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Heavy-Metal-Ion Sensor Using Graphene Field-Effect Transistor Decorated with Thiacalix[4]arene

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Abstract

Heavy-metal-ion sensors ware developed by decorating thiacalix[4]arene (TCA) on graphene field-effect transistors (G-FETs). Since TCA is known to have an ability to bind heavy metal ions, the devices are useful for detecting heavy metal ions in solution. In this study, we utilized Cu in heavy-metal ions as targets, and investigated changes in the transfer characteristics by introducing Cu^{2+}. The transfer characteristics of the G-FETs decorated with TCA shifted with increasing the concentration of Cu^{2+}. In contrast, alkali metal ions such as Na^{+} and K^{+} were not detected at all using the devices. In these devices, Cu^{2+} at pH 7.0 were detected with higher sensitivity compared with that at pH 7.9. Therefore, the devices are expected to be portable and highly sensitive sensors for detecting heavy metals.

1. Introduction

Heavy metals pollute the environment and are harmful to human. Currently, large-size instruments such as an atomic absorption spectrophotometer are generally used for detecting heavy metal ions with high sensitivity. Thus, novel devices that is low cost and has short time measurements are required. To realize a highly sensitive and portable sensor for detection of heavy metal ions, we developed graphene-based devices. Graphene, a one-atom-thick two-dimensional carbon sheet, is characterized by high mobility, chemical stability and device miniaturization. Recently, it has been attracting attention as sensor materials [1-3]. However, selectivity is not obtained using only graphene. It has been reported that Na^{+} was detected by modifying graphene with valinomycin [4]. In this study, we focused on thiacalix[4]arene (TCA), composed of benzene rings linked via sulphide bridges (Fig. 1), which is known to form complex ions with heavy metal ions by bridging sulfur which has the lone pair of electrons and phenol O^{-}, and heavy metal ions were detected by using TCA [5-7]. In this study, heavy-metal-ion sensors ware developed by depositing TCA on graphene field-effect transistors (G-FETs).

2. Experimental Methods

First, graphene was synthesized by chemical vapor deposition [8], transferred onto a Si/SiO_2 substrate, and electrodes were formed to fabricate G-FETs [9]. Then, a solution was prepared by dissolving TCA in chloroform, and the graphene was decorated with TCA by immersing the G-FETs in the solution. After the G-FETs were taken out from the solution and dried, graphene-based sensors were developed. Finally, a silicon rubber pool was attached to the G-FETs, and a Tris-HCl buffer (pH 7.9) was introduced. A saturated Ag/AgCl was used as a reference electrode. The transfer characteristics were measured by applying a drain voltage of 50 mV.

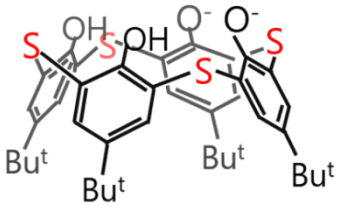

Fig. 1. Schematic structure of thiacalix[4]arene (TCA).

3.Results and Discussion

Figures 2(a) and 2(b) show transfer characteristics of G-FETs decorated with TCA before and after introducing Cu^{2+} at 100 μM, respectively, revealing that the transfer characteristics shifted in the positive direction by introducing Cu^{2+}, and the shift amount was as large as approximately 80 mV. The results indicate that after introducing Cu^{2+}, TCA formed complex ions with Cu^{2+}, resulting in the detection of Cu^{2+}. Therefore, the devices are capable of monitoring Cu.

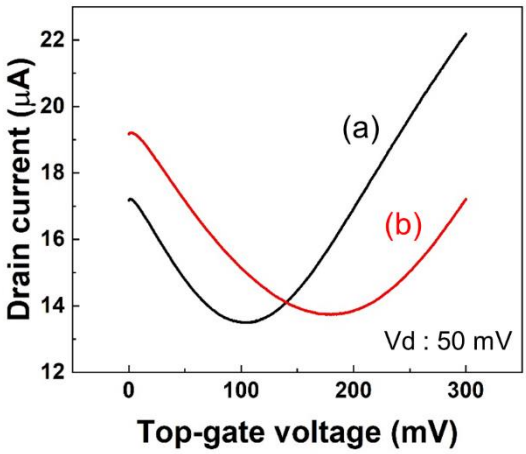

Fig. 2. Transfer characteristics (a) before and (b) after 100 μM injection of Cu^{2+}.

Figure 3 shows the voltage shift at the Dirac-point voltage (V_{DP}) of the transfer characteristics as a function of the concentration of Cu^{2+}. The result reveals that the V_{DP} shifted toward the positive direction with increasing the concentration of Cu^{2+}. Detection of alkali-metal ions such as Na^+ and K^+ were also investigated using the same device and the data were plotted in Fig.3. After introduction of Na^+ and K^+ with various concentrations, no shift in V_{DP} was observed. The results indicate that the device has selectively detected Cu^{2+}. Both the bridging sulfur and phenol O^- form complex ions with the vacant 3d orbital of Cu^{2+}. In contrast, since alkali-metal ions do not have vacant 3d orbitals, they do not bind TCA. As a result, Cu^{2+} was selectivity detected using G-FETs decorated with TCA.

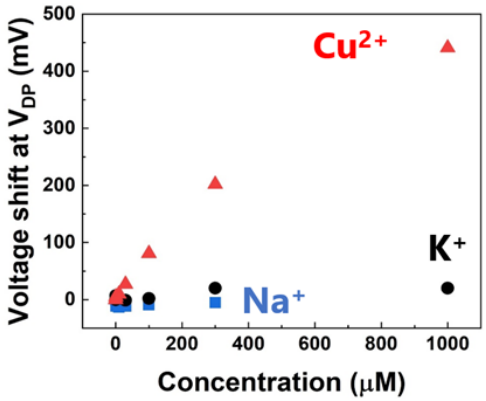

Fig. 3. V_{DP} shift depend on each concentration of Cu^{2+}, Na^+ and K^+.

Then, pH dependence of Cu^{2+} detection was investigated using the devices. Figure 4 shows the voltage shift at Dirac-point voltage as a function of the concentration of Cu^{2+} at pH 7.0 and 7.9. The result reveals that the V_{DP} shifted toward the positive direction with increasing the concentration of Cu^{2+} at pH 7.0 and 7.9, respectively. However, the amount of the V_{DP} shift was larger at pH 7.0 than that at pH 7.9. In the solution of pH 7.9, TCA is considered to have a higher proportion of phenol O^- as compared with that at pH 7.0. As a result, TCA has become difficult to detect Cu^{2+} owing to the occurrence of the structural distortion.

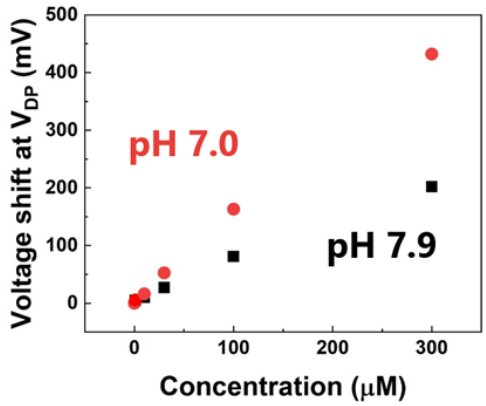

Fig. 4. V_{DP} shift depend on concentration of Cu^{2+} at pH 7.9 and 7.0.

3. Conclusions

We have developed heavy-metal-ion sensors using G-FETs decorated with TCA. The devices have succeeded in detection of Cu^{2+}, and the amount of V_{DP} shifts increased with the concentration of Cu^{2+}. In contrast, the devices do not detect alkali-metal ions. The results indicate that the devices have selectivity detected Cu^{2+}. In addition, Cu^{2+} was detected with higher sensitivity at pH 7.0 as compared with that at pH 7.9. Therefore, the G-FETs decorated with TCA are expected to highly sensitive and portable sensors for detection of heavy metal ions.

Acknowledgements

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