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Detection of Cysteine in Water using an Extended-gate Organic Field Effect Transistor

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Abstract

We report cysteine detection in water using an extended-gate type organic field-effect-transistor (FET). The fabricated organic FET can be operated at below 3 V. The cysteine-sensing-part of the designed device is the extended-gate electrode made of Au. Cysteine can bind on the Au electrode through chemisorption. As a consequence, we have successfully observed a shift of threshold voltage of the organic FET upon addition of cysteine in an aqueous solution. The detection limit for cysteine was several tens of ppb.

1. Introduction

Cysteine is known as a sulfur containing nonessential amino acid, which plays important roles in living systems. The concentration of cysteine has significant effects on health conditions. For example, low levels of cysteine cause various diseases, such as lethargy, liver damage, muscle and fat loss, slowed growth in children, hair depigmentation, edema, skin lesions, and weakness [1]. In addition, elevated cysteine levels are associated with neurotoxicity, which was investigated in animals with immature blood-brain barriers and in cultured neurons [2]. Moreover, cysteine induced hypoglycemic brain damage was studied as a putative mechanism to excitotoxicity [3]. The reasons for these effects on the brain are relatively unclear.

The detection of cysteine is conventionally performed by liquid chromatography-mass spectrometry [4], or gas chromatography-mass spectrometry [5]. Unfortunately, these techniques are relatively expensive and require trained personnel. Therefore, methods amenable to simple assays that require low-cost instrumentation are desirable.

Organic FET based sensors can readily detect biomolecule concentrations captured onto semiconductor layers or gate electrodes, because the charge carrier concentrations in semiconductor layers are affected by the charge of biomolecules [6]. As part of our ongoing program is on the assumption that cysteine detection is done in water using organic FETs, we designed an extended-gate type organic FET. At the designed device, the main organic FET part is separated from the detection site (= the extended-gate) and the device can be operated at a low voltage. Therefore, degradation of organic transistor by water can be prevented. Furthermore, an Au thin-film was employed as the extended-gate electrode, which allowed that the thiol moiety of cysteine can chemisorb on the Au extended-gate electrode. Here, we report for the first time simple and reliable detection of cysteine by the extended-gate type organic FET sensor.

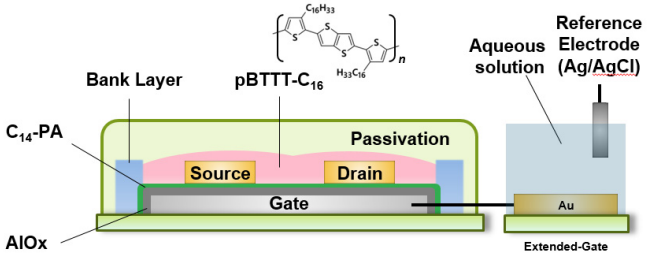

Fig. 1 Schematic structure of the designed extended-gate type organic FET.

2. Results and Discussion

The device structure of the extended-gate type organic FET is shown in Fig. 1. The transistor was designed to achieve low-voltage operation. An Al gate electrode was deposited on a glass substrate by thermal evaporation (30 nm in thickness). The gate dielectric consists of a thin-film of aluminum oxide (5 nm) and a tetradecylphosphonic acid (1.7 nm) self-assembled monolayer (SAM). 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 tetradecylphosphonic acid at room temperature. Au source-drain electrodes were deposited on the gate dielectric layer by evaporation (30 nm) and patterned using photolithography. The channel width and length were 500 and 20 μm, respectively. To prepare bank layers, a 1 wt% solution of an amorphous fluoropolymer (Teflon® AF1600) in FC-43 was dispensed using a dispenser system. Subsequently, a semiconducting polymer, pBTTT-C_{16} (poly(2,5-bis(3-hexadecylthiophene-2-yl)thieno[3,2-*b*]thiophene)), was drop-casted from a 0.03wt% solution of *o*-dichlorobenzene, and then annealed at 175 ºC for 30 min under nitrogen atmosphere. To passivate the device, Cytop® (CTL-809M) was spin-coated on the device and baked at 100 ºC for 10 min (100 nm in thickness). Finally, an Au extended-gate electrode on a PEN film substrate (125 μm) was prepared by thermal evaporation. The size of sensing area on the extended-gate was 15 mm^2.

The electrical characteristics of the organic FET devices were measured. As expected, the fabricated organic FET was reproducibly operated at below 3 V, which means that the organic FET can be applied to analyte detection in water. Then, we used the extended-gate type organic transistor as a sensor for cysteine detection. An Ag/AgCl electrode was employed as a reference electrode. A HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid) buffer solution of cysteine was casted onto the extended-gate electrode. Fig. 2 (top panel) shows the transfer characteristics of an organic FET upon titration with the cysteine solution. Intriguingly, we observed that clear negative shift of the transfer curve with increasing the cysteine concentration, although the change in the field effect mobility was very small. The observed negative shift is attributed to the carrier concentration in the FET channel changed by the charged cysteine on the extended-gate electrode. Fig. 2 (bottom panel) shows the relationship between the cysteine concentration and change in the threshold voltage estimated from the transfer characteristics. The resulting titration isotherm was fitted to Langmuir adsorption model to obtain an equilibrium constant (K), which exhibited a K value of 4.5×10^5 M^{-1}. Furthermore, the limit of detection for cysteine was estimated to be 39 ppb.

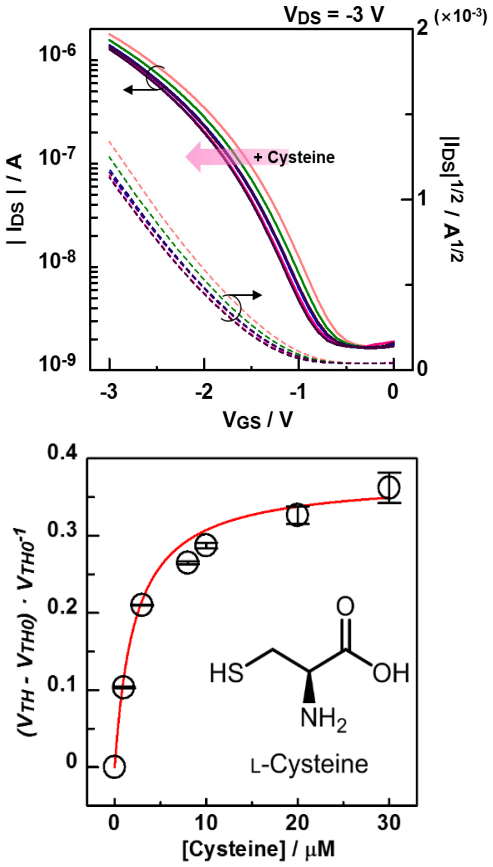

Fig. 2 Top: Transfer characteristics (I_{DS}-V_{GS}) of the organic FET upon titration with cystene in a HEPES buffer solution (10 mM) with NaCl (100 mM) at pH 7.4. [Cysteine] = 0-30 μM. Bottom: Threshold voltage of the organic FET by cysteine at various concentrations in a HEPES buffer solution (10 mM) with NaCl (100 mM) at pH 7.4.

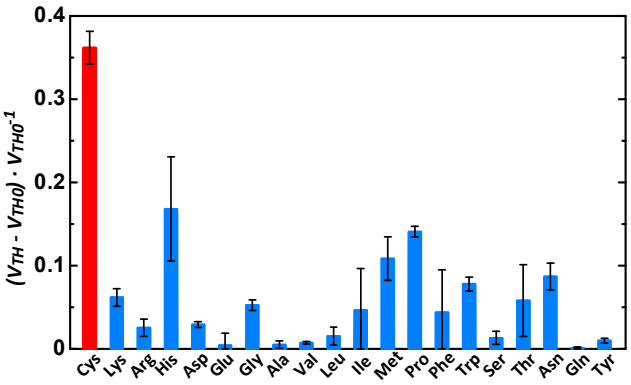

Fig. 3 Threshold voltage changes in the fabricated organic FET-sensor after addition of amino acids in a HEPES buffer solution (10 mM) with NaCl (100 mM) at pH 7.4. [Amino acid] = 30 μM.

We investigated the selectivity of the sensor toward amino acids in water. Aqueous solutions of standard amino acids (30 μM) such as Alanine (Ala), Arginine (Arg), Asparagine (Asn), Aspartic acid (Asp), Cysteine (Cys), Glutamic acid (Glu), Glutamine (Gln), Glycine (Gly), Histidine (His), Isoleucine (Ile), Leucine (Leu), Lysine (Lys), Methionine (Met), Phenylalanine (Phe), Proline (Pro), Serine (Ser), Threonine (Thr), Trptophan (Trp), Tyrosine (Tyr), and Valine (Val) were examined. As shown in Fig. 3, the sensor exhibited the best response to cysteine. Other amino acids induced no or weaker changes in the threshold voltage. This suggests that the selective response is derived from thiol chemisorption.

3. Conclusions

We demonstrated the first cysteine detection in water using the extended-gate type organic FET device operated at low voltage. The high sensitive sensing of cysteine was successfully accomplished. We believe that this result is worthwhile for developing organic FET-based sensors, which is ultra-flexible and low-cost by fabricating with printing technology on a plastic film.

Acknowledgements

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