Electrolyte-gated organic field effect transistor with functionalized lipid monolayer for novel sensors

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論 文 内 容 の 要 旨

Nowadays, urban and industrial growth causes critical water issues through the contamination of radioactive ions, heavy metal ions, and organic compounds. Especially, the pollution from radioactive ions can cause serious problems for the environment and humans even with a small amount of them. The detection and monitoring of radioactive ions are critical for protecting the environment and humans. The conventional chromatographic techniques are well known for the identification and quantification of ions. However, these techniques are limited by expensive instrumentation, intricate sample preparations, and expert manpower. Therefore, small size sensors with a low-cost fabrication and easy for handling, are highly needed as an alternative tool for the detection of the radioactive ions.

Electrolyte-gated organic field-effect transistors (EG-OFET) have been gained much attention for the development of the sensor due to their intrinsic advantages. OFET technology provides a high throughput fabrication process with a large printable area on a flexible substrate and a capable of integration to an electrical circuit. Here, electrolyte solutions are used as electrical gates of the EG-OFET provides the high capacitor (1-20 μFcm^{-2} scale) at the interface of organic semiconductor channel and electrolyte solution. EG-OFET, therefore, can operate at an ultra-low voltage under 1 V. However, a stable operation of EG-OFET remains a challenge due to the doping of electrolyte ions into the organic semiconductor channel. Furthermore, the specific probes for the detection of analytes are required for sensor applications. The functionalization of transistors channels with probing molecules is necessary.

This dissertation provides a new sensor structure based on EG-OFET functionalized by an ultra-thin lipid monolayer for various sensing purposes. Poly(3-hexylthiophene-2-5-dily) (P3HT) films are employed as the channel layers of the EG-OFET because of its stability in the aqueous environment. For the reduction of the doping effect of electrolyte ions, the P3HT surface is modified by depositing the ultra-thin lipid monolayer (2.2 nm) to protect the channel layers from the electrolyte solution. Furthermore, the head groups of lipid monolayer can be further functionalized by attaching the specific probes for sensor applications. As proof of concept, the sensor for the detection of Cs^+ ions is developed.

This dissertation includes five chapters. Chapter 1 describes the general introduction including background, problems, purposes, and approaches for this work.

Chapter 2 discusses the formation and properties of lipid monolayer on the P3HT film. Due to the amphipathic property, lipid molecules can self-assemble a monolayer on the P3HT film. The existence of lipid monolayer on the P3HT film is confirmed by using ATR-FTIR and water contact angle measurements. During the sensor fabrication, the stability of the lipid monolayer is necessary against the rinsing forces from pipets. The lipid monolayer is, therefore, polymerized at middle and head groups of lipid molecules to improve the mechanical stability of lipid monolayer. The mechanical stability and thickness of lipid monolayer are characterized by force measurements. The thickness of the lipid monolayer is confirmed again by the X-ray deflection method. Moreover, the influence of lipid monolayer on the electrical double layer is also investigated by electrochemical impedance spectroscopy.

In chapter 3, a fundamental operation of water-gated OFET (WG-OFET) functionalized by a lipid monolayer is established. For this transistor, the de-ionized water is used as electrical gates because the ion-free of the highly pure water can minimize the doping effect. The electric double layer (EDL) at the interface between water and channel plays an important role in allowing WG-OFET to operate on the millivolt range. However, the EDL strongly depends on the flatness of the P3HT film due to its sub-nanometer thickness. It is necessary to understand the influence of P3HT on the performance of WG-OFET for long-term stable operation. Another key factor is the gate electrode metal to be immersed in water. The intrinsic work function of metal can modulate the threshold voltage (V_{th}) of WG-OFET. Therefore, two kinds of gate electrodes metal, tungsten (W) and gold (Au), are utilized to investigate the influence of metal on the performance of WG-OFET. Additionally, the influence of lipid monolayer on the operation of WG-OFET also needs to be evaluated. The lipid monolayer is expected to eliminate the doping effect.

Chapter 4 discusses the performance of EG-OFETs functionalized by lipid monolayers for sensor applications. Because the detection of ions and biomolecules is typically carried out in the presence of interfering ions, the electrolyte solution is employed as a gating medium. However, the electrolyte ions are aggressive to organic semiconducting materials. In this case, the benefit of lipid monolayer becomes more important for the protection of the P3HT film from the doping of electrolyte ions. Additionally, the lipid monolayers with functionalized head groups provide the capability for pH sensors. Therefore, the understanding of the pH sensitivity of different lipid monolayers is investigated. However, the pH sensitivity is a disadvantage for ion sensors because the pH dependence of devices can change the output signal of ion sensors. Therefore, it is necessary to eliminate the pH sensitivity of lipid monolayers. Here, I passivate head groups of lipid monolayers by methyltrichlorosilane (MTS), which is inert to pH variation. This method is also employed for grafting the specific probes to lipid monolayers. Here, the Cs^+ probes are attached to lipid monolayers through MTS molecules for ion sensor applications. The sensor will be characterized in different environments to demonstrate the highly sensitive detection of Cs^+ ions even in the presence of interfering ions.

Finally, chapter 5 summarizes this dissertation.

This study achieves the stable operation of EG-OFET functionalized by the lipid monolayer in the electrolyte solution for ion sensor applications. Notably, the sensor demonstrates high sensitivity for the detection of Cs^+ ions in pseudo-practical conditions. The findings in this study will pave the new way for the development of new sensor applications in chemical and biological fields.