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# Valinomycin-Modified Graphene Field-Effect Transistors for Potassium Ion Sensors

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## 1. Introduction

Graphene is a two-dimensional material, and its electrical characteristic shows very high sensitivity for environmental condition. In our previous works, we have reported that graphene field-effect transistors (GFETs) have a potential to detect positively charged ions in electrolytes [1, 2]. In this study, we have fabricated highly sensitive and selective K (potassium) ion sensors based on valinomycin-modified GFETs (VGFETs). Valinomycin is one of ionophores, which has cyclic structure. For its shape and size, valinomycin forms complexes much more readily with K ion than other kinds of ions. K ion is an essential element for biological activity including human life. For example, K ion plays an essential role to control the electrostatic charge on cell membranes, and the excessiveness or the insufficiency of K ion concentration in body lead to critical diseases like high blood pressure or consciousness disorder. Therefore, selective K ion sensors are required in medical field.

## 2. Experimental

Graphene single-layers were obtained from kish graphite by mechanical exfoliation. GFETs were fabricated by conventional e-beam lithography and lift-off method on highly p-doped Si substrates covered by thermally grown $SiO_2$ layer. To achieve selective detection, the graphene channels were covered with ion selective membrane (ISM), as shown in Fig. 1. ISM was constructed from a mixture of polyvinyl chloride and valinomycin, a K ion binding protein shown in the inset of Fig 1.

After preparing the VGFET, a silicone rubber frame was placed on the VGFET so that a graphene channel was filled with a solution, and an Ag/AgCl reference electrode was used as a top-gate electrode, as shown in Fig. 2.

## 3. Results and Discussion

First, we measured transfer characteristics of VGFETs in the 100 mM Tris-HCl buffer solution with various KCl concentrations. Figure 3(a) shows transfer characteristics of VGFET as a function of the top-gate voltage with various K ion concentrations over the range from 0 to 1.0 mM. With increasing K ion concentration, the top-gate voltage at the Dirac point shifted toward negative direction. The leakage current in the VGFETs in a solution were negligible (less than 1 nA). The shift of voltage at the Dirac point toward negative direction is due to the accumulation of K ions caused by valinomycin on the graphene surfaces, as shown in Fig. 3(b). These results indicate VGFETs detected K ions with concentration from 10 nM to 1.0 mM.

Second, Na ion concentration dependence of transfer characteristics in VGFETs was investigated. The transfer characteristic of VGFETs remained almost constant over the Na ion concentration range between 0 to 1.0 mM, as shown in Fig. 4(a). These results indicate that virtually no Na ions were bound by valinomycin in the ISM, as shown in Fig 4(b).

Figure 5 shows the top-gate voltages at the Dirac point ($V_{TG}$) as a function of K ion concentration (red dots) and Na ion concentration (blue dots). It was found that the top-gate voltages have a roughly linear relationship with K ion concentration on logarithmic scale. On the contrary, increasing of Na ion concentration, VGFET shows almost constant in transfer characteristic. These results show that the electrostatic potential of graphene surfaces exhibit a rather linear dependence on log[K], and the selective accumulation of K ions on the graphene surface was demonstrated.

## 4. Conclusions

We fabricated VGFETs and electrically detected K ion in the electrolyte. The transfer characteristics indicate VGFETs detected K ions with high sensitivity over the wide concentration range. In contrast, VGFET maintain almost the same transfer characteristic while increasing of Na ions. These results indicate VGFET selectively detected K ions. Therefore, VGFETs are useful to fabricate K ion sensors with high sensitivity and selectivity.


## Acknowledgement

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## References


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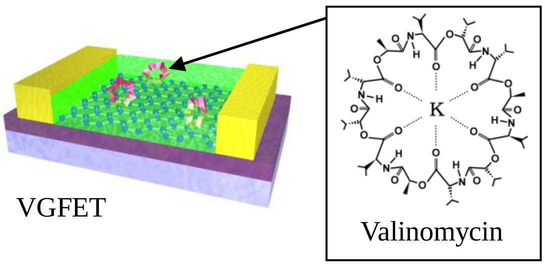


**Fig. 1.** Schematic image of VGFET. The inset shows a molecular structure of valinomycin.

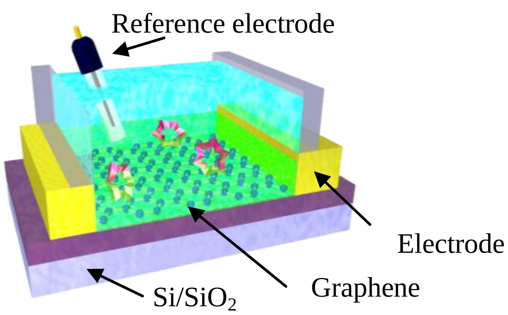


**Fig. 2.** Schematic image of a measurement set up.

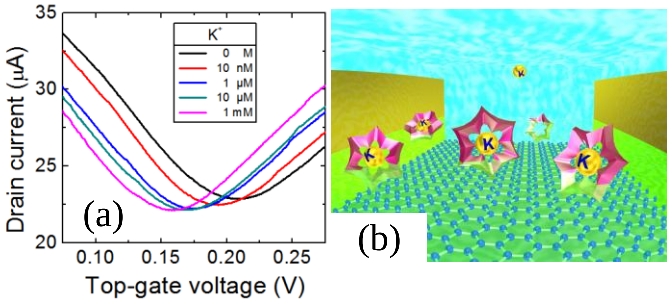


**Fig. 3.** (a) Drain currents as a function of the top-gate voltage of the VGFET with various K ion concentrations from 0 to 1.0 mM. (b) Schematic image of the ISM with K ions.

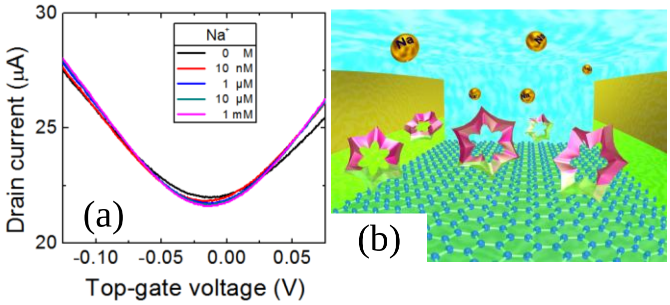


**Fig. 4.** (a) Drain currents as a function of the top-gate voltage of the VGFET with various Na ion concentrations from 0 to 1.0 mM. (b) Schematic image of the ISM with Na ions.

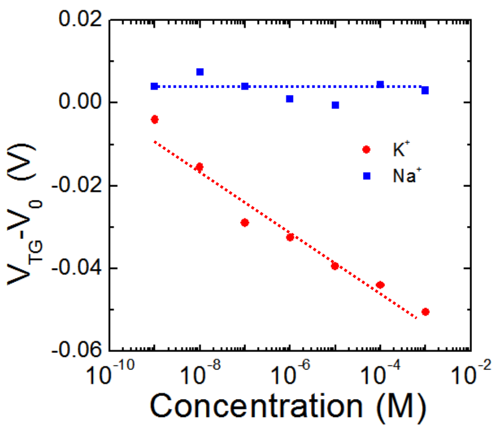


**Fig. 5.** Top-gate voltages at the Dirac point ($V_{TG}$) as a function of K ion concentration (red dots) and Na ion concentration (blue dots). $V_0$ shows the top-gate voltage at the Dirac point with no K and Na ion.