

# Complementary Reduced Graphene Oxide-Based Inverter for Ion Sensing †

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† Presented at the 2nd International Electronic Conference on Biosensors (IECB), 14–18 February 2022; Available online: <https://iecb2022.sciforum.net/>.

**Abstract:** Graphene, a 2D material with high conductivity and stability in aqueous media could complement silicon as raw material for sensing with transistor-based devices in liquids. Furthermore, the fabrication of graphene-transistors is affordable with low-cost techniques such as inkjet printing from graphene oxide (GO)-based inks. Deposited on plastic conformable substrates, graphene-based logic gates are standing as attractive and compelling candidates in the field of biosensing, to make electrical transduction and binary operations match with aqueous media and facilitate diagnostic operations.

**Keywords:** Electrolyte-gated field-effect transistors; Chemical Logic; reduced graphene oxide-based inverters; sweat sensor

## 1. Introduction

Graphene-based transistors are well known for being ambipolar devices stable in aqueous media, with high channel conductivity and charge carrier mobility, in comparison with organic semiconductor-based ones [1]. Electrolyte-Gated Graphene-based Field-Effect-Transistors (EG-GFET) are composed of 3 electrodes, named source, drain and gate as in the case of conventional FETs but they possess a few specificities of their own [2]. First of all, graphene cannot be considered as a semiconductor regarding its electrical behavior; in addition to that, the electrolyte separating the gate from the transistor's channel is easily tunable and modifiable and that stands for both dielectric and sensing medium [3]. This latter property is particularly remarkable as the nature of the electrolyte induces a change of the electrochemical double layer capacitance at the interfaces between gate/electrolyte and graphene/electrolyte which, in turn, leads to a modification of the electrical properties of the transistor itself [4]. The use of graphene transistors as biological or ionic sensors has already been highly reported [5], however logic gates built from graphene transistors have never been described for such purpose, even though few articles are already pointing out the interest of such devices to perform basic logic operations in aqueous media [6]. In this study, we investigate the design of a logic gate for ion-sensing purposes from graphene-based electrical devices on flexible substrates, to further extend the application field to skin patches or bandage-type sensors, for instance.

## 2. Materials and Method

Transistors are designed with a coplanar gate configuration (Figure 1, left). The fabrication steps, from the electrodes patterning by photolithography to the electrochemical reduction of the GO ink-coated channel, by drop-casting or inkjet printing method, are described elsewhere [7]. All electrolytes used are DI-water-based solutions, containing K<sup>+</sup> and/or Na<sup>+</sup> at various concentrations. Valinomycin (VMC) ion-selective membrane,

**Citation:** Boukraa, R.; Mattana, G.; Battaglini, N.; Piro, B. Complementary reduced Graphene Oxide-based inverter for ion sensing. *2022*, *4*, x. <https://doi.org/10.3390/xxxxx>

Published: date

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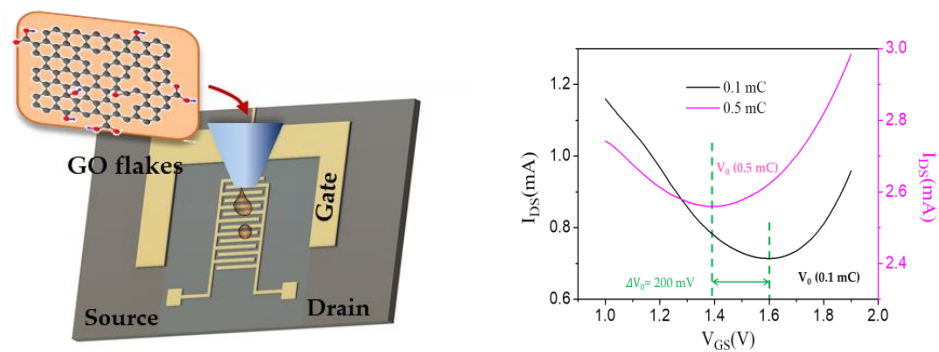
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specific to  $K^+$ , is deposited on the gate of each transistor by using the KELENN DMD100 printer. The composition is adapted from the method of Kisiel et al. [8]: 1.0% ( $w/w$ ) of valinomycin, 0.5% of potassium tetrakis [3,5-bis(trifluoromethyl) phenyl]borate (KTBP) selectophore to improve VMC selectivity, 31.5% of poly (vinyl chloride) polymer and 67.0% of 2-nitrophenyl octyl ether plasticizer in cyclohexanone instead of THF as solvent to prevent fast evaporation in the dispenser syringe. The conventional silicon wafer playing the role of the substrate is replaced here by a flexible polymer foil of polyimide to match with on-skin patch application perspectives. A commercial silver ink (purchased from PV Nano Cell) is affording the interconnections between the transistors. All electrical measurements are performed with a 4200-A-SCS Keithley analyzer. The biased supply voltage to acquire inverter characteristics is applied through an external power source (Basetech BT-305 DC).

### 3. Results and Discussion

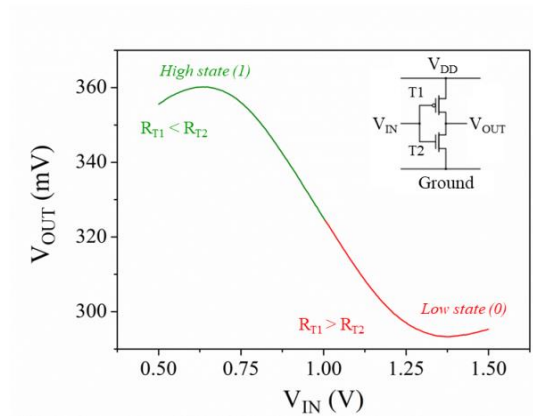
#### a. Electrical Characteristics of the EG-GFET Inverter

Regarding the ambipolar behavior of rGO, one expects an increase of drain current  $I_{DS}$  apart from a minimum value which occurs at  $V_{GS} = V_0$ , corresponding to the situation where Fermi level crosses the so called Dirac point [1]. The electrochemical reduction of GO to rGO is controlled by measuring the amount of charge passed at a constant reduction voltage, showing a good control of the  $V_0 = V_{GS}$  (at  $I_{DS,min}$ ).  $V_0$  can be tuned as shown below (Figure 1, right), the higher the amount of charge, the less positive  $V_0$ . However, even with a significant value of charge injected,  $V_0$  stays positive, which indicates that the rGO built following this process is still p-doped [5,7].



**Figure 1.** Coplanar gate configuration (**left**) and transfer characteristics for different charges during the electrochemical reduction process (**right**).

The difference of  $V_0$  from one to another transistor may be caused by a difference of the doping state. Therefore, a slight shift of a few tens of mV is enough to build an inverter out of two graphene transistors made from two different reduction charges: The two gates are connected together and the drains too, so that the transistor with the highest  $V_0$  is taken as the  $p$  transistor and connected to  $V_{DD}$  from its source, the second one, still p-doped even if less, is connected to the ground and acts as the  $n$  transistor of a usual NOT-gate. The electrical characteristic of the resulting gate is shown on Figure 2.

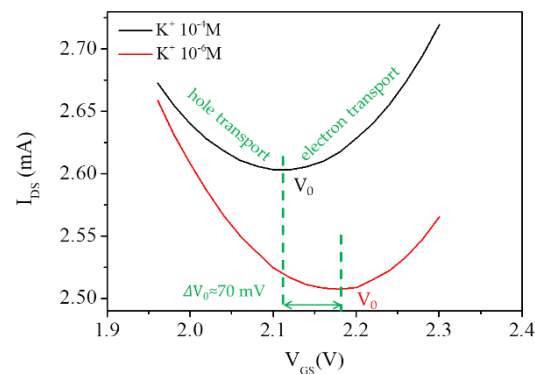


**Figure 2.** Graphene-based inverter input (IN) versus output (OUT) characteristic. Inset: electrical circuit with T1 (p-type, slightly reduced) and T2 (“n-type-like”, more reduced, see text for explanation) transistors.

### b. The EG-GFET inverter as $K^+$ sensor

One way to study inverters is to consider each transistor T1 and T2 as a variable resistor. The competition between those two connected transistors is related to the ratio  $R_{T1}$  versus  $R_{T2}$ : when the upper transistor, connected to the biased supply voltage  $V_{DD}$ , is driving the device, i.e.,  $R_{T1} < R_{T2}$  happening for low input  $V_{IN}$ , the output is connected to the supply voltage corresponding to the ON state. On the other side, when  $R_{T2} < R_{T1}$ , the bottom transistor connects the ground to the output resulting in the OFF state.

We have seen right above that different reduction levels lead to the shift of the  $V_0$  of the two transistors; however, this shift can also be obtained by changing the capacitance at the gate/electrolyte interface which is the way that we investigated in order to build a proper sensor out of the rGO inverter.



**Figure 3.** Transfer characteristic of VMC-modified rGO-EGFET for two different concentrations of  $K^+$  ion.

Functionalization of the gate electrode with ionophores or other specific hydrogel modifies the capacitance at the gate/electrolyte interface that induces a change of the effective gate voltage at the input of the modified transistor.

Figure 3 gives an example of ion-sensing with rGO transistors, as the transfer characteristic is directly impacted by a change in the concentration of  $K^+$  ions of the electrolyte, from  $10^{-6}$  to  $10^{-4}$  M, with a VMC gate-modified transistor.

We plan to use the rGO-based inverters to assist ion-sensing, following the above-mentioned principle, which consists in performing the switch from OFF state to ON state, for a fixed  $V_{IN}$ , thanks to the capacitance changes occurring at the gate/electrolyte interface of one of the two transistors, resulting in a change of the  $V_0$ . In this configuration, the ion

concentration involved in the capacitance change is standing for the input information of the sensor. The main interest of sensing with inverters instead of isolated transistors is to take advantage of the Boolean Algebra applied to graphene logic gates, that could allow us to design complex circuits stable in aqueous media and thus to perform Chemical Logic which is an ingenious method to produce basic mathematical operations in solution or more concretely to get a unique sensor built from the output response of several ones in the same medium.

#### 4. Conclusions

In this study, we reported a way to perform ion sensing with the most elementary logic gate that is the inverter, from two interconnected transistors. To overcome heavy and costly processes of graphene deposition, we formulated a graphene oxide surfactant-free ink that can be directly inkjet printed on the channel. As a perspective, we are now investigating the way to make the inverter switch occur, and therefore to estimate the sufficient threshold value of capacitance or ion concentration change needed to go from OFF to ON output state, through both experimental work and simulation.

**Author Contributions:** Conceptualization, G.M., N.B., B.P.; methodology, R.B., G.M., N.B., B.P.; investigation, R.B.; writing, R.B., G.M., N.B., B.P.; supervision, G.M., N.B., B.P. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received funding from the Consortium of French higher education and research institutions for the development of USTH, under the framework “Collaborative S&T projects 2021”, entitled “*Functionalized Graphene for Electrolyte-Gated Field Effect Transistors. Application to Wearable Sweat Sensors*”.

**Institutional Review Board Statement:**

**Informed Consent Statement:**

**Data Availability Statement:**

**Acknowledgments:** R.B thanks Ecole Doctorale ED388 *Chimie Physique et Chimie Analytique de Paris Centre* for providing a PhD grant.

**Conflicts of Interest:** The authors declare no conflict of interest.

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