Selective ion-sensing with membrane-functionalized electrolyte-gated carbon-nanotube field-effect transistors

K. Melzer, A. M. Münzer, E. Jaworska, K. Maksymiuk, A. Michalska, and G. Scarpa

Technische Universität München, Institute for Nanoelectronics, Arcisstraße 21, 80333 München, Germany.

University of Warsaw, Faculty of Chemistry, Pasteura 1, 02-093 Warsaw, Poland

1. Response of ISE in an all-solid-state arrangement

The ion-selective membranes (ISMs) were also characterized with respect to sensitivity and selectivity in an all-solid-state ion-selective electrode configuration. All-solid state ion-selective electrodes were prepared by drop-casting a THF based CNT solution on top of a glassy carbon electrode (for the electrode placed in position with glassy carbon layer facing up). The total amount of 0.08 mg of CNTs was applied per electrode. After drying of the solvent, the CNT layer was covered with 30 µl of the ion-selective membrane cocktail (in portions of 10 µl). After drying the membrane solvent in lab atmosphere the as obtained ion-selective electrodes were conditioned in a $10^{-3}$ M solution of the respective primary ion for 12 h priori measurement.

To investigate the sensitivity towards the primary ions, the ion activity was decreased stepwise while recording the potentiometric responses. Additionally, the response of the membranes towards different interfering ions (K$^+$-selective membrane: Na$^+$ and Ca$^{2+}$, Ca$^{2+}$-selective membrane: Na$^+$ and Mg$^{2+}$) was tested. The results for the K$^+$-selective membrane are presented in Figure S1 a, proving the sensitive and selective response towards K$^+$. A lower detection limit for the primary ion of $10^{-7}$ M is achieved. Between $10^{-1}$ M and $10^{-7}$ M the response shows a linear behavior with a slope of 59.8 mV/dec, which is relatively close to the theoretical response limit of 59.5 mV/dec for monovalent cations. The response curve towards the interfering ion Na$^+$, revealed a smaller slope (49.9 mV/dec) within a much smaller activity range. The response curve towards Ca$^{2+}$ has a slope of 75.5 mV/dec.
The results for the Ca\textsuperscript{2+}-selective membrane are presented in Figure S1 b, proving the sensitive and selective response towards Ca\textsuperscript{2+}. A lower detection limit for the primary ion of 10\textsuperscript{-6} M is achieved. Between 10\textsuperscript{-5} M and 10\textsuperscript{-6} M the response shows a linear behavior with a slope of 21.1 mV/dec, which is relatively close to the theoretical response limit of 29.8 mV/dec for divalent cations. The response curve towards Mg\textsuperscript{2+} has a slope of 32.1 mV/dec within a much smaller activity range.

The response curve towards the interfering ion Na\textsuperscript{+}, revealed a bigger slope (45.4 mV/dec). The results for the anion-selective membrane are presented in Figure S1 c. A lower detection limit for the primary ion Cl\textsuperscript{-} of 10\textsuperscript{-5} M is achieved. Between 10\textsuperscript{-1} M and 10\textsuperscript{-5} M the response shows a linear behavior with a slope of -51.3 mV/dec, which is relatively close to the theoretical limit.

2. Changes in transconductance

Figure 3a-d shows transfer curves I\textsubscript{SD} vs. V\textsubscript{EG} recorded in different types of electrolytes with a CNT-FET gated with either a Pt-wire or a gate electrode, which was further modified with a K\textsuperscript{+}-selective polymeric membrane. To quantify the shift of the transfer curves, we extracted the threshold voltage V\textsubscript{th} by fitting the linear regime and extracting the intercept with the x-axis. In Figure S2 the response of the K\textsuperscript{+}-selective CNT-FET towards the ions K\textsuperscript{+}, Na\textsuperscript{+} and Ca\textsuperscript{2+} is exemplarily shown for two different concentrations.

The slope of the LinearFit $\Delta I_{SD}/\Delta V_{EG}$ (Figure S2, left panel) gives us the value of the transconductance. According to the following equation,

$$ g_m = \frac{\Delta I_{SD}}{\Delta V_{EG}} = \frac{W}{L} \mu \varepsilon_0 \varepsilon_{eff} V_D $$

a change in the transconductance can be attributed to either a change in the charge carrier mobility or it goes along with a change of the effective gate capacitance $C_{eff}$, which is mainly given by the in-series capacitances of the semiconductor/electrolyte and the electrolyte/gate-electrode interface. The transfer curves of the K\textsuperscript{+}-selective CNT-FET show a significant change in the transconductance, if they are recorded upon different concentrations of an interfering ion with the same valency, in this case Na\textsuperscript{+} (see Figure S2 and S3).

![Figure S2](image-url)

Figure S2. Transfer curves recorded with a K\textsuperscript{+}-selective CNT-FET in 10\textsuperscript{-3} M and 10\textsuperscript{-5} M of KCl (left panel), NaCl (middle) or CaCl\textsubscript{2} (right panel). For KCl a clear shift of the threshold voltage V\textsubscript{th} (intercept of the LinearFit with the x-axis) towards more positive gate voltages with increasing ion activities is obtained. For NaCl the transconductance (slope of LinearFit) decreases with decreasing ion activity, whereas V\textsubscript{th} stays almost constant. For CaCl\textsubscript{2} the change in the transconductance is rather small and V\textsubscript{th} shifts slightly towards more positive gate voltages with decreasing ion activity.
Figure S3. Transconductance change of the K$^+$-selective CNT-FET for different activities of the primary ion K$^+$ or the interfering ions (Na$^+$ and Ca$^{2+}$). The black data points correspond to a normal Pt-gated CNT-FET. For a better comparison the data were normalized with respect to the transconductance at an activity of $10^{-4}$ M. The right panel shows the difference between the normalized value for an activity of $10^{-2}$ M and $10^{-1}$ M. The most significant change of the transconductance was observed for the interfering ion with the same valency, in this case Na$^+$.

The same behavior was observable for the Ca$^{2+}$-selective CNT-FET, when operated in different activities of Mg$^{2+}$ (see Figure S4). Since an ion-activity dependent change of the CNT-FET’s mobility should be independent on the type of membrane used as modification and should rather depend on the valency of the ion (see the different response of the either K$^+$- or Ca$^{2+}$-selective CNT-FET towards sodium in Figure S3 and S4), we are suggesting that especially interfering ions with the same valency as the primary ion influence the membrane/solution interface, which results in a change of the membrane capacity.

Figure S4. Transconductance change of the Ca$^{2+}$-selective CNT-FET for different activities of the primary ion Ca$^{2+}$ or the interfering ions (Mg$^{2+}$ and Na$^+$). The black data points correspond to a normal Pt-gated CNT-FET. For a better comparison the data were normalized with respect to the transconductance at an ion activity of $10^{-5}$ M. The right panel shows the difference between the normalized value for an activity of $10^{-2}$ M and $10^{-1}$ M. The most significant change of the transconductance was observed for the interfering ion with the same valency, in this case Mg$^{2+}$.

3. Leakage current between modified gate-electrode and source contact

Figure S5 displays that the leakage current $I_{GS}$ is about two orders of magnitude ($I_{GS} < 100$ nA) lower than the drain current. The curves were recorded in a KCl concentration of $10^{-2}$ M. The leakage current of the membrane-modified CNT-FET is comparable to the one obtained with a normal Pt-gated CNT-FET.
Leakage current $I_{GS}$ between gate and source contact for a $K^+$-selective CNT-FET and a normal Pt-gated CNT-FET. The corresponding transfer curves $I_{SD}$ vs. $V_{EG}$ are depicted in Figure 2.