Selective Detection of Cu$^{2+}$ Ions by Immobilizing Thiacalix[4]arene on Graphene Field-Effect Transistors

Yuki Takagiri, Takashi Ikuta,* and Kenzo Maehashi*†

Institute of Engineering Tokyo University of Agriculture and Technology, 2-24-16, Nakacho, Koganei, Tokyo 184-8588, Japan

ABSTRACT: Highly accurate quantitative detection of heavy metals is essential for environmental pollution monitoring and health safety. Here, for selective detection of Cu$^{2+}$ ions with high sensitivity, thiacalix[4]-arene (TCA) immobilized on graphene field-effect transistors (G-FETs) are developed. Our proposed TCA-immobilized G-FETs are successfully used to detect Cu$^{2+}$ ions at concentrations ranging from 1 μM to 1 mM via changes in their transfer characteristics. Moreover, the measured transfer characteristics clearly shift only when Cu$^{2+}$ ions are introduced in the buffer solution despite it containing other metal ions, including those of Na$^+$, Mg$^{2+}$, Ni$^{2+}$ and Cd$^{2+}$; this selective detection of Cu$^{2+}$ ions is attributed to the planar arrangement of TCA on graphene. Therefore, TCA-immobilized G-FETs selectively detect Cu$^{2+}$ with high sensitivity.

INTRODUCTION

Detection of heavy metal ions is necessary for environmental monitoring and health safety. In the same vein, identification and quantification of heavy metal ions is crucial for determining water quality. Currently, conventional analytical approaches such as atomic absorption spectrometry and inductively coupled plasma mass spectrometry have been utilized in laboratory settings to identify and quantify heavy metal ions in environmental and biological samples. However, these approaches are not suitable for onsite analysis of heavy metal concentrations owing to the size of the equipment used for them. In addition, heavy metal analysis is not straightforward owing to the complexity of the analytical processes and relatively long measurement times. Considering this, portable devices that can be used for highly sensitive onsite detection of heavy metal ions are needed. Thus, in this study, we developed graphene-based devices to achieve this.

Graphene is a one-atom-thick two-dimensional carbon sheet characterized by high carrier mobility and chemical stability, which can also be used for device miniaturization. Owing to these properties, in recent times, graphene has attracted considerable attention as a sensor material in sensor devices. An example of such a device is the graphene field-effect transistor (G-FET). In particular, when charged molecules are adsorbed on graphene channels in G-FETs, the adsorbed molecules induce carriers on the graphene channels, resulting in a shift in the charge neutrality point of G-FETs. In addition, because of the high carrier mobility of graphene, these shifts lead to significant changes in the drain current. Consequently, G-FETs can be used to detect molecules with high sensitivity. However, graphene alone cannot be used for selective detection of different target molecules. Therefore, to obtain selectivity, different types of receptors, such as antibodies, aptamers, enzymes, DNA, and supramolecules, immobilized on graphene have been used in previous studies.

RESULTS AND DISCUSSION

Detection of Cu$^{2+}$ Ions Using TCA-Immobilized G-FETs. In this study, we demonstrated the detection of Cu$^{2+}$ ions using TCA-immobilized G-FETs. Figure 1 shows the transfer characteristics of TCA-immobilized G-FETs before...
and after introducing Cu$^{2+}$ ions at concentrations of 1, 10, 30, 100, and 300 μM. Bipolar characteristics were observed for the buffer solutions at all Cu$^{2+}$ concentrations. Because the leakage current of G-FETs is 1000 times smaller than the drain current, the leakage current is negligible for detection of Cu$^{2+}$. The results revealed that the transfer characteristics shifted in the positive gate-voltage direction when Cu$^{2+}$ ions are introduced, indicating that G-FETs can be used to detect Cu$^{2+}$ ions based on these electrical measurement changes. Furthermore, the shifts in the transfer curves increased with increasing Cu$^{2+}$ concentration; in particular, the shift at a Cu$^{2+}$ concentration of 300 μM was as large as ~200 mV. Also, the average of the shifts at 300 μM was 186 ± 20 mV; the results indicated that G-FETs have repeatability for detection of Cu$^{2+}$ ions. The observed positive shifts in Figure 1 were different from the results in a previous study that used G-FET-based sensors, wherein the accumulation of positive charges on graphene channels in G-FETs led to negative shifts in transfer curves. In contrast, our results shown in Figure 1 imply that the charge distribution in TCA changed because of the formation of complexes between Cu$^{2+}$ and TCA, as shown in Figure 2. In turn, this change in the charge distribution induced potential changes in the graphene channel, resulting in the positive shift in transfer characteristics.

**Cu$^{2+}$ Concentration Dependence.** Next, the dependence of Cu$^{2+}$ ion concentration on voltage characteristics of TCA-immobilized G-FETs was investigated. The transfer characteristics were measured every 5 min, and the Dirac-point voltage ($V_{DP}$) was plotted. Figure 3a shows the shifts in $V_{DP}$ with time for various ion concentrations of Cu$^{2+}$ ranging from 0 to 1 mM; the results shown in the figure reveal that the shift in $V_{DP}$ increased with increasing Cu$^{2+}$ ion concentration. Furthermore, change in $V_{DP}$ almost stopped within 15 min at each Cu$^{2+}$ concentration. This occurs because the adsorption of Cu$^{2+}$ ions on TCA attains an equilibrium state. Therefore, G-FETs with TCA can be used to detect Cu$^{2+}$ ions in a concentration range of 1 μM to 1 mM within 15 min. Figure 3b shows the amount of $V_{DP}$ shift as a function of concentration of Cu$^{2+}$ ranging from 0 to 1 mM. The result reveals that the $V_{DP}$ shift increases linearly with the concentration of Cu$^{2+}$ ranging from 0 to 300 μM. On the other hand, the $V_{DP}$ shift at 1 mM is slightly deviated from the linearity, indicating that the $V_{DP}$ shift gradually saturated over 300 μM.

**Selectivity of TCA-Immobilized G-FETs for Cu$^{2+}$ Ions.** To investigate the selectivity of TCA-immobilized G-FETs for Cu$^{2+}$, the shifts in $V_{DP}$ were measured in Tris-HCl buffer containing other metal ions (Na$^+$, Mg$^{2+}$, Ni$^{2+}$, and Cd$^{2+}$). Figure 4a shows these shifts in $V_{DP}$ when Na$^+$, Mg$^{2+}$, Ni$^{2+}$, and Cd$^{2+}$ ions at concentrations of 500 μM each were sequentially added to the solution, after which Cu$^{2+}$ ions at concentrations of 50 and 500 μM were added; the results show that $V_{DP}$ did not clearly shift when Na$^+$, Mg$^{2+}$, Ni$^{2+}$, and Cd$^{2+}$ ions were introduced in the solution. In contrast, a clear $V_{DP}$ shift was observed when Cu$^{2+}$ ions were introduced in the solution. Therefore, TCA-immobilized G-FETs showed selective detection of Cu$^{2+}$ ions even in a solution containing other metal ions. Figure 4b shows the changes in $V_{DP}$ for each metal ion (Na$^+$, Mg$^{2+}$, Ni$^{2+}$, Cd$^{2+}$, and Cu$^{2+}$) at concentrations of 500 μM in the form of a bar graph. In particular, the $V_{DP}$ shift at 500 μM was observed to be over 100 mV for Cu$^{2+}$ ions, which was more than 10 times larger than those recorded when Na$^+$, Mg$^{2+}$, Ni$^{2+}$, and Cd$^{2+}$ ions were introduced. This selectivity for Cu$^{2+}$ ions results from the immobilization of TCA on the graphene channel. The recognition of Cu$^{2+}$ ions using TCA immobilized on graphene can be explained using the hard and soft acids and bases (HSAB) theory and the ligand field theory. According to the HSAB theory, soft metal ions (Cu$^{2+}$, Ni$^{2+}$, and Cd$^{2+}$) tend to easily coordinate with sulfur atoms. Results from previous works indicate that TCA dispersed in solution captures not only Cu$^{2+}$ ions, but also...
Ni²⁺ and Cd²⁺ ions through the liquid–liquid extraction method. However, it is interesting to note that, compared with these previous works, our results indicate that TCA on the graphene surfaces capture only Cu²⁺ ions, which, in turn, implies that the space degrees of freedom of TCA were limited by immobilizing it on graphene surfaces. In particular, in the case of the liquid–liquid extraction method, the orientation and position of TCA changes relatively freely in solutions; consequently, several different heavy metal ions are surrounded by three TCA molecules leading to their adsorption. However, when immobilized on G-FETs, TCA was planarly placed on the graphene surfaces; therefore, TCA cannot surround and adsorb several types of heavy metal ions when it is immobilized so. The coordination between Cu²⁺ ions and G-FETs occurs via the host–guest interaction. As depicted in Figure 5, Cu²⁺ ions are generally coordinated in a square shape, as are the bridging sulfur atoms in TCA leading to the coordination of the bridging sulfur atoms with Cu²⁺ ions and their subsequent adsorption. On the contrary, coordination forms of the other heavy metal ions are not of square type, but instead are of tetrahedron and octahedron types, which is why they do not coordinate with TCA immobilized on graphene. In summary, the selectivity of G-FETs for Cu²⁺ ions is attributed to the immobilization of TCA on graphene surfaces in G-FETs. Therefore, G-FETs can be successfully used in the selective detection of Cu²⁺.

### CONCLUSIONS

In this study, we fabricated Cu²⁺ sensors using TCA-immobilized G-FETs. The transfer characteristics shifted in the positive gate-voltage direction on introducing Cu²⁺ ions in the solution; in addition, the V_DP shift increased as the Cu²⁺ concentration increased from 1 μM to 1 mM, which indicates that G-FETs can be used for quantitative analysis of Cu²⁺. Furthermore, TCA-immobilized G-FETs were able to successfully detect Cu²⁺ ions selectively in a buffer solution containing several different metal ions, viz., Na⁺, Mg²⁺, Ni²⁺, and Cd²⁺ ions. In particular, the amount of V_DP shift on introducing Cu²⁺ ions at a concentration of 500 μM was about 10 times larger than that on introducing Na⁺, Mg²⁺, Ni²⁺, and Cd²⁺ ions at the same concentration. Therefore, our results indicate that the TCA-immobilized G-FETs provide high sensitivity and selectivity for the detection of Cu²⁺ ions, making them promising candidates as portable Cu²⁺ sensors. Moreover, our research shows the importance of coordination structures between TCA and metal ions for the detection of specific metal ions using G-FETs. Moreover, in a manner similar to the approach followed in our study, other heavy metal ion sensors could be realized by adjusting the molecular structure to ensure the formation of a coordinate structure between the molecule and metal ions.

### EXPERIMENTAL METHODS

**Fabrication Process for G-FETs.** First, monolayer graphene was synthesized on Cu foil (JX Nippon Mining & Metals, HA) via chemical vapor deposition. Before use, the Cu foil was annealed under a flow of 3% H₂ and 97% Ar at 500 sccm for 41 min to remove any native oxide so that Cu exhibits catalytic activity. Graphene was synthesized at 1035 °C by cracking CH₄ under both 3% H₂ and 97% Ar flow at 15 sccm, and 5% CH₄ and 95% Ar flow at 1500 sccm for 35 min. Next, the graphene was transferred onto a Si/SiO₂ substrate using poly(methyl methacrylate) (PMMA) and annealed at 330 °C for 1 h under a 3% H₂ and 97% Ar flow to remove impurities such as residual PMMA. Subsequently, Ni(10 nm) and Au(30 nm) were deposited as sources and drain electrodes via a photolithography technique. The channel distance and width for the source and drain were approximately 5 and 15 μm, respectively.

**Adsorption of TCA on Graphene and Measurement Methods.** After G-FETs were fabricated, a 50 μM solution was prepared by dissolving TCA (Tokyo Chemical Industry Co.) in chloroform. Then, the G-FETs were immersed in this prepared solution to immobilize TCA on graphene through π–π interactions between them. These G-FETs were then taken out of the solution and dried to obtain the required graphene-based sensors. Next, a silicon rubber pool was attached to the G-FETs so that the graphene channel could be immersed in a Tris-HCl buffer (20 mM, pH 8.0). A saturated Ag/AgCl electrode was used as the reference electrode. NaCl, MgCl₂, CdSO₄, NiSO₄, and CuSO₄ solutions at various concentrations were added to the Tris-HCl buffer solution to increase the Na⁺, Mg²⁺, Cd²⁺, Ni²⁺, and Cu²⁺ concentrations in the reagent solution, respectively. The transfer characteristics of the G-FETs were measured by applying a drain voltage of 50

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**Figure 4.** (a) V_DP as a function of time with other metal ions (Na⁺, Mg²⁺, Ni²⁺, and Cd²⁺) at 500 μM and Cu²⁺ at 50 and 500 μM. (b) Shifts in V_DP due to different metal ions (Na⁺, Mg²⁺, Ni²⁺, Cd²⁺, and Cu²⁺) at 500 μM.

**Figure 5.** Coordination of TCA with Cu²⁺ ions.
mV using a semiconductor parameter analyzer (Keysight Technologies, B2912).

**AUTHOR INFORMATION**

**Corresponding Authors**

*E-mail: ikuta@go.tuat.ac.jp (T.I.).
*E-mail: maehashi@cc.tuat.ac.jp (K.M.).

**ORCID**

Kenzo Maehashi: 0000-0002-9925-8874

**Notes**

The authors declare no competing financial interest.

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