biofunctionalization by X-Ray Photoelectron Spectroscopy (XPS)**

The XPS study indicated a successful surface modification. **Table S1** shows the atom content in percentage extracted from the XPS survey scan. The 11-MUA deposition brought an increase of the carbon content from 23.35% to 52.64%. Sulphur atoms that belong to the thiol group also appeared with 2.36%, which were hardly visible on the bare gold surface (0.31%). After the oligonucleotide immobilization, the nitrogen and phosphorus concentrations increased due to their presence in the DNA structure. After each surface modification step, the gold percentage was also decreasing. High resolution spectra of the C1s (**Figure S2a**), S2p (**Figure S2b**), N1s (**Figure S3a**) and P2p (**Figure S3b**) regions were also recorded. The introduction of 11-MUA increased the peak at 289 eV, which corresponds to the C=O bonds of the carboxylic groups. This peak was slightly visible on the bare gold surface, which is ascribed to contamination with hydrocarbon pollutants to which gold is prone when it is exposed to environmental conditions,[1] and it is later shielded under the thicker biomolecule layer after the DNA deposition. Additionally, the doublet that appeared in the S2p spectrum also indicated the presence of the thiolated molecule. This doublet consists of the S2p3/2 and S2p1/2 peaks at 162 eV and 163 eV, respectively. The first one typically arises when sulphur is bonded as a thiolate to gold (S-Au),[2] while the second one is attributed to the creation of new sulphur species by the progressive Au-S bond damage with increasing X-ray radiation time.[3] Finally, the presence of DNA was confirmed by the presence of nitrogen and phosphorus atoms as seen in the N1s and P2p spectra. The N1s spectrum showed a core-level peak between 398 and 402 eV, consistent with previously published results, in which the different bonding states of the nitrogen atoms belonging to the nucleotides present a narrow distribution. The signal between 398 and 399 eV corresponds to the imino species (N=C) while the one above 400 eV can be attributed to N atoms with single bonds.[4]

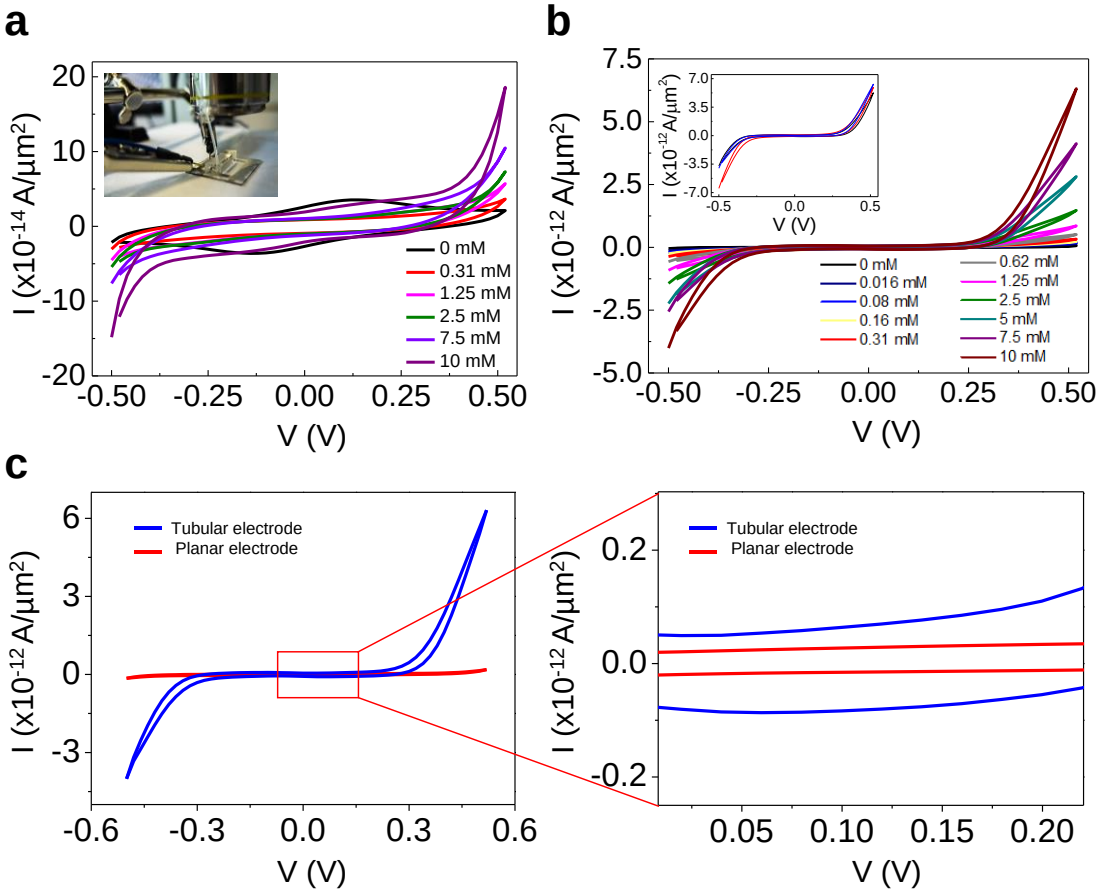


**Figure S1.** Characterization of unmodified electrodes with ferricyanide. Cyclic voltammograms of (a) planar and (b) rolled-up electrodes. Inset in (a) shows setup of contacting needles with the complete microfluidic chip. Inset in (b) shows the average of three cyclic voltammograms for three different electrodes, and (c) comparison of the voltammograms at 10mM ferricyanide with a zoom showing the increased of capacitive currents of the tubular electrodes compared to the planar ones.

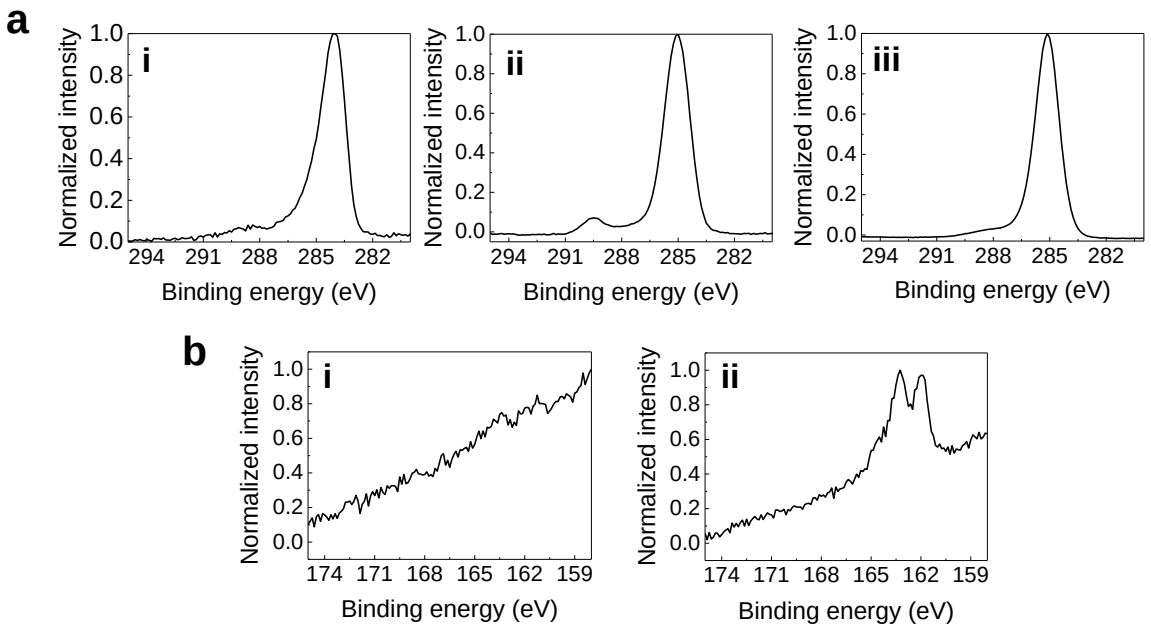


**Figure S2.** XPS measurements. (a) High resolution spectra of C1s electron for (i) bare electrode, (ii) 11-MUA SAM, and (iii) DNA probe. (b) High resolution spectra of S2p electron for (i) bare electrode and (ii) 11-MUA SAM.

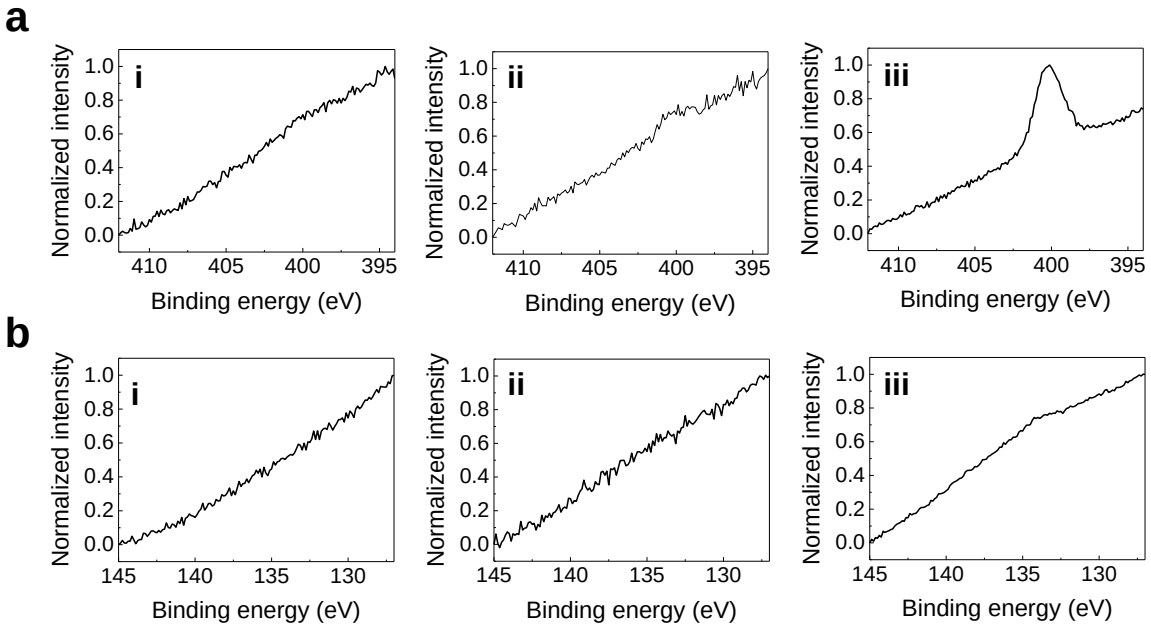


**Figure S3.** XPS measurements. (a) High resolution spectra of N1s electron for (i) bare electrode, (ii) 11-MUA SAM, and (iii) DNA probe. (b) High resolution spectra of P2p electron for (i) bare electrode, (ii) 11-MUA SAM and (iii) DNA probe.

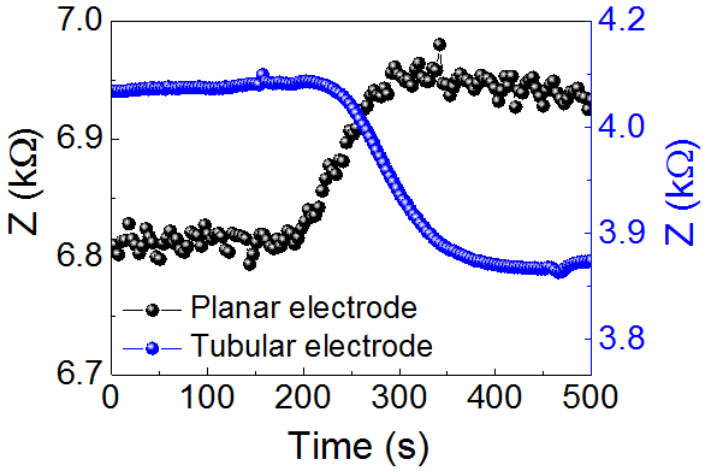


**Figure S4.** Chronoimpedance at 5 kHz of 2 pM target DNA injection on biofunctionalized electrodes (planar and tubular). Opposite behavior can be observed when DNA reaches the biomolecule layer at electrode surface.

**EIS modelization parameters**

The impedance relates to the fitting parameters as follows:

Constant phase elements $Z = 1/(Q\, j\omega)^n$

Warburg impedance $Z = 1/(W\, (j\omega)^{1/2})$

Where W relates to the diffusion coefficient and $\omega$ is the angular frequency.

n is an index that varies from 0 to 1. The case n = 1 describes an ideal capacitor while the case n = 0 describes a pure resistor.

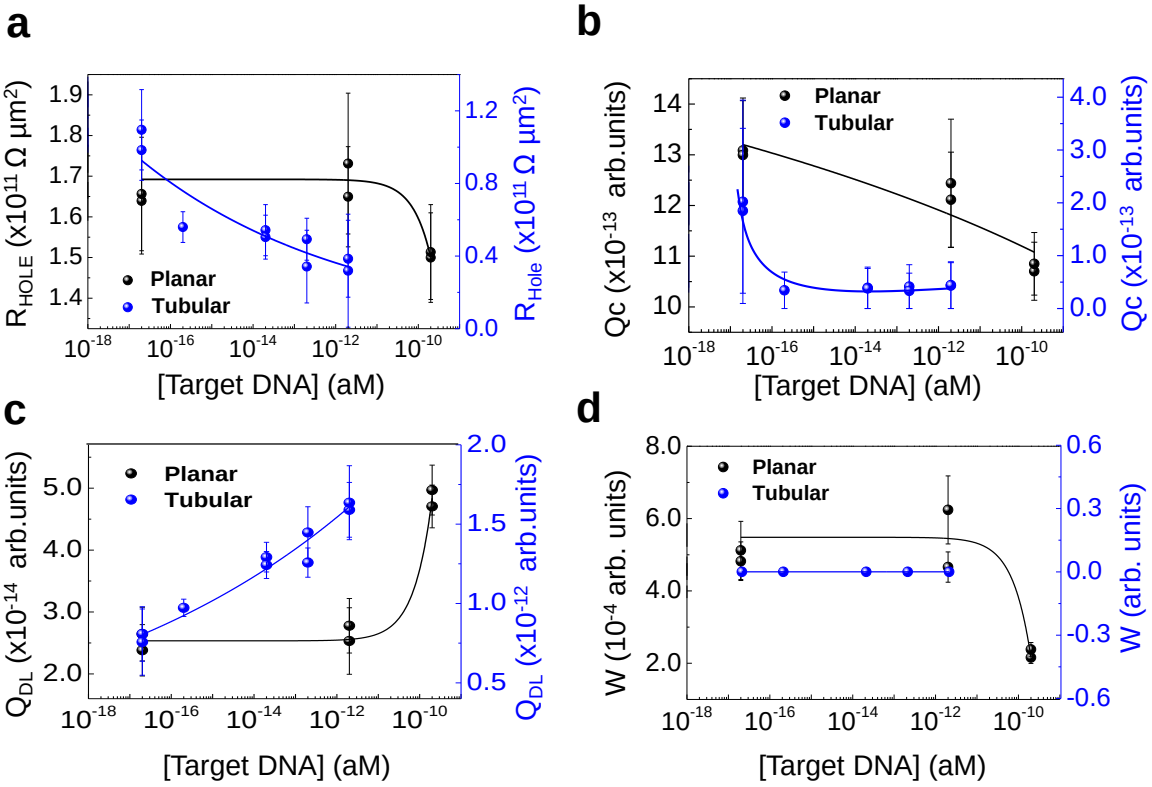


**Figure S5.** Variation of fitting parameters after hybridization of different DNA concentrations: (a) $R_{HOLE}$, (b) Capacitance component of the organic coating ($Q_C$), (c) capacitance component of the associated to the double layer ($Q_{DL}$), and (d) Warburg fitting coefficient

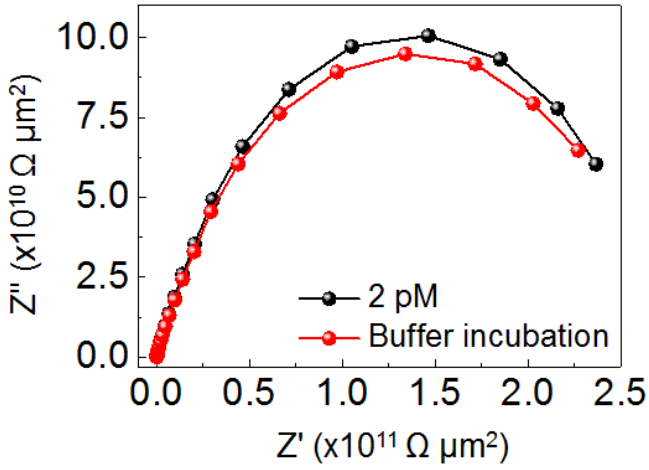


**Figure S6.** Comparison of impedance measurements after 2pM target DNA hybridization and after further buffer incubation, showing that the results from the calibration were not caused by the buffer itself or by electrode degradation through time.

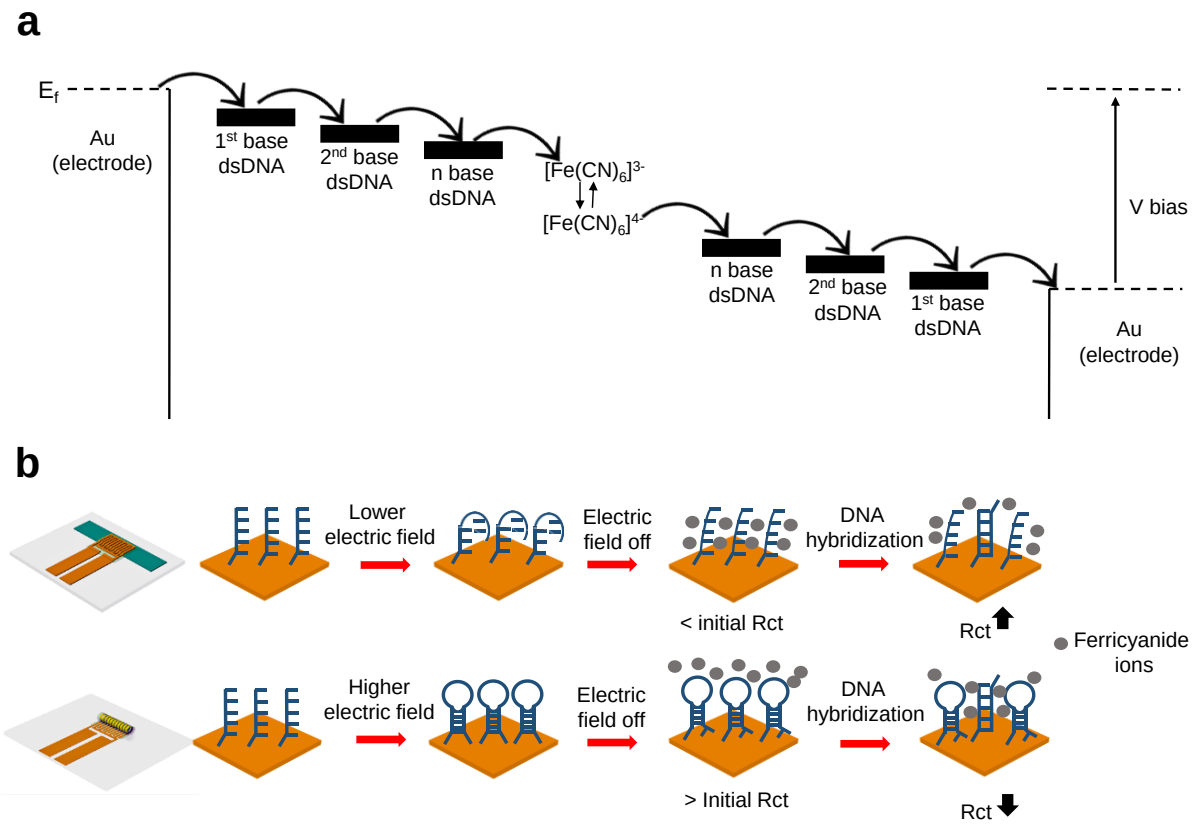


**Figure S7.** (a) Charge transport from and to gold electrodes in rolled-up electrodes. The first electrode provides the charge that is transported through the hybridized DNA base pairs, allowing reaching the ferricyanide for its oxidation/reduction. The double stranded DNA from the second electrode also permits the transport to the gold for the readout of the signal. (b) Conformational changes of DNA through the different experiment steps. The short oligonucleotides tend to expand in the planar electrodes, and after hybridization a simple organic coating occurs, maintaining the ferricyanide ions far from the gold. In the rolled-up electrodes, the DNA forms a self-entangled form due to the higher electric field during the cyclic voltammetry test to check the performance of the electrode. This self-entangled form finds it more difficult to recover the expanded form, happening only during the hybridization event and allowing only then the access of the ferricyanide ions to the gold surface.

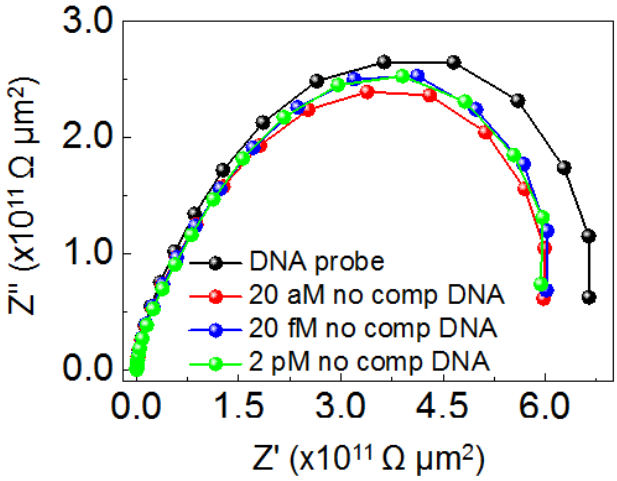


**Figure S8.** Impedance values after incubation of biofunctionalized tubular electrodes with non-complementary target DNA.

**Table S1.** Atomic concentration (%) of the surface after each modification step, obtained from the survey scan of the XPS.

| Sample | C1s [%] | N1s [%] | O1s [%] | P2p [%] | S2p [%] | Au4f [%] |
|---|---|---|---|---|---|---|
| Bare gold | 23.35 | 0.11 | 1.12 | 0.00 | 0.31 | 75.11 |
| 11-MUA | 52.64 | 0.25 | 7.33 | 0.01 | 2.36 | 37.39 |
| DNA | 65.36 | 2.04 | 3.33 | 0.97 | 1.85 | 26.44 |

## References

(1) Canaria, C. A; So, J.; Maloney, J. R.; Yu, C. J.; Smith, J. O.; Roukes, M. L.; Fraser, S. E.; Lansford, R. *Lab Chip* **2006**, *6* (2), 289–295.

(2) Snow, A. W.; Jernigan, G. G.; Ancona, M. G. *Analyst* **2011**, *136* (23), 4935-4949.

(3) Büttner, M.; Belser, T.; Oelhafen, P. *J. Phys. Chem. B* **2005**, *109* (12), 5464–5467.

(4) Ptasińska, S.; Stypczyńska, A.; Nixon, T.; Mason, N. J.; Klyachko, D. V; Sanche, L. *J. Chem. Phys.* **2008**, *129* (6), 065102.