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Selective ion sensors based on ionophore-modified graphene field-effect transistors

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Abstract

Selective potassium (K) ion sensors were fabricated by modifying graphene field-effect transistors (FETs) with valinomycin, a selective K ionophore. The valinomycin-modified graphene FETs demonstrated highly sensitive, selective electrical detection of K ions in electrolytes. The K ions bound to the valinomycin in the graphene channel and affected the electrical potential of the channel. The transfer curves were shifted in a negative direction as the K ion concentration increased, indicating that K ions in solution were effectively detected over a wide concentration range, from 10 nM to 1.0 mM. The addition of Na ions did not cause any change in the transfer characteristics. We have thus demonstrated the utility of graphene FETs as highly sensitive, selective K ion sensors.

Key words: graphene field-effect transistors, selective ion sensors, potassium, ionophore, valinomycin

Introduction

A highly sensitive detection of biomolecules or chemical molecules has recently attracted much attention for various applications. Label-free electrical monitoring of biorecognition events provides a promising platform, which is simpler, less expensive and requires less energy. Rapid testing of different proteins is required in various applications, including clinical diagnostics, environmental testing, food analysis, bioterrorism detection technologies, etc [1-5].

Graphene is a two-dimensional material [6]. Electrical characteristics in graphene field-effect transistors (FETs) are expected to be very sensitive for modulation of surface potentials in graphene channels [7]. Thus, graphene FETs are attractive as electric-readout biological, or chemical sensors owing to their superior properties such as high sensitivity, high conductance, and fast response [8-11]. In this paper, we have fabricated graphene FET-based chemical sensors with high sensitivity. Moreover, we report the integration of valinomycin into graphene FETs to achieve ion selectivity. Valinomycin has a high affinity for K relative to other alkali metal ions [12,13]. We report the fabrication and electrical characterization of valinomycin-modified graphene FET-based chemical sensors, and the investigation of their selective detection of K ions. The valinomycin-modified graphene FETs responded differently to K and Na ions over a wide concentration range, demonstrating their utility for monitoring K ions in solutions.

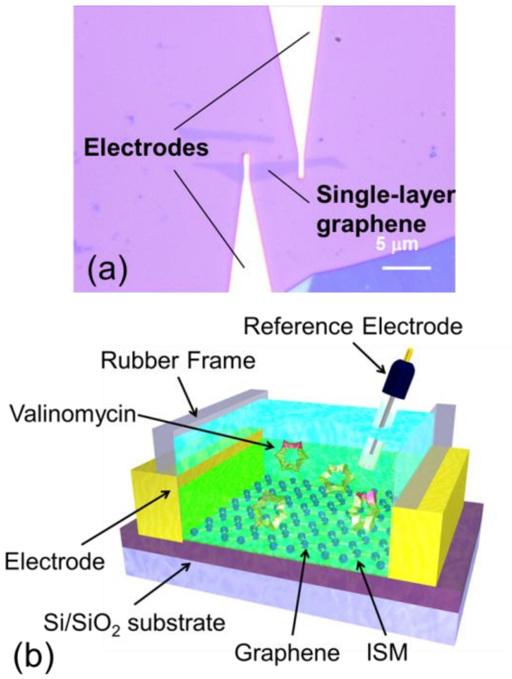

Fig. 1. (a) Scanning electron microscope image of a graphene-based FET and (b) schematic image of a measurement system.

Experimental

A graphene was obtained by mechanical exfoliation. Only monolayer graphene was used for the channel to obtain high sensitivity. The number of graphene layer was confirmed by Raman spectroscopy [14,15]. Figure 1(a) shows graphene FETs fabricated by e-beam lithography and lift-off method on a SiO_2 layer. Au was used for source and drain electrodes.

Figure 1(b) shows a schematic image of a measurement system. A silicone rubber was placed on the graphene FET so that the graphene channel was immersed in a buffer solution. An Ag/AgCl reference electrode was used as the top-gated electrode to minimise environmental effects [16,17]. To achieve selective detection, the graphene channels were covered with ion selective membrane (ISM), constructed from a mixture of polyvinyl chloride and valinomycin. The electrical characteristics in the graphene FET were measured with a semiconductor parameter analyzer. All experiments were carried out in a supporting electrolyte of tris-(hydroxymethyl)-aminomethane and HCl (Tris-HCl) buffer solution (0.1 M, pH 8.6) at room temperature. KCl solutions of various concentrations were added to the Tris-HCl buffer solution to increase the K ion concentration in the reagent solution.

Transfer characteristics in a solution

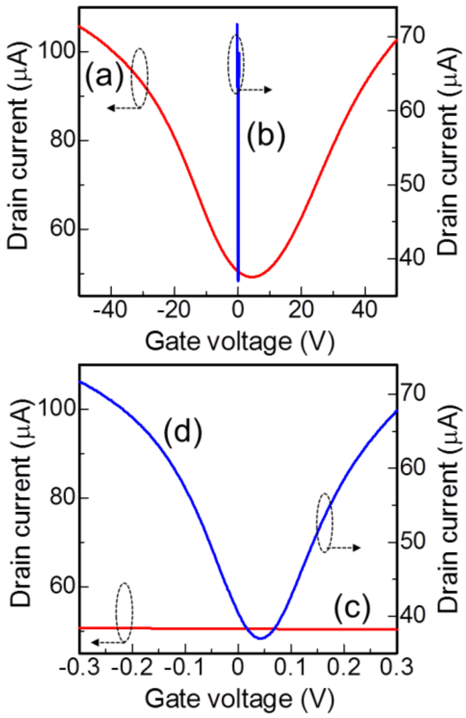

Fig. 2. Transfer characteristics in graphene FET against back-gate voltage in vacuum (a) and top-gate voltage in a solution. (c) and (d) show the enlarged view of (a) and (b), respectively.

Figure 2 shows transfer characteristics in the graphene FET at room temperature. A typical ambipolar characteristic against back-gated voltage was observed in vacuum, as shown in Fig. 2(a). The transconductance was estimated to be 1.8 μS in a vacuum. The drain current in the graphene FETs was plotted against the top-gate voltage in an electrolyte, as shown in Fig. 2(b). Figures 2(c) and 2(d) show the enlarged view of Figs. 2(a) and 2(b), respectively, which were obtained by sweeping from -0.30 to 0.30 V of the gate voltage. The transconductance in the top-gated graphene FET was estimated to be 190 μS, which is 100-fold larger than that in vacuum. This indicates that the electrical double layers act as thin insulators [18,19]. As a result, graphene FETs are useful to detect chemical and biological molecules with high sensitivity.

Selective ion sensors

Figure 3 shows transfer characteristics of valinomycin-modified graphene FETs in the 100 mM Tris-HCl buffer solution with various KCl 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, which is due to the accumulation of K ions caused by valinomycin on the graphene surfaces. The electrostatic potential of graphene surfaces exhibit that the K ion concentration dependence of the top-gate voltage at the Dirac point of valinomycin-modified graphene FETs is roughly linear on a semilogarithmic scale, indicating an equilibrium between the K ions in the valinomycin sites and in solution. These results show valinomycin-modified graphene FETs detected K ions with concentration from 10 nM to 1.0 mM.

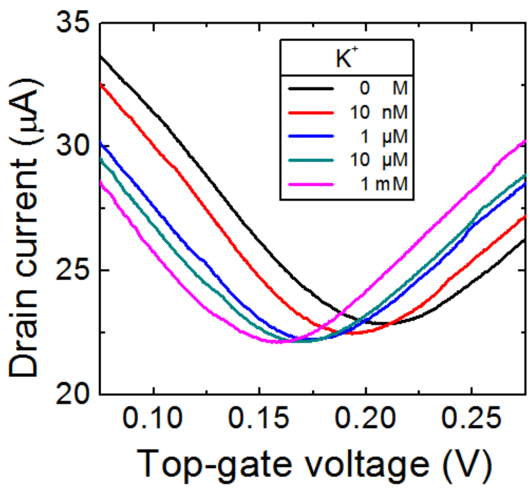

Fig. 3. Transfer characteristics of a valinomycin-modified graphene FET in the 100 mM Tris-HCl buffer solution with various K ion concentrations over the range from 0 to 1.0 mM.

To verify the ion selectivity of valinomycin-modified graphene FETs, Na ion concentration dependence of transfer characteristics in graphene FETs was investigated, as shown in Fig. 4. The transfer characteristics of valinomycin-modified graphene FETs were almost unchanged; almost no Dirac point shifts were found over the Na ion concentration range between 0 and 1.0 mM, indicating that the ISM membrane suppressed the nonspecific binding of nontarget cations to the surface of the graphene channels. Therefore, valinomycin-modified graphene FETs are useful to fabricate ion sensors with high sensitivity and selectivity.

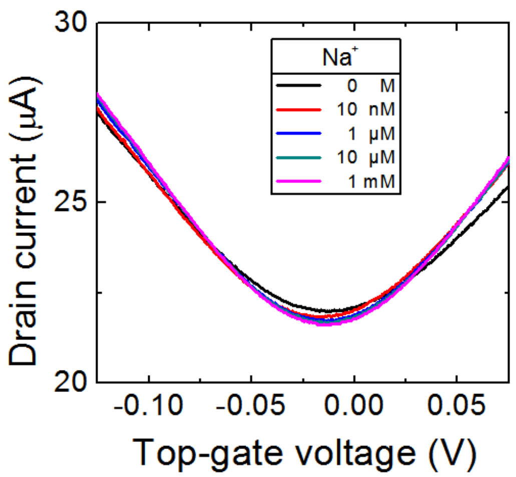

Fig. 4. Transfer characteristics of a valinomycin-modified graphene FET in the 100 mM Tris-HCl buffer solution with various Na ion concentrations over the range from 0 to 1.0 mM.

Conclusions

We have demonstrated that graphene FETs modified with valinomycin are highly sensitive and selective for the electrical detection of K ions in the electrolyte. The K ion concentration dependence of the valinomycin-modified graphene FET transfer characteristics revealed that the transfer curves were negatively shifted as the K ion concentration increased, and a semilogarithmic dependence between the top-gate voltage at the Dirac point and the K ion concentration was observed. Furthermore, the valinomycin-modified graphene FETs effectively detected K ions over a wide concentration range from 10 nM to 1.0 mM. These observations can be explained by the accumulation of positive charge on the surface of the graphene channel, because of the specific binding of K ions to valinomycin in the ISM. In contrast, the valinomycin-modified graphene FET transfer characteristics showed no change when the concentration of Na ions was increased. These results indicate that the valinomycin-modified graphene FETs responded specifically to K ions in solution, and will prove useful for high sensitivity, selective ion sensors.

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