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

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ABSTRACT

Electrolyte-gated graphene field-effect transistors (FETs) were fabricated to demonstrate highly sensitive electrical detection of K or Na ions in a solution. Moreover, selective K ion sensors were fabricated by modifying graphene 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 potential utility of graphene FETs as highly sensitive, selective K ion sensors.

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1. Introduction

Graphene exhibits excellent electrical, mechanical and chemical properties [1], such as extraordinary high carrier mobility [2], low optical absorption [3], and excellent thermal strength [4]. Then, graphene is highly expected to be a promising electronic material in next generation electronics; field-effect transistors (FETs) [5], high frequency electronic devices [6,7], transparent electrodes [8,9], and so on. Since single-layer graphene has a perfect two-dimensional structure formed by a single layer of carbon atoms, electrical characteristics in graphene FETs, in which graphene single layers are incorporated as channels, are expected to be highly sensitive for modulation of surface potentials in graphene channels [10]. Moreover, graphene has high potential window and chemical stability, and thus graphene FETs will operate in a solution without insulators on channels. For these reasons, change in tiny charges owing to adsorption or desorption of analyte on the graphene channel in a solution will be detected [11–13]. Therefore, graphene FETs will be used as electric-readout biological, or chemical sensors.

Label-free electrical detections of chemical and biological species have attracted significant attention for genomics, clinical diagnosis, and practical pharmacy applications during the past decade because they are simpler, less expensive and require less energy than conventional methods, and can be miniaturized for the development of hand-held electrochemical multiplex sensors [14–22]. In this paper, electrolyte-gated graphene FETs were

fabricated, and electrical detections of potassium (K) or sodium (Na) ions in solutions were demonstrated. K and Na are essential elements for biological activity including human life [23–27]. For example, these ions are important in transport of nerve impulses, and in controlling electrostatic charges on cell membranes through ion channels or ion pumps. Moreover, we report the integration of valinomycin into graphene FETs in order to achieve ion selectivity. Valinomycin ($C_{54}H_{90}N_6O_{18}$) is a dodecadepsipeptide synthesized by several *Streptomyces* strains, which has a high affinity for K relative to other alkali metal ions [28,29]. Valinomycin has previously been used in ion sensors, because of its unique structure and ion binding properties [30,31]. 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 potential utility for monitoring K ions in solutions.

2. Experimental

The following graphene FET fabrication processes were employed. Single-layer graphene samples were deposited on a silicon wafer with a top layer of thermally formed SiO_2 (~280 nm) by the mechanical exfoliation of Kish graphite (Covalent Materials Corp., Tokyo, Japan) with adhesive tape. The number of graphene layers was initially identified with an optical microscope, using a method known as optical contrast identification. Graphene layers show a distinct change in the reflected light contrast compared with the underlying SiO_2 top layer, which depends on the number of

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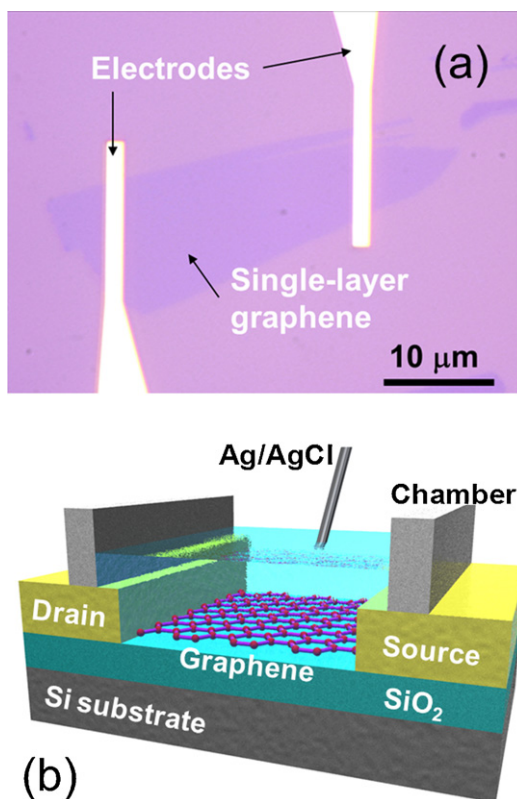


Fig. 1. (a) Optical microscopy image of a graphene FET fabricated by e-beam lithography and lift-off method on a SiO₂ layer and (b) schematic image of a measurement system in a solution.

graphene layers [32–34]. The exact number of graphene layers can be determined by Raman spectroscopy; a characteristic intensity ratio of the 2D Raman peak at 2700 cm⁻¹ to the G peak at 1582 cm⁻¹ indicates that a single-layer graphene was obtained [35,36]. Fig. 1a shows graphene FETs fabricated by e-beam lithography and lift-off method on a SiO₂ layer. Ni/Au (5 nm/30 nm) source and drain electrodes were prepared on the opposite sides of the graphene channel.

Fig. 1b 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 (Cypress Systems) was used as the electrolyte-gated electrode to minimize environmental effects [37,38]. The electrical characteristics in the graphene FET were measured with a semiconductor parameter analyzer (B1500A; Agilent Technologies Ltd.). 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 and NaCl solutions of various concentrations were added to the Tris–HCl buffer solution to increase the K and Na ion concentrations in the reagent solution, respectively.

3. Results and discussion

3.1. Electrolyte-gated graphene FETs

Fig. 2 shows transfer characteristics in the graphene FET in air or in an electrolyte (phosphate buffer solution: 10 mM) at a source-drain voltage of 0.1 V. When the back-gated voltage using the Si substrate was swept from –50 to 50 V, an ambipolar characteristic was observed in vacuum, as shown in Fig. 2a. The result is consistent with other reports, which arises from the band structure of

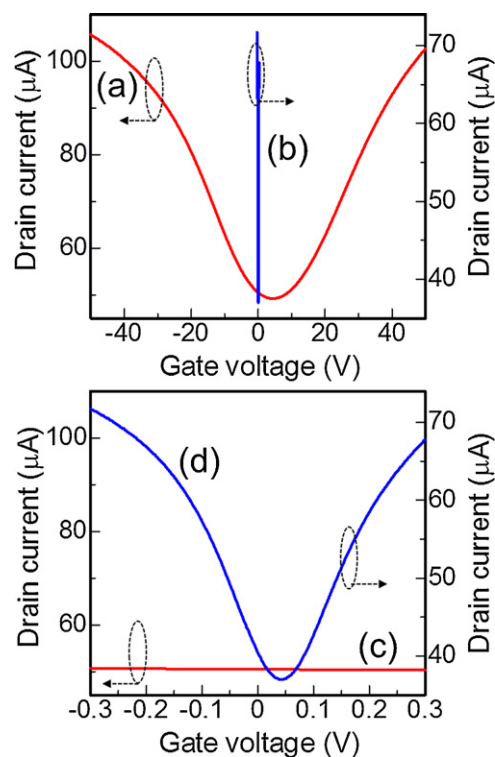


Fig. 2. Transfer characteristics of a graphene FET against back-gate voltage in vacuum (a) and electrolyte-gate voltage in a solution (b). (c) and (d) show the enlarged view of (a) and (b), respectively.

graphene [39]. The transconductance was estimated to be 1.8 μS in vacuum. The drain current in the graphene FETs was plotted against the electrolyte-gate voltage in the solution, as shown in Fig. 2b. Fig. 2c and d shows the enlarged view of Fig. 2a and b, respectively, which was obtained by sweeping from –0.30 to 0.30 V of the gate voltage. It is found that an ambipolar characteristic was obtained in the electrolyte. It is noted that the current through the electrolyte from the graphene FET to the reference electrode was negligible (less than a few nA). The transconductance in the electrolyte-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 [40]. As a result, graphene FETs will be useful to detect chemical and biological molecules with high sensitivity.

K or Na ion concentration dependence of the transfer characteristics in graphene FETs was investigated. After introduction of the 100 mM Tris–HCl buffer solution with various KCl and NaCl concentrations ranging from 0 to 1.0 mM, the drain currents versus electrolyte-gate voltage characteristics were measured, as shown in Fig. 3a and b, respectively. The source–drain voltage was set at 0.1 V and the back-gate voltage was grounded during the measurements. The measurements reveal that all transfer curves show ambipolar characteristics and that the curves have almost the same transconductances, indicating that defects were not induced into the graphene channels and the carriers in the graphene channels were not scattered by K or Na ions. Moreover, the transfer curves shifted toward the negative direction of electrolyte-gate voltage with increasing K or Na ion concentration. The negative shifts of the curves with increasing the ion concentration can be due to the negative shifts of the Fermi level, indicating that graphene FETs detected K or Na ions from 1.0 nM to 1.0 mM by electrical measurements. The detection mechanism of K or Na ions using graphene FETs is not clear at present. However, when some carbon atoms bind hydroxyl groups in a solution, the mechanism may be interpreted using a site binding model [41]. As the K or Na ion concentrations increase,

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