

# From Rigid to Flexible: Solution-Processed Carbon Nanotube Deposition on Polymeric Substrates for the Fabrication of Transistor-Based Ion Sensors

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**Abstract**—Electrolyte-gated field-effect transistors (EG-FETs) are widely used in the growing field of biochemical sensing applications, due to their manifold advantages, such as large specific capacitance, low operating voltage, and intrinsic signal amplification. In this work, carbon nanotube (CNT) EG-FET (EG-CNTFET)-based sensors for ammonium ( $\text{NH}_4^+$ ) detection are reported. The active semiconducting single-walled CNTs layer was manufactured through a cost-effective and scalable spray deposition technique. To achieve high-quality semiconducting networks, the CNT ink was optimized. Atomic force microscopy (AFM) analysis was used to optimize the CNT concentration and significantly reduce the posttreatment time from the previously reported 12 to 1 h. The optimized ink was then used to fabricate EG-CNTFETs first on standard rigid Si/SiO<sub>2</sub> substrate and then on flexible polyimide (PI) foils. Both devices showed typical p-type behavior with an on-off ratio in the order of magnitude of  $1 \times 10^3$  A/A. Furthermore, as proof of concept, we demonstrated the detection of the  $\text{NH}_4^+$  ions with EG-CNTFETs fabricated on a flexible substrate and functionalized with nonactin ion-selective membrane. The calibration curve of the fabricated sensors showed a linear detection range for ammonium from 0.01 to 10 mM, covering the entire range of physiological concentrations of interest, with an average sensitivity of 0.346  $\mu\text{A}/\text{decade}$  and a 94.35% coefficient of determination.

**Index Terms**—Biosensors, carbon nanotubes (CNTs), ion-selective membranes, planar gate, sweat sensing, wearable electronics.

## I. INTRODUCTION

ELECTROLYTE-GATED field-effect transistors (EG-FETs) have recently attracted paramount interest in the field of biosensing, thanks to several distinctive features such as superior electronic properties, intrinsic signal amplification, suitability for small-scale integration with in vitro systems, low operating voltages ( $<|1|$  V) allowing operation in physiological solutions (i.e., water-based electrolytes) [1], [2], [3], [4], [5].

Among the available channel materials for EG-FETs, carbon nanotubes (CNTs) have demonstrated high potential for sensitive biosensing applications. CNTs are 1-D nanomaterials, with a diameter that varies from 0.4 to 100 nm and a length up to tens of micrometer [6]. The nanometric dimensions, comparable to the ones of the analytes of interest, and the high aspect ratio make them especially interesting for biosensing. Moreover, the large surface area offered for the immobilization of the bio-recognition elements can be exploited to achieve an enhancement of the overall biosensor sensitivity [7], [8]. Another extremely important feature is the solution processability that allows CNTs to be unobtrusively integrated into almost any type of substrate, from traditional rigid substrates (e.g., glass and Si/SiO<sub>2</sub>), to flexible polymeric foils including, among the others, polyimide (PI) and polyethylene terephthalate (PET) [9], [10]. Furthermore, such flexible substrates facilitate the design and integration of EG-CNTFETs for example in wearable platforms of arbitrary shape.

Over the past few years, wearable sensors have become more and more widespread, thanks to the possibility to perform noninvasive and real-time monitoring of various physiological parameters (e.g., heart rate, temperature, and blood pressure). One of the most interesting sources of information for wearables is sweat, due to its richness of helpful analytes, such as metabolites, proteins, and ions. [11]. In a recent study, we developed an EG-CNTFET-based biosensor for ammonium ( $\text{NH}_4^+$ ) detection, which was presented at IEEE IFETC 2022 [12]. Among the different

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analytes, ammonium ( $\text{NH}_4^+$ ) has recently been explored as a possible marker for the starting point of the metabolic breakdown of the proteins caused by the depletion of the carbohydrates (especially in the physiological concentrations: 0.12–2.17 mM) [13].

Here, we report our initial steps toward developing EG-CNTFET-based  $\text{NH}_4^+$  sensors on flexible substrate. To do so, first, the fabrication process was established on standard Si/SiO<sub>2</sub> substrate. In fact, Si/SiO<sub>2</sub> represents an ideal substrate for the optimization of a fabrication process, thanks to its manifold favorable properties, such as low roughness, good wettability, mechanical, and thermal stability. The semiconducting channel was deposited through a cost-effective and scalable spray deposition technique compatible with rigid/polymeric surface coating. We focused our efforts on the preparation of the CNT ink, to achieve high-quality thin semiconducting CNT network. The fabrication process was subsequently adapted to fabricate EG-CNTFETs on flexible PI substrate.

Finally, as proof of concept, the EG-CNTFETs were functionalized with a nonactin ion-selective membrane for the detection of  $\text{NH}_4^+$ . Only the specific ions (i.e.,  $\text{NH}_4^+$ ) can be transported across the ion-selective membrane, hence ensuring sensitivity and selectivity [14], [15]. The fabricated sensors were tested for the detection of  $\text{NH}_4^+$  over a range of concentrations from 0.01 to 100 mM. The calibration curve of the fabricated sensors showed a linear detection range for ammonium from 0.01 to 10 mM, with an average sensitivity of 0.346  $\mu\text{A}/\text{decade}$  and a coefficient of determination of 94.35%.

## II. MATERIALS AND METHODS

All chemicals were purchased from Sigma-Aldrich, unless otherwise stated. All solutions and dispersions were prepared using deionized (DI) water with a resistivity of 18.2 M $\Omega$  cm produced by a Milli-Q system (Millipore, SAS, France). The main steps of the fabrication of the proposed EG-CNTFET-based sensors are depicted in Fig. 1, while an overview of each separate process is presented in the following Sections.

### A. Semiconducting CNT Ink Preparation

For the preparation of the main dispersion of CNTs, 0.05%wt CNTs (95% semiconducting, catalog number 773735) were dispersed in DI water using 0.5%wt sodium carboxymethyl cellulose (CMC) as surfactant [16], [17]. The detailed description of the preparation of the CNT dispersion is given in Section 1.1 of the Supporting Information. Before the spray deposition, the CNT main dispersion was diluted in 1.3 mM CMC using different dilution ratios, for the preparation of five inks: 1:15, 1:30, 1:75, 1:150, and 1:300.

### B. Electrode Fabrication

The layout of the EG-CNTFETs consists of a planar gate electrode and interdigitated electrodes (IDEs) for the source and drain (channel length  $L = 50 \mu\text{m}$ , channel width  $W = 57 \mu\text{m}$ ), with an active area of 8.85 mm<sup>2</sup>.

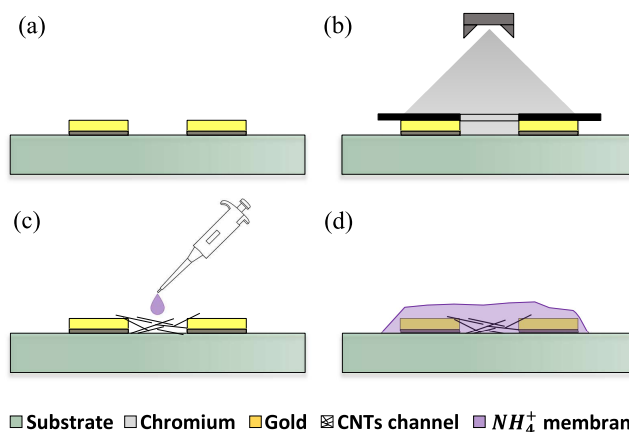


Fig. 1. Schematic representation of the electrolyte gated field-effect transistors (EG-CNTFETs) fabrication process: (a) thermally evaporated layer of 10 nm of chromium (adhesion layer) and 50 nm of gold, structured by lift off, (b) spray deposition of the semiconducting CNTs through a metallic shadow mask, employed to pattern the active area of the devices, (c) drop-casting of 10  $\mu\text{L}$  of  $\text{NH}_4^+$ -selective membrane on top of the active area of the devices, and (d) schematic side-view of the obtained EG-CNTFET-based  $\text{NH}_4^+$  sensor.

The three electrodes were patterned by one step of standard negative photolithography on Si/SiO<sub>2</sub> (100 nm oxide thickness, Microchemicals GmbH, Germany) or PI substrates (50  $\mu\text{m}$  thickness, Kapton<sup>1</sup> EN, DuPont<sup>2</sup>, USA), followed by thermal evaporation (MBRAUN ProVap 5G, equipped with an INFICON SQM-160 rate-thickness monitor) of 10 nm of chromium (Cr) and 50 nm of gold (Au). The Cr was employed as adhesion layer between the substrate and the Au.

### C. Spray Deposition of the Semiconducting CNT Ink

The spray deposition was carried out by means of an automated system equipped with an industrial air atomizing spray valve (Nordson EFD 781S, USA). The experimental parameters of the spray deposition process are given in Section 1.2 of the Supporting Information. The spraying valve was programed to describe a serpentine shape above the active area of the device, to ensure homogeneous deposition of the ink. A complete cycle of the spraying valve is what is hereby defined as a “layer” of CNTs. After spraying, to remove the CMC surfactant and, at the same time, enhance the conductivity of the nanotubes (via acid doping), the devices were immersed in 2.90 M nitric acid ( $\text{HNO}_3$ ) for respectively 1, 6, and 9 h at room temperature [18], followed by a water bath for 30 min, and a final drying step on a hot plate at 100  $^\circ\text{C}$  for 30 min as well. From now on, this posttreatment will be synthetically recalled as  $\text{HNO}_3 + \text{H}_2\text{O}$  treatment.

The quality of the spray-deposited CNT layers was analyzed by atomic force microscopy (AFM) imaging (Nanosurf Core-AFM, Switzerland) after the acid posttreatment, as discussed in Section III-A.

### D. EG-CNTFETs Electrical Characterization

The electrical characterization of the EG-CNTFETs was carried out by means of a probe station, connected to a

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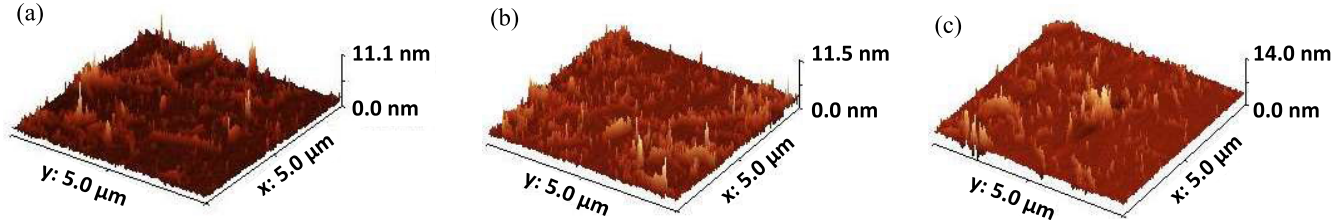


Fig. 2. Three-dimensional AFM topography of the spray-deposited CNT ink (1:30 dilution) on Si/SiO<sub>2</sub> after the removal of the CMC matrix through the HNO<sub>3</sub> + H<sub>2</sub>O treatment for (a) 1 h, (b) 3 h, and (c) 6 h of HNO<sub>3</sub> + H<sub>2</sub>O treatment time. The thicknesses of the three CNT random networks, reported in the z-axis scale, were similar between the three treatment times.

Keysight B1500A Semiconductor Device Parameter Analyzer. The source–drain resistance  $R_{DS}$  of the devices was measured, by sweeping the drain-source voltage  $V_{DS}$  from  $-0.5$  to  $0.5$  V and measuring the drain-source current  $I_{DS}$ . The transfer characteristics were recorded by sweeping the gate-source voltage  $V_{GS}$  from  $0.8$  to  $-0.8$  V, while maintaining the  $V_{DS}$  constant at  $-0.1$  V. The output characteristics were recorded varying the  $V_{DS}$  from  $0$  to  $-0.6$  V for different values of  $V_{GS}$  (from  $0.2$  to  $-0.8$  V, with  $-0.2$  V steps). The devices were then characterized in terms of threshold voltage  $V_{TH}$  and  $I_{ON}/I_{OFF}$  ratio.

#### E. EG-CNTFETs Functionalization

An NH<sub>4</sub><sup>+</sup>-selective membrane, based on the nonactin ionophore, was employed for the functionalization of the fabricated EG-CNTFETs on flexible PI. The membrane cocktail was prepared according to the procedure reported in [19], with some modification. The details on membrane preparation and subsequent device functionalization are given in Section 1.3 of the Supporting Information. The thickness of the drop-casted NH<sub>4</sub><sup>+</sup>-selective membrane was measured by means of a contact profilometer (Tencor<sup>2</sup> P-6 Stylus Profiler, KLA Instruments, California, USA).

#### F. EG-CNTFET-Based NH<sub>4</sub><sup>+</sup> Sensors Characterization

A custom-made polyethylene chamber was mounted to ensure the full coverage of the three electrodes with  $200 \mu\text{L}$  of DI water. Transfer and output characteristics were recorded immediately after the addition of DI water. While the initial electrical characterization described in Section II-D provided comprehensive information on the EG-FET characteristics, not all voltages were relevant for their use as sensors. To achieve more efficient testing during the sensor characterization, the voltage ranges were narrowed down: the transfer characteristics were recorded sweeping the  $V_{GS}$  from  $0.2$  to  $-0.8$  V, while maintaining the  $V_{DS}$  constant at  $-0.1$  V, while the output characteristics were recorded varying the  $V_{DS}$  from  $0$  to  $-0.5$  V for different values of  $V_{GS}$  (from  $0$  to  $-0.8$  V, with  $-0.2$  V steps). Afterward, the transfer characteristics were continuously recorded for 100 min, with 110 s interval between consecutive measurements, to let the devices stabilize. The devices were then tested as a sensor for the detection of five different NH<sub>4</sub><sup>+</sup> concentrations: 0.01, 0.1, 1, 10 and 100 mM. After the addition of each new

concentration, 3 transfer curves were recorded, keeping the 110 s interval between consecutive curves. For the extraction of the calibration curve, only the last two curves were taken into account, to correctly discard the transient caused by the injection of the new NH<sub>4</sub><sup>+</sup> concentration.

### III. RESULTS

#### A. Optimization of the Semiconducting CNT Ink

The key aspect of a semiconducting CNT network for transistor-oriented applications is the uniformity of the dispersion, in terms of adequate coverage of the surface [20], [21] and absence of bundles (i.e., agglomerates of CNTs). The presence of bundles, in particular, can lead to the formation of conductive pathways, being the electrical behavior of such bundles mainly determined by the metallic nanotubes present in the random network. The conductivity of such pathways does not respond to the applied gate voltage, reducing thus the ability to modulate the  $I_{DS}$  by tuning the applied  $V_{GS}$ , and ultimately hindering the performance of the devices [22]. The quality of the spray-deposited CNT network can be controlled through a fine tuning of the ink composition (e.g., CNT concentration), of the process parameters of the ink preparation (e.g., power and time of sonication and centrifugation), and of the parameters of the spray deposition itself (e.g., the thickness of the deposited layer and the regime of deposition) [16].

As a first step in the optimization of the semiconducting CNT ink, we focused on the optimization of the concentration of the CNTs, using Si/SiO<sub>2</sub> as substrate. Starting from the main 0.05%wt dispersion, we prepared five different inks with different dilutions. Considering that the properties of the spray-deposited layer are largely determined by the choice and concentration of the surfactant [23], [24], [25], we kept the concentration of the CMC constant to 1.3 mM.

After the deposition, the CMC matrix needs to be completely removed, since the presence of the surfactant (inherently insulating) lowers the conductivity of the spray-deposited CNT network. It was previously reported that the samples need to be immersed for 12 h in the HNO<sub>3</sub> + H<sub>2</sub>O treatment to completely remove the surfactant [26]. In this work, we explored the possibility of reducing this processing time, testing three possible posttreatment times: 1, 3, and 6 h.

For this purpose, we prepared samples with different CNT inks (spray depositing eight layers of the inks) and tried



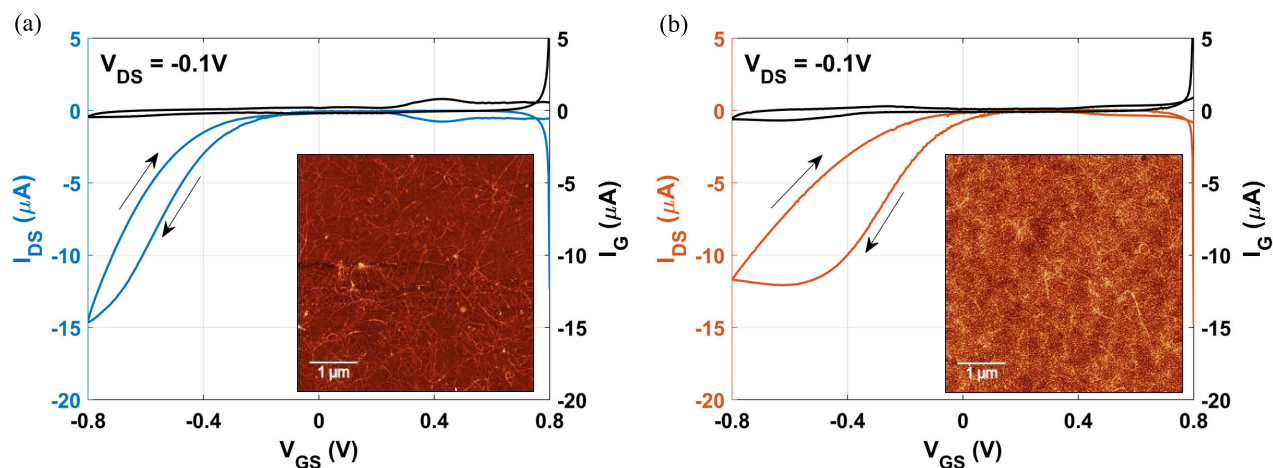


Fig. 3. Transfer characteristics for the fabricated EG-CNTFETs for (a) 18 layers of CNTs on rigid Si/SiO<sub>2</sub> substrate and (b) 24 layers of CNTs on flexible PI foil. Inset the 2-D AFM color map of the CNT channel, on Si/SiO<sub>2</sub> and PI, respectively.

different duration of the  $HNO_3 + H_2O$  treatment. The quality of the resulting CNT network was evaluated by means of AFM microscopy. The 2-D AFM color maps are reported in the supplementary Figs. S1 (1 h treatment), S2 (3 h treatment) and S3 (6 h treatment). The CNT networks looked already completely residual-free after 1 h of  $HNO_3 + H_2O$  treatment, as further proved by the 3-D AFM topography in Fig. 2. The thickness of the CNT layer was not affected by the time of treatment. Furthermore, Fig. S4(a) and (b) of the Supporting Information report the direct comparison of the AFM color maps before and after the  $HNO_3 + H_2O$  treatment: the removal of the CMC matrix from the spray-deposited CNT network can be clearly observed. This is further verified from the measurement of the  $R_{DS}$ , reported in Fig. S4(c). The measured  $R_{DS}$  reduces drastically after the removal of the insulating CMC surfactant.

As expected, the density of the deposited network lowered by increasing the ratio of the dilution, as proven by the roughness values extracted from the AFM images (Table S5). The random networks deposited from the three highest dilution ratios (i.e., 1:75, 1:150, and 1:300) were characterized by very few CNTs effectively deposited on the surface. On the other hand, the CNT networks deposited from the 1:15 dilution showed the presence of CNT bundles. For this reason, the 1:30 dilution and 1 h  $HNO_3 + H_2O$  treatment were selected as the best CNT concentration and process parameters for the development of EG-CNTFET on rigid and flexible substrates.

### B. From Rigid to Flexible Substrates

The optimized CNT ink (i.e., 1:30 dilution and 1 h of  $HNO_3 + H_2O$  treatment) was employed for the deposition of the channel of the EG-CNTFET fabricated on standard Si/SiO<sub>2</sub> substrate. We tested different number of layers of the spray-deposited CNT random networks. When depositing less than 18 layers, the devices did not show an EG-CNTFET behavior with the  $I_{DS}$  in the same range as the  $I_G$  [Fig. S6(a)]. The low conductivity of the CNT channel ( $R_{DS} = 107$  k $\Omega$ ) did

not allow the formation of the required electrical double layers (EDLs), i.e., not enough ions were attracted at the interface between the semiconducting channel and the electrolyte [17]. The minimum deposition thickness allowing the targeted EG-CNTFET behavior was 18 layers, which yielded  $R_{DS} = 16.3$  k $\Omega$  and an  $I_{ON}/I_{OFF}$  of  $1.22 \times 10^3$  A/A (Fig. 3(a), with corresponding 2-D AFM color map in the inset. The corresponding semilog plot can be found in Fig. S7(a) of the Supporting Information).

To be able to integrate EG-CNTFETs in wearable platforms of arbitrary shape, it is necessary to fabricate them on conformal substrates, e.g., thin PI foil. For this reason, the fabrication process developed on the standard Si/SiO<sub>2</sub> substrate was adapted to the PI substrate. The EG-CNTFET fabricated on PI using the same parameters of the Si/SiO<sub>2</sub> device (i.e., 18 layers of CNTs) did not show the expected EG-CNTFET behavior [see Fig. S6(b)]. The measured  $R_{DS}$  was 356 k $\Omega$ , more than one order of magnitude bigger than the resistance measured on Si/SiO<sub>2</sub>. The observed reduced channel conductivity on PI was most probably a result of the increased roughness of the polymeric surface with respect to Si/SiO<sub>2</sub>. In fact, according to what was reported in the datasheet provided by the respective manufacturers, the root mean square (rms) roughness of the Si/SiO<sub>2</sub> wafer is <1 nm, while the rms roughness of the PI foil is in the 0.02–0.07  $\mu$ m range. Being the rms roughness of the PI foil in the same order of magnitude of the spray-deposited CNT random networks (few tens of nanometer), more layers of material are required to overcome the substrate ridges and form a connected semiconducting path.

To obtain higher density of CNTs in the spray-deposited network, we increased the number of layers to 24. With the increased CNT density (drain–source resistance  $R_{DS}$  of 4.83 k $\Omega$ ). The device fabricated on PI substrate showed typical EG-FET behavior, as shown in Fig. 3(b) (with corresponding 2-D AFM color map in the inset), with  $I_{ON}/I_{OFF}$  ratio of  $2.52 \times 10^3$  A/A (the corresponding semilog plot can be found in Fig. S7(b) of the Supporting Information).

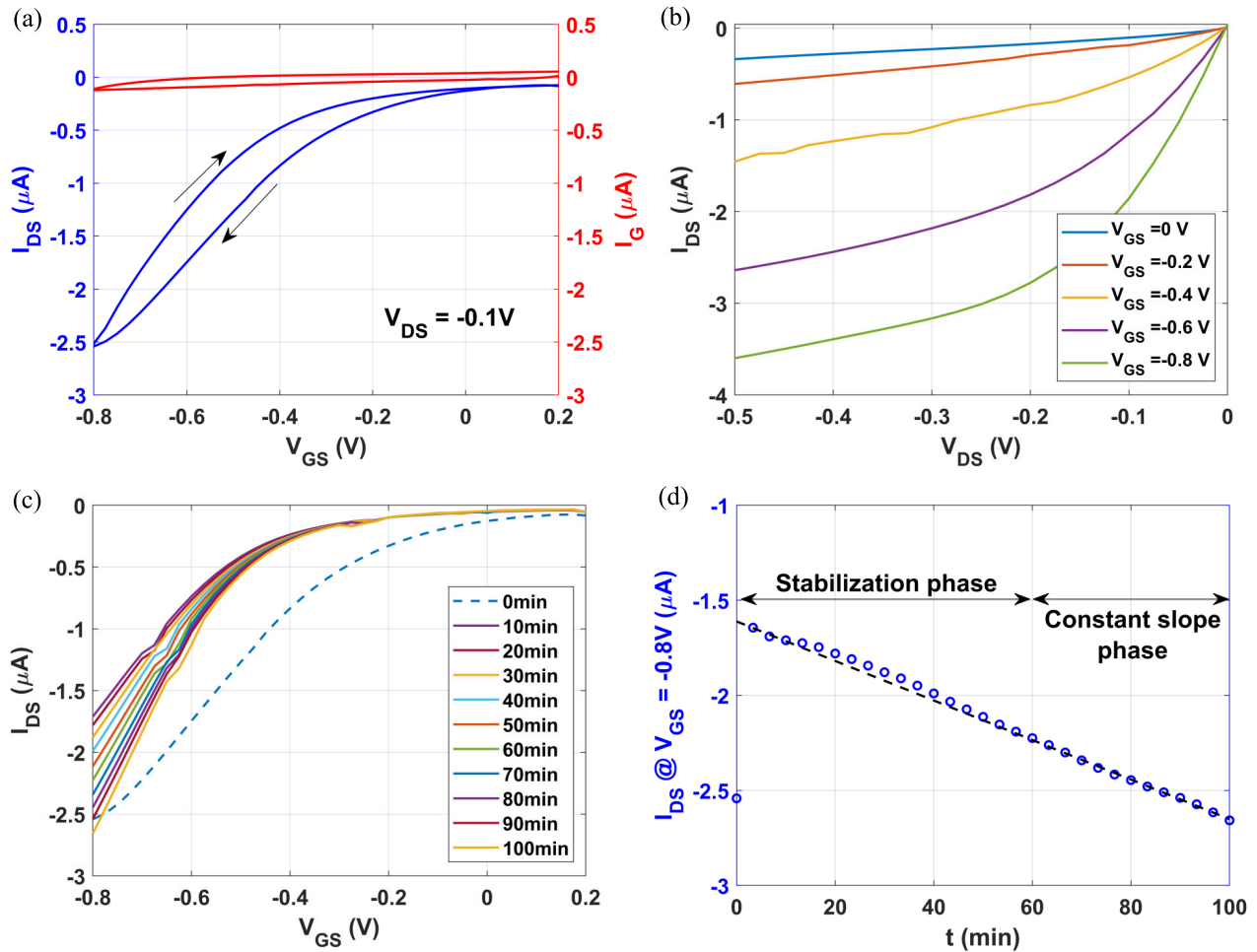


Fig. 4. (a) Transfer and (b) output characteristics of the fabricated EG-CNTFET fabricated on flexible substrate, functionalized with the  $\text{NH}_4^+$ -sensitive membrane. 200  $\mu\text{L}$  of DI-water, directly drop-casted on top of the active area of the device, were used as electrolyte. The output characteristics show typical p-type behavior and absence of contact resistance. (c) Consecutive transfer characteristics recorded with only DI-water as electrolyte, to investigate the stability of the proposed EG-CNTFET-based  $\text{NH}_4^+$  sensors. (d) Time dependence of the  $I_{DS}$  at the minimum  $V_{GS}$ , (i.e.,  $V_{GS} = -0.8$  V). After the stabilization phase, there is the onset of a stable linear trend that can be extracted by means of a linear fitting.

From the analysis of the transfer curves, a clear hysteresis can be observed both on rigid Si/SiO<sub>2</sub> and flexible PI substrate. Hysteresis can be originated either by charge transfer into the semiconducting layer from neighboring adsorbates or charge injection into trap sites on the dielectric substrate, as discussed by Wang et al. [27]. However, a proper analysis of this phenomenon would require a dedicated set of experiments, going thus beyond the scope of this article.

### C. EG-CNTFET-Based $\text{NH}_4^+$ Sensors

Having successfully transferred the fabrication process from Si/SiO<sub>2</sub> to PI, we fabricated a new batch of devices ( $N = 3$  devices), and we functionalized them by means of an  $\text{NH}_4^+$ -selective membrane to test them as  $\text{NH}_4^+$  sensors. The thickness of the drop-casted  $\text{NH}_4^+$ -selective membrane was of 5.06  $\mu\text{m}$ , with a standard deviation of 0.99  $\mu\text{m}$ . A representative profilometer measurement can be observed in Fig. S8 of the Supporting Information.

Before testing the functionalized EG-CNTFETs on PI as  $\text{NH}_4^+$  sensors, electrical characterization was performed. It can be observed, both in Fig. 3(a) and (b), how the  $I_{DS}$  and the  $I_G$  were symmetrical for the first part of the measurement

( $0.8 \text{ V} > V_{GS} > 0.2 \text{ V}$ , approximately). This was indicative of the very early stages of the onset of the EDLs at the semiconductor-electrolyte and gate-electrolyte interfaces: until enough ions rearranged under the influence of the  $V_{GS}$  the current passed through the electrolyte. For this reason, we changed the characterization procedure, starting the sweep of the  $V_{GS}$  from 0.2 V and adding a brief hold time (i.e., the time during which the bias is applied to the device before starting the sweep) of 5 s to help the formation of the EDLs.

The transfer and output characteristics recorded in DI water showed typical p-type behavior [Fig. 4(a), with the corresponding semilog plot depicted in Fig. S9(a) of the Supporting Information, and 4(b)]. Comparing the recorded transfer curves with the ones of the bare devices [i.e., Fig. 3(b)], a clear decrease in the  $I_{DS}$  can be observed. This is to be ascribed to the penetration of the polymeric membrane, inherently insulating, into the CNT network, with the consequent reduction of the number of semiconducting paths and the overall reduction of the network conductivity, which is in turn reflected in a decrease of the  $I_{ON}$ . Moreover, the output characteristics proved the formation of stable ohmic contacts between the gold IDEs and the CNTs [28], [29].

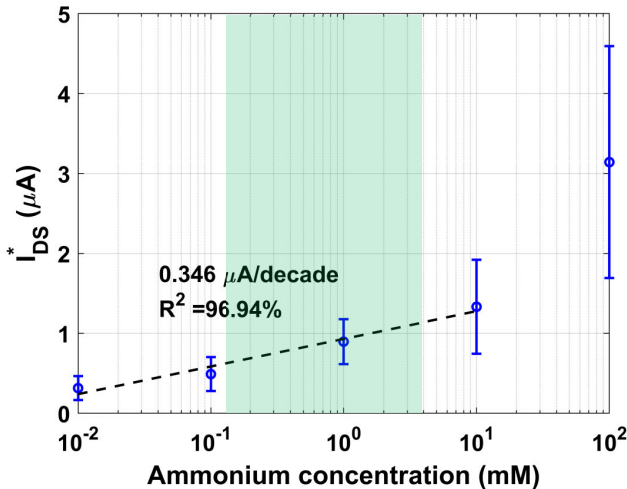


Fig. 5. Calibration curves representing the average corrected response of the EG-CNTFET-based sensors ( $I_{DS}^*$ ) versus different concentrations of  $NH_4^+$ . All the devices were tested using DI water as electrolyte. The green box highlights the physiological range of concentrations of  $NH_4^+$  during physical exercise [13]. The response of the devices toward  $NH_4^+$  diverged from linearity when the highest concentration (100 mM) was tested, showing signs of saturation. This concentration was hence excluded from the calculation of the sensitivity. Here, the error bars represent the standard errors of the mean, with  $N = 3$  devices.

When employing EG-CNTFETs for biosensing applications, it is crucial to assess the device stability to have reliable biosensing data [30]. Therefore, transfer characteristics were recorded for 100 min (Fig. 4(c)), with the corresponding semilog plot depicted in Fig. S9(b) of the Supporting Information) prior to the exposure to the target analyte  $NH_4^+$ .

The response of devices (i.e., the value of the  $I_{DS}$  at  $V_{GS} = -0.8$  V) stabilized after 1 h of measurements [Fig. 4(d)], similar to what reported in [31]. After 1 h, i.e., after the stabilization phase, the  $I_{DS}$  showed a linear increase (i.e., constant slope phase) of 10.4 nA/min, with a coefficient of determination of 99.75%. During the same time interval, the gate current  $I_G$  went through a similar stabilization, probably due to the continuous dynamic re-arrangement of the ions in the electrolyte in response to the applied  $V_{GS}$ . Nevertheless,  $I_G$  was  $<10$  nA (in absolute value) during the whole measurement time, so at least three orders of magnitude lower than the  $I_{DS}$ , proving reliable EG-CNTFET operation of the tested devices [1]. The onset of the constant slope phase, and the possibility to extract the trend of the  $I_{DS}$  for each device by means of a linear fitting, enabled the possibility to subtract such trend and obtain the corrected response  $I_{DS}^*$  [32].

Different  $NH_4^+$  concentrations were injected at the end of the constant slope phase. As shown in Fig. 5, exposure of the sensor to  $NH_4^+$  led to concentration-dependent changes in  $I_{DS}^*$ : the  $I_{DS}^*$  increased for increasing concentrations of  $NH_4^+$ . Such behavior was likely driven by the ability of the ion-selective membrane to exchange the  $NH_4^+$  ions of the electrolyte (a representative plot of the  $I_{DS}^*$  in real time can be found in Fig. S10 of the Supporting Information). The build-up of positive  $NH_4^+$  ions inside the membrane, together with the corresponding increase in negative charge in the electrolyte (i.e., the depletion of positive charge) leads to the onset of an electrical potential difference across the membrane. This established potential difference causes a reduction in

the conductivity of the semiconducting channel [33]. The response of all the tested EG-CNTFET-based  $NH_4^+$  sensors was linear for concentrations up to 10 mM, with a sensitivity of 0.346  $\mu A/decade$  (relative standard deviation of 69.2%) and a coefficient of determination of 94.35%. The response diverged from this linear behavior when 100 mM  $NH_4^+$  was tested, the reason for this can be the saturation of the sensor: when the available sites of the nonactine ionophore inside the membrane are fully occupied by  $NH_4^+$ , the remaining free  $NH_4^+$  cations react only electrostatically with the membrane in close proximity of the channel. This interaction, being regulated by the randomly distributed the  $NH_4^+$  cations inside the solution, is intrinsically chaotic, leading to an increase in the standard error.

#### IV. CONCLUSION

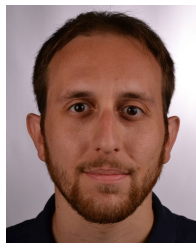
In this work, we presented the fabrication and characterization of EG-CNTFETs on rigid and flexible substrate. The semiconducting channel was made of solution-processed CNTs and deposited through cost-effective and scalable spray deposition technique. To achieve high-quality semiconducting nanotube networks, we focused on the optimization of the CNT ink. We chose the optimal CNT concentration and significantly reduced posttreatment time from the previously reported 12 to 1 h. The optimized ink was then used to fabricate EG-CNTFET first on standard rigid Si/SiO<sub>2</sub> substrate and later on flexible PI foil. Both devices showed typical p-type behavior with an on-off ratio in the order of magnitude of  $10^3$  A/A. Furthermore, as a proof of concept, we demonstrated the detection of the  $NH_4^+$  ions with EG-CNTFETs functionalized with nonactin ion-selective membrane. To have reliable sensing data, the sensor stability was thoroughly investigated, and a facile data analysis protocol was established. The sensors reached stability after 1 h of continuous transfer characteristics recording, which allowed for the baseline correction of the  $I_{DS}$ . Upon reaching stability, sensors were tested for the detection of  $NH_4^+$  over the range of concentrations from 0.01 to 100 mM. The sensors showed sensitive detection of  $NH_4^+$  in the range of interest from 0.01 to 10 mM with average sensitivities of 0.346  $\mu A/decade$  and 94.35% coefficient of determination. Future work will involve the characterization with a narrower range of concentrations, possibly increasing the number of concentrations tested inside the physiological range from 0.12 to 2.17 mM, as well as performing the characterization with more complex electrolytes (i.e., artificial sweat), to explore the selectivity (i.e., the effect of interfering ions on the sensor response) [32], [34]. Another aspect that needs to be studied is the re-usability of the sensor, by studying possible mechanisms to induce recovery of the membrane after exposure to  $NH_4^+$ . The results shown in this work demonstrate the potential of using EG-CNTFETs fabricated on a flexible substrate, functionalized with nonactine-based membrane, opening a pathway for the development of a wearable platform.

#### REFERENCES

- [1] B. Shkodra et al., "Electrolyte-gated carbon nanotube field-effect transistor-based biosensors: Principles and applications," *Appl. Phys. Rev.*, vol. 8, no. 4, 2021, Art. no. 041325.



- [2] C. Zhao, T. Man, Y. Cao, P. S. Weiss, H. G. Monbouquette, and A. M. Andrews, "Flexible and implantable polyimide aptamer-field-effect transistor biosensors," *ACS Sensors*, vol. 7, no. 12, pp. 3644–3653, 2022.
- [3] G. Elli, S. Hamed, M. Petrelli, P. Ibba, M. Ciocca, P. Lugli, and L. Petti, "Field-effect transistor-based biosensors for environmental and agricultural monitoring," *Sensors*, vol. 22, no. 11, p. 4178, 2022.
- [4] N. Nakatsuka et al., "Aptamer–field-effect transistors overcome debye length limitations for small-molecule sensing," *Science*, vol. 362, no. 6412, pp. 319–324, 2018.
- [5] L. Suo et al., "'Water-in-salt' electrolyte enables high-voltage aqueous lithium-ion chemistries," *Science*, vol. 350, no. 6263, pp. 938–943, 2015.
- [6] L. Hu, D. S. Hecht, and G. Gruner, "Carbon nanotube thin films: Fabrication, properties, and applications," *Chem. Rev.*, vol. 110, no. 10, pp. 5790–5844, 2010.
- [7] I. V. Zaporotskova, N. P. Boroznina, Y. N. Parkhomenko, and L. V. Kozhitov, "Carbon nanotubes: Sensor properties. A review," *Mod. Electron. Mater.*, vol. 2, no. 4, pp. 95–105, 2016.
- [8] B. Shkodra et al., "Polymeric integration of structure-switching aptamers on transistors for histamine sensing," *Faraday Discuss.*, Jul. 2023, doi: 10.1039/D3FD00123G.
- [9] M. Petrelli et al., "Novel gate electrode design for flexible planar electrolyte-gated field-effect transistor-based sensors for real-time ammonium detection," in *Proc. IEEE Sensors*, Jul. 2022, pp. 1–4.
- [10] C.-S. Lee, Y. Ju, J. Kim, and T. H. Kim, "Electrochemical functionalization of single-walled carbon nanotubes with amine-terminated dendrimers encapsulating Pt nanoparticles: Toward facile field-effect transistor-based sensing platforms," *Sensors Actuators B, Chem.*, vol. 275, pp. 367–372, Aug. 2018.
- [11] A. J. Bandodkar, W. J. Jeang, R. Ghaffari, and J. A. Rogers, "Wearable sensors for biochemical sweat analysis," *Annual Rev. Anal. Chem.*, vol. 12, pp. 1–22, Jun. 2019.
- [12] M. Petrelli et al., "Flexible, planar, and stable electrolyte-gated carbon nanotube field-effect transistor-based sensor for ammonium detection in sweat," in *Proc. IEEE Int. Flexible Electron. Technol. Conf. (IFETC)*, Jul. 2022, pp. 1–2.
- [13] E. Renner, N. Lang, B. Langenstein, M. Struck, and T. Bertsch, "Validating sweat ammonia as physiological parameter for wearable devices in sports science," in *Proc. 42nd Annu. Int. IEEE Eng. Med. Biol. Soc. (EMBC)*, Jun. 2020, pp. 4644–4647.
- [14] M. Cuartero, N. Colozza, B. M. Fernández-Pérez, and G. A. Crespo, "Why ammonium detection is particularly challenging but insightful with ionophore-based potentiometric sensors—An overview of the progress in the last 20 years," *Analyst*, vol. 145, no. 9, pp. 3188–3210, 2020.
- [15] B. Martínez-Haya, J. R. Avilés-Moreno, F. Gámez, G. Berden, and J. Oomens, "Preferential host-guest coordination of nonactin with ammonium and hydroxylammonium," *J. Chem. Phys.*, vol. 149, no. 22, 2018, Art. no. 225101.
- [16] A. Falco, L. Cinà, G. Scarpa, P. Lugli, and A. Abdellah, "Fully-sprayed and flexible organic photodiodes with transparent carbon nanotube electrodes," *ACS Appl. Mater. Interfaces*, vol. 6, no. 13, pp. 10593–10601, 2014.
- [17] B. Shkodra et al., "Optimization of the spray-deposited carbon nanotube semiconducting channel for electrolyte-gated field-effect transistor-based biosensing applications," *IEEE Sensors J.*, early access, Mar. 29, 2022, doi: 10.1109/JSEN.2022.3162706.
- [18] L. Zhang, M. Rao, J. Kochupurackal, N. Mathews, Y. M. Lam, and S. G. Mhaisalkar, "Effect of nitric acid concentration on doping of thin film single-walled carbon nanotubes for electrode application in transparent, flexible dye sensitized solar cells," *MRS Online Proc. Library (OPL)*, vol. 1436, Jan. 2013, Art. no. mrss12-1436-k06-03.
- [19] T. Guinovart, A. J. Bandodkar, J. R. Windmiller, F. J. Andrade, and J. Wang, "A potentiometric tattoo sensor for monitoring ammonium in sweat," *Analyst*, vol. 138, no. 22, pp. 7031–7038, 2013.
- [20] H. Okimoto et al., "Tunable carbon nanotube thin-film transistors produced exclusively via inkjet printing," *Adv. Mater.*, vol. 22, no. 36, pp. 3981–3986, 2010.
- [21] F. Loghin et al., "Scalable spray deposition process for highly uniform and reproducible CNT-TFTs," *Flexible Printed Electron.*, vol. 1, no. 4, 2016, Art. no. 045002.
- [22] T. Haeberle, F. Loghin, U. Zschieschang, H. Klauk, and P. Lugli, "Carbon nanotube thin-film transistors featuring transfer-printed metal electrodes and a thin, self-grown aluminum oxide gate dielectric," in *Proc. IEEE 15th Int. Conf. Nanotechnol. (IEEE-NANO)*, Jul. 2015, pp. 160–163.
- [23] A. Abdelhalim, A. Abdellah, G. Scarpa, and P. Lugli, "Fabrication of carbon nanotube thin films on flexible substrates by spray deposition and transfer printing," *Carbon*, vol. 61, pp. 72–79, Sep. 2013.
- [24] E. J. Lavernia and Y. Wu, *Spray Atomization and Deposition*. Hoboken, NJ, USA: Wiley-Blackwell, 1996.
- [25] A. H. Lefebvre and V. G. McDonell, *Atomization and Sprays*. Boca Raton, FL, USA: CRC Press, 2017.
- [26] F. Loghin, A. Rivadeneyra, M. Becherer, P. Lugli, and M. Bobinger, "A facile and efficient protocol for preparing residual-free single-walled carbon nanotube films for stable sensing applications," *Nanomaterials*, vol. 9, no. 3, p. 471, 2019.
- [27] H. Wang, Y. Wu, C. Cong, J. Shang, and T. Yu, "Hysteresis of electronic transport in graphene transistors," *ACS Nano*, vol. 4, no. 12, pp. 7221–7228, 2010.
- [28] G. Horowitz, "Interfaces in organic field-effect transistors," in *Organic Electronics*. Springer, 2010, pp. 113–153.
- [29] H. Chen et al., "Aptamer-functionalized carbon nanotube field-effect transistor biosensors for Alzheimer's disease serum biomarker detection," *ACS Sensors*, vol. 7, no. 7, pp. 2075–2083, 2022.
- [30] F. Torricelli et al., "Electrolyte-gated transistors for enhanced performance bioelectronics," *Nature Rev. Methods Primers*, vol. 1, no. 1, pp. 1–24, 2021.
- [31] A. Molazemhosseini et al., "A rapidly stabilizing water-gated field-effect transistor based on printed single-walled carbon nanotubes for biosensing applications," *ACS Appl. Electron. Mater.*, vol. 3, no. 7, pp. 3106–3113, 2021.
- [32] M. Petrelli et al., "Method for instability compensation and detection of ammonium in sweat via conformal electrolyte-gated field-effect transistors," *Organic Electron.*, vol. 122, Nov. 2023, Art. no. 106889.
- [33] K. Melzer et al., "Flexible electrolyte-gated ion-selective sensors based on carbon nanotube networks," *IEEE Sensors Journal*, vol. 15, no. 6, pp. 3127–3134, Jun. 2015.
- [34] M. Petrelli et al., "Flexible sensor and readout circuitry for continuous ion sensing in sweat," *IEEE Sensors Lett.*, vol. 7, no. 6, May 2023, Art. no. 5501804.



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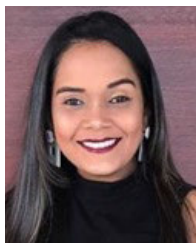
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