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An Extended-Gate Type Organic Transistor Based on a Solution Processable Small-Molecule Semiconductor Capable of Detecting Glutathione in Water

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Abstract

We herein report glutathione detection in water using an organic field-effect-transistor (OFET) based on a solution processable small-molecule semiconductor. The fabricated OFET can be operated at below |3| V. The glutathione-sensing-portion of the fabricated OFET is an extended-gate electrode made of Au. Owing to the strong binding affinity of glutathione onto gold through chemisorption, we have successfully observed a shift of threshold voltage of the OFET upon addition of glutathione in an aqueous solution. Because glutathione plays important roles in our body, the device would be applied to various research fields including molecular biology, analytical chemistry, and medical diagnostics in the near future.

1. Introduction

Glutathione is a tripeptide formed from cysteine, glutamic acid, and glycine, which mostly exists in mammalian tissues [1]. The tripeptide has crucial roles as an antioxidant, a free radical scavenger and a detoxifying agent. Furthermore, glutathione is a substrate for glutathione *S*-transferases recognized as detoxifying enzymes. Harmful chemical species such as halides and epoxides are reacted with glutathione in the presence of the enzyme to form harmless products. Because such significant biological roles of glutathione in our body, the peptide has been investigated as a biomarker for various diseases including Parkinson's disease, cancer, etc. To-this-date, one of the most common methods for the detection of glutathione is liquid chromatography-mass spectrometry. Although the above method is reliable, the instrument is expensive and requires trained personnel. In this regard, a fluorescent assay kit for glutathione has been commercialized as an alternative method. However, the price of the kit is still expensive ($ 800/kit)[2]. Therefore, we decided to use an extended-gate type organic field-effect transistor (OFET)[3] for the glutathione detection, owing to its simplicity and low-fabrication cost. The extended-gate electrode made of gold (Au) allowed for chemisorption of the thiol moiety of glutathione, resulting in changes in OFET characteristics. The very simple detection method of glutathione based on the OFET is herein reported.

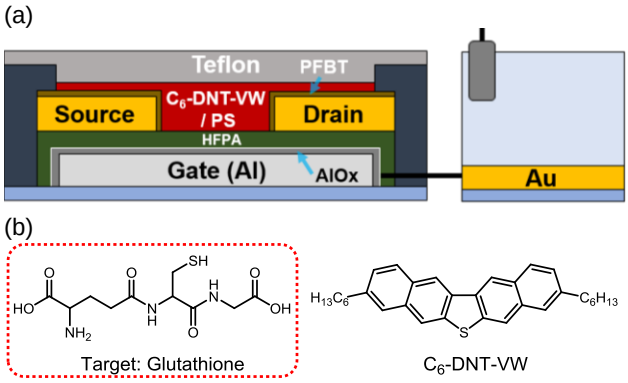

Fig. 1. (a) Schematic structure of the designed extended-gate type OFET. (b) Chemical structures of glutathione and the organic semiconductor material.

2. Results and Discussion

Device fabrication process

The device structure of the extended-gate type OFET is illustrated in Fig. 1. The low-voltage driven OFET was fabricated as follows. An aluminum (Al; Furuya Metal) gate electrode was deposited on a glass substrate by thermal evaporation (30 nm). The gate dielectric was a double layer made of a thin-film of aluminum oxide (4 nm) and a self-assembled monolayer (SAM) of (1*H*,1*H*,2*H*,2*H*-heptadecafluoro decyl)phosphonic acid (HFPA; Tokyo Chemical Industry) (1.5 nm). The aluminum oxide film was prepared by a reactive ion etching treatment of the Al gate electrode. The plasma power was 150 W, and the duration of treatment was 30 min. The SAM was prepared by immersing the substrate in a 2-propanol (IPA) solution of HFPA at room temperature (RT). Source and drain electrodes made of Gold (Au; Tanaka Kikinzoku) 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. The gold electrodes were fully functionalized using a IPA solution of pentafluorobenzenthiol (PFBT; Tokyo Chemical Industry) (0.1 vol%). A 1 wt% solution of an amorphous fluoropolymer ((Dupont™ Teflon® AF1600) in FC-43 (3 M) was robotically dispensed onto the gate dielectric layer for the preparation of a bank layer (0.6 mm in width). Subsequently, a solution-processable semiconducting molecule, 3,9-dihexyldinaphtho[2,3-*b*:2',3'-*d*]thiophene (C_6-

DNT-VW) [4], was robotically dispensed on the inside of the bank layer at 100 °C. To fabricate the active layer, 0.05wt% of C_6-DNT-VW and 0.02wt% of polystyrene (PS; Mw: 3,000, Sigma-Aldrich) in a mixture solution of 1,2-dichlorobenzene and toluene (1: 2, v/v) was used. Such solution processability of C_6-DNT-VW offered high-throughput but relatively easy fabrication of the active layer under ambient conditions. The layer was annealed at 120 °C for 10 min, which was then covered by Teflon® AF1600. Finally, the Teflon layer was baked at 110 °C for 10 min. To fabricate the detection portion, 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.

Characterization of OFET and Glutathione Chemisorption

The electrical characteristics of the fabricated OFET were firstly measured by a Keithley 2602B source meter. As anticipated, the OFET was reproducibly operated at below |3| V, which indicates that the OFET can be applied to chemical detection in aqueous media.

Next, we investigated the chemisorption properties of glutathione on the Au electrode by the water contact angle on the Au electrode using a Kyowa CA-X contact angle goniometer; the water contact angle on the electrode treated with glutathione (15°) was lower than that on the untreated electrode (40°). Here, the chemisorption of glutathione significantly affects the contact angle. The measurment reveals that the contact angle did not decrease after 30 sec of immersion in the glutathione solution. This indicates that glutathione was fully chemisorbed onto the Au electrode after 30 sec. In other words, the quick detection of glutathione can be possibly achieved in the OFET-based electrical detection. In addition, the Au electrode after immersion in the glutathione solution was characterized by attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR) using a Thermo Fisher Scientific Nicolet iS5 FTIR spectrometer. The results showed absorption peaks at 1732 cm^{-1}, 1650 cm^{-1}, 1540 cm^{-1}, and 1520 cm^{-1}, which could be identified as –COOH (stretching vibration), –C=O (amide I), –NH– (amide II), and –NH (bending vibration), respectively. We successfully confirmed that the changes in the contact angle measurements were derived from the chemisorption of glutathione onto the Au surface.

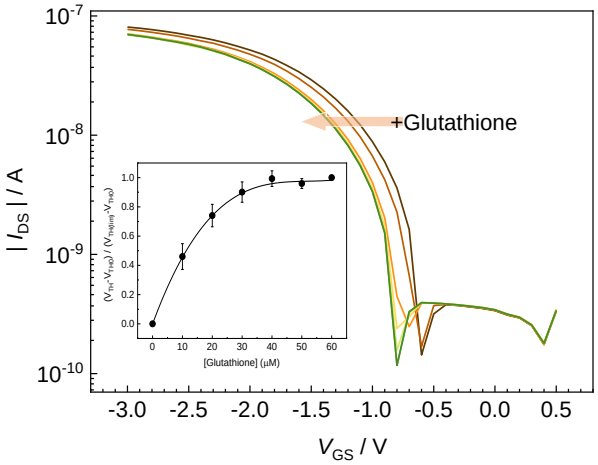

Fig. 2. Transfer characteristics (I_{DS}–V_{GS}) of the OFET upon titration with glutathione in a HEPES buffer solution (10 mM) with NaCl (100 mM) at pH 7.4. [Glutathione] = 0–60 μM. Inset: Changes in threshold voltage of the OFET by glutathione at various concentrations.

Glutathione Detection

The characterization data as mentioned above encouraged us to detect glutathione in water by using the fabricated OFET. The OFET was connected to the extended-gate electrode through a copper cable. An Ag/AgCl electrode was employed as a reference electrode. The extended-gate electrode was dipped into a HEPES (= 4-(2-hydroxyethyl)- 1-piperazineethanesulfonic acid) buffer (10 mM) solution (with NaCl (100 mM)) of glutathione at a pH of 7.4 at RT. Figure 2 exhibits the OFET transfer characteristics upon titration with the glutathione solution. Interestingly, we observed that clear negative shift of the transfer curve with increasing the glutathione 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 charged glutathione on the extended-gate electrode. The inset in Fig. 2 shows the relationship between the glutathione concentration and change in the threshold voltage, as estimated from the transfer characteristics. The titration isotherm was fitted with the Langmuir adsorption model to calculate an equilibrium constant (K), which exhibited a K of 1.2×10^5 M^{-1}.

Finally, we evaluated the selectivity of the sensor for various amino acids in water. Aqueous solutions of amino acids (30 μM) such as alanine (Ala), arginine (Arg), aspartic acid (Asp), cysteine (Cys), glycine (Gly), histidine (His), isoleucine (Ile), leucine (Leu), lysine (Lys), methionine (Met), phenylalanine (Phe), proline (Pro), serine (Ser), and valine (Val) were examined. As predicted, the sensor possessed the highest response to glutathione, while other amino acids induced little or no change of the threshold voltage. We could distinguish glutathione from cysteine, glutamic acid, and glycine.

3. Conclusions

We demonstrated for the first time detection of glutathione in water using the extended-gate type OFET. We believe that the results are useful for developing printed chemical sensors based on OFETs of the future.

Acknowledgements

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