Detection of Mercury (II) Ion in Water using an Organic Field Effect Transistor with a Cysteine-functionalized Gold Electrode

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Abstract

Mercury (II) ion (Hg^{2+}) in water was detected electrically by an organic field effect transistor (OFET). The fabricated OFET possesses an extended-gate electrode functionalized by cysteine, which shows a selectivity for Hg^{2+} over alkali or alkaline-earth metal ions. OFETs could be fabricated on low-cost plastic film substrates using printing technologies, meaning that OFETs can potentially be applied to practical heavy metal ion sensor devices in the near future.

1. Introduction

For several decades, environmental pollution by heavy metal ions has been a major concern in the world [1]. One of the significant metal pollutants is Hg²⁺ because of its high toxicity. To analyze environmental water contaminated by heavy metal ions, several highly sensitive and accurate methods, such as atomic absorption spectroscopy (AAS), atomic fluorescence spectrometry (AFS), and inductively coupled plasma mass spectrometry (ICP-MS), have been developed [3]. However, their disadvantages are expensive, time-consuming, and require trained personnel, so methods amenable to simple, fast, and easy assays that require low-cost instrumentation are desirable. Toward that end, we believe that organic field effect transistors (OFETs) [4-6] are one of the more promising candidates for chemical sensors capable of detecting heavy metal ions. OFETs possess attractive properties such as printability, mechanical flexibility, and low manufacturing costs. To date, OFETs have been thus originally applied to rollable displays [7]. However, interest in OFETs and their advantages have extended beyond displays to sensor applications. Although sensor application of OFETs has been recently investigated [8], heavy metal ion sensors based on OFETs are still their infancy. Herein we report for the first time an extended-gate type OFET chemical sensor for the detection of Hg²⁺ in water. The extended-gate electrode is functionalized by an amino acid, cysteine [9], which can be expected to bind Hg^{2+} in aqueous media.

2. Results and Discussion

The structure of the extended-gate type OFET is exhibited in Fig. 1. The designed transistor could be operated at low-voltages. An Al gate electrode was deposited on a



Fig. 1 Schematic structure of the designed extended-gate type organic FET.

glass substrate by thermal evaporation (30 nm). The gate dielectric consists of a thin-film of aluminum oxide (5 nm) and a tetradecylphosphonic acid (C₁₄-PA, 1.7 nm) self-assembled monolayer (SAM) [10]. The aluminum oxide film was prepared by oxygen-plasma treatment of the Al gate electrode. The plasma power was 300 W, and the duration of treatment was 50 min. The SAM was prepared by immersing the substrate in a 2-propanol solution of C14-PA at r.t. Au source-drain electrodes were deposited on the gate dielectric layer by thermal evaporation (30 nm) and patterned using a shadow mask. The channel width and length were 1000 and 50 µm, respectively. A 1 wt% solution of an amorphous fluoropolymer (Teflon® AF1600) in FC-43 was dispensed for the preparation of bank layers. Subsequently, a solution-processable semiconducting polymer, poly(2,5-bis(3-hexadecylthiophene-2-yl)thieno[3,2b]thiophene) (pBTTT-C₁₆) [10], was drop-casted from a 0.03wt% solution of o-dichlorobenzene, and then annealed at 175 °C for 30 min under nitrogen atmosphere. Cytop[®] (CTL-809M) was spin-coated on the device and baked at 100 °C for 10 min (100 nm). In addition, An Au extended-gate electrode on a PEN film substrate (125 µm) was prepared by thermal evaporation. The extended-gate electrode was immersed in a HEPES (= 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid) buffer (100 mM) solution (with NaCl (100 mM)) of cysteine (10 mM) for 1 h at pH 7.4 at r.t. Finally, the electrode was washed by a HEPES buffer solution. The size of sensing area on the extended-gate was 15 mm².



Fig. 2 XPS spectra for C1s, N1s, S2p, and O1s regions of the cysteine-treated Au electrode.



Fig. 3 Output characteristics ($I_{DS}-V_{DS}$) of the OFET upon addition of incremental amounts of Hg²⁺ in a HEPES buffer solution solution (100 mM) with NaCl (100 mM) at pH 7.4 at r.t. [Hg²⁺] = 0–30 μ M.

First, the prepared extended-gate was characterized by X-ray photoelectron spectroscopy (XPS). The XPS results revealed that the presence of carbon, oxygen, sulfur, and nitrogen on the gold electrode (Fig. 2), suggesting that cysteine was successfully immobilized on the gold electrode.

The fabricated OFET was reproducibly operated below 1 V, which means that the OFET can be employed for sensing of metal ions in water. The OFET was connected to the extended-gate electrode through a conducting cable, and the gate voltage was applied through a silver chloride electrode (Fig. 1). Fig. 3 shows changes in the output characteristics of the OFET upon addition of incremental amounts of Hg²⁺ in a HEPES buffer solution at pH 7.4. As a result, the output current decreased with an increase in the concentration of Hg²⁺. These observed changes of the output current decreased with an increase of the output current decreased with an increase in the concentration of Hg²⁺.

put current are attributed to changes in conductance within the OFET channel by the positively charged mercury ions (Hg^{2+}) captured on the extended-gate electrode, such that the operating mechanism of extended-gate type FETs can be explained as a shift in surface potential at the gate/electrolyte interface [11]. It is worth noting that the detection of Hg^{2+} was successfully achieved even in the presence of large excess amounts of interferent Na⁺ (100 mM) (100,000~3,300 equivalent amount of Hg^{2+}). Furthermore, Ca^{2+} (which is a representative alkaline-metal ion) titration was carried out as a control experiment. As a consequence, the response to Ca^{2+} is weaker than that to Hg^{2+} . This suggests that the changes in the OFET characteristics is derived from the chelating ability of cysteine on the extended gate electrode.

3. Conclusions

In conclusion, we successfully demonstrated the first detection of Hg^{2+} in water using the extended-gate type OFET. The obtained results indicate that the OFET based sensors have high potential for developing flexible and low-cost chemical sensors.

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