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Label-Free Direct Electrical Detection of a Histidine-Rich Protein with Sub-Femtomolar Sensitivity using an Organic Field-Effect Transistor

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There is a growing interest in achieving sensor systems to enable on-site testing of biomarkers. Herein, a new strategy for highly sensitive protein detection at sub-femtomolar levels without any labelling has been demonstrated by using an organic field-effect transistor (OFET). An artificial histidine-rich protein receptor (Ni^{II}-nitrilotriacetic acid complex, Ni^{II}-nta) functionalizes a detection portion (i.e. an extended-gate electrode) of the fabricated OFET device. The OFET responds electrically and selectively to a target analyte (bovine serum albumin), meaning that the binding processes at the Ni^{II}-nta on the extended-gate electrode for the analyte affect the field-effect properties of the device. Our results demonstrate that the combination of the OFET with the artificial receptor is an ideal approach for label-free and immune-free protein detection.

Development of analytical methods for biomarkers such as proteins and peptides has great significance in the fields of clinical diagnostics,[1a,b] environmental monitoring,[1c] food safety tests,[1d] and proteomics.[1e] Immunoassays,[2] which are those of the most common methods for protein analyses, can sensitively detect desired analytes, because proteins are recognized through antigen–antibody interactions in measurement systems. Although the features (a high sensitivity and reliability) of general immunoassays are useful for the accurate detection of proteins, the assays have difficulty in the application to on-site detection at various situations (such as outdoor sites or developing countries) for the following reasons. 1) Labelling processes for analytes are complicated. 2) It takes time for users (i.e. analysts, patients, and researchers) to acquire analysis results, because pre-treatments of immune proteins are time-consuming processes. 3) For quantitative analysis, relatively large equipment and expensive reagents are required; for instance, spectroscopic apparatus and naturally derived substances are generally essential to optical-based assays such as enzyme-linked immunosorbent assays (ELISAs).[3]

To solve the above problems, micro-total analysis systems (μTAS) toward an on-site detection of biomarkers have been demonstrated in the fields of analytical chemistry and device engineering.[4] Especially, microfluidic technology of μTAS is a useful approach for reducing the total measurement time of proteins. In those devices, various transducing mechanisms for the detection signal of proteins can be employed. For example, fluorometric[4b] and/or electrochemical-based[4c] μTAS are vigorously researched. Moreover, organic field-effect transistor (OFET)-based sensing platforms for biomarkers (e.g. ricin,[5a] C-reactive protein,[5b] chromogranin A,[5c] α-casein,[5d] etc.) have been demonstrated in recent years. OFETs,[6a] which consist conjugated organic materials as an active layer, can be easily fabricated on elastic substrates using wet processes. These electrical switchers are not only valuable transducers for chemo-/biosensors, but also the prospective devices for flexible displays[6b] and low-cost radio frequency identification (RFID) tags.[6c] Thus, the components of the sensing system (i.e. a detector, transducer, transmitter, and display) could be integrated into a single chip by using OFET-based circuits. To date, OFET-based sensors usually rely on the above-mentioned immunoassays, whereas the development of the detection system using artificial receptors in the field of OFET devices is still in its early stage.

Coordination-bonding-based artificial receptors[7a] [e.g. zinc(II)-dipicolylamine (Zn^{II}-dpa),[7b] nickel(II)-nitrilotriacetic acid (Ni^{II}-nta),[7c] copper(II)-iminodiacetic acid (Cu^{II}-ida),[7d] etc.] are often employed for protein recognition. These receptors are generally utilized for optical chemosensory systems. In our approach, we have attempted to combine such receptors with OFETs toward the development of label-free and immune-free sensor devices.[5d] In this regard, the Ni^{II}-nta complex, which is known as a receptor for histidine-rich proteins (ex. albumin) (K_d: about 10^{-8} M),[8a] could be a promising candidate for the development of label-free and immune-free OFET-based sensors.[8] Histidine-rich proteins are known as the biomarkers for serious diseases such as acquired immune deficiency syndrome (AIDS),[9a] advanced liver cirrhosis,[9b] disorders of the lung,[9c] thrombosis,[9d] malaria,[9e] and so forth. Although surface plasmon resonance (SPR) of a Ni^{II}-nta-functionalized gold substrate detected histidine-rich proteins successfully,[10] compact, simple, and disposable sensor devices for such proteins have

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not yet been fully established. Toward that end, we herein demonstrate the fabrication of an easy-to-use sensor device based on an OFET modified with a Ni^{II}-nta self-assembled monolayer (SAM) for the detection of bovine serum albumin (BSA).

The Ni^{II}-nta-functionalized OFET sensor was fabricated as described in the Supporting Information (Figure 1). To apply the OFET for the accurate detection of proteins, it is necessary to stabilize and homogenize electrical signals of the fabricated device.[11] Toward this end, the OFET was constructed with

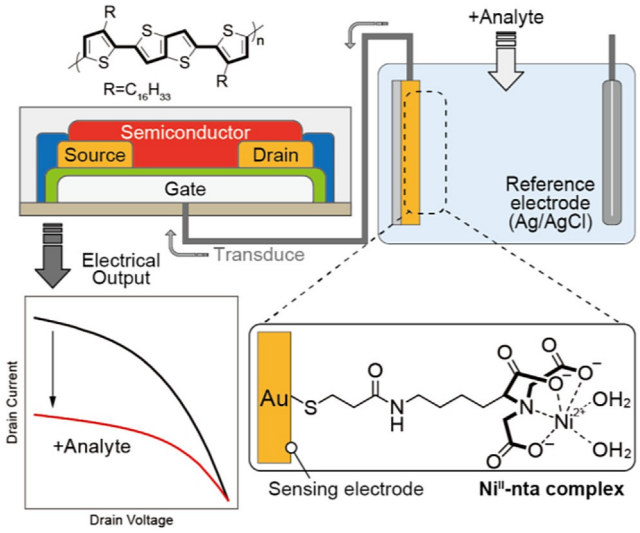

Figure 1. Schematic representation of the OFET-based protein sensor with the sensing electrode. The sensing electrode is functionalized with a Ni^{II}-nta monolayer.

a conjugated polymer-based active layer[12a,b] and a SAM-based dielectric layer, which provides high electric capacity.[12c,d] Furthermore, it became possible to take an accurate measurement of output signals, because the transducer (the OFET) is separated from the detection portion (the extended-gate), which can prevent degradation of the active layer by water.[11a] By repetitive measurements of the fabricated OFET, we found that the OFET was stably operated at below 1 V (Figure S1). The results obtained indicate that the designed device could be applied for protein detection in water. Next, the chemical functionalization of the gold extended-gate electrode toward the recognition of the histidine-rich protein was carried with a thiol-terminated nta with Ni^{II} (Ni^{II}-nta SAM). The modification procedure for the SAM was carried out by following a previously reported method (see the Experimental Section).[10a] The formation of the Ni^{II}-nta complex on the gold electrode was confirmed by measuring the contact angle, photoelectron yield spectroscopy (PYS) in air, X-ray photoelectron spectroscopy (XPS), and the OFET-based electrical titration of Ni^{II}[13] (Figure S2–S5). From these results, it appears that the Ni^{II}-nta SAM successfully formed on the extended-gate electrode.

The sensing ability of the fabricated OFET device was assessed through an electrical analysis of the protein-induced current changes in output characteristics before and after the addition of BSA (Figure 2a). Serum albumin, which is one of

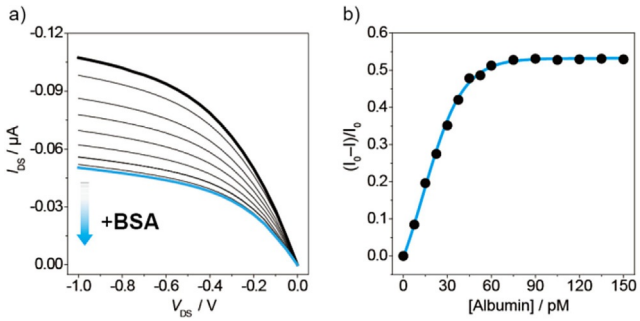

Figure 2. a) The *I–V* curves (i.e. output characteristics) of the fabricated OFET upon the addition of albumin in a HEPES buffer solution (10 mM) with NaCl (100 mM), pH 7.0, at 25 °C; [Albumin] = 0–150 pM. b) Titration isotherm corresponding to the albumin-induced drain current (I_{DS}) change. Three repetitions were measured for each concentration. Relative standard deviation ($n = 3$) of the response was estimated to be 1–2%.

the histidine-rich proteins used as a target in this work, is involved in many physiological processes. Albumin is not only known to aid the regulation of osmotic pressure[14a] and pH in blood,[14b] but it also supports lipid metabolism,[14c] isolates toxins,[14d] and acts as an antioxidant.[14e] As an abnormal lowering of albumin concentration in blood is caused by many disease (e.g. liver disease,[15a] nephrotic syndrome,[15b] malnutrition,[15c] etc.), the detection of the albumin level is important for diagnosis. Additionally, as the molecular properties of BSA are well-characterized in the field of biology, BSA is a suitable analyte model for the investigation of the protein recognition ability of the OFET.

An electrical titration experiment revealed a distinct decrease in the output current (I_{DS}) of the OFET upon addition of BSA in a HEPES buffer solution (Figure 2a). The limit of detection (*LOD*)[16] for BSA was estimated to be 6.0×10^{-13} M (= 40 pg mL^{-1}). The *LOD* was estimated in accordance with the IUPAC rule (see the Experimental Section). To the best of our knowledge, this is the lowest value ever reported for OFET-based protein sensors without labeling processes.[17] Furthermore, it is comparable to, or lower than, those of recently reported immunoassays or luminescent probes for BSA.[18] As the long and hydrophobic linker group of the Ni^{II}-nta monolayer could be accessible to histidine residues of BSA, it is assumed that the obtained *LOD* was lower than our previous OFET-based sensor for a protein.[5d] In this regard, molecular design of the linker group of the SAM as well as that of the terminated group (i.e. the recognition site) is important for OFET-based sensors.[19]

Changes in electrical characteristics associated with increasing the BSA concentration were supported by PYS results (Figure 3a). The work function of the gold electrode was clearly shifted by adding BSA (5.0 → 4.7 eV), which means that such electrical change in the OFET characteristics occurred through BSA-induced changes of surface potential on the extended-gate electrode (Figure 3b).[5d,20] Recently, a similar electrical response related to the BSA concentration in a dual-gated OFET was reported by Choi et al.[21] They demonstrated BSA detection by using physical adsorption on the surface of a dielectric

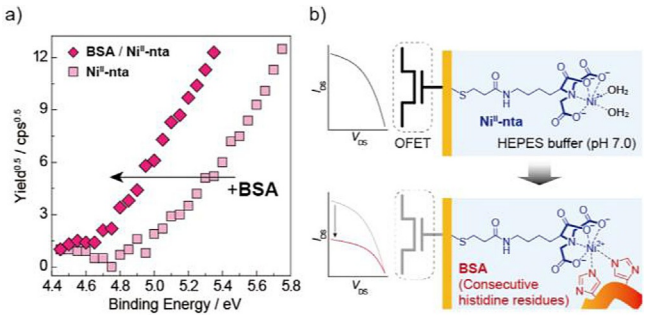

Figure 3. a) PYS measurement of the Ni^{II}-nta-functionalized electrode before and after immersion in the HEPES buffer solution with BSA. [BSA] = 1 μg mL^{-1}. b) A plausible mechanism of the electrical detection of BSA. BSA can be bound onto the extended-gate electrode modified with the Ni^{II}-nta SAM, which triggers the decrease in channel conductance in the OFET.

over-layer. Numerical simulations of BSA-induced changes of an electrical performance in the dual-gated OFET suggested that these responses can be attributed to changes in the channel conductance of the OFET induced by the charge property of BSA. According to this experimental evidence, we conclude that the observed changes of the output characteristics are ascribed to shifts in the field-effect behavior of the OFET device caused by the electron-donating properties of BSA captured on the Ni^{II}-nta-modified extended-gate electrode.[22]

Finally, we investigated the protein selectivity of the OFET sensor device. The Ni^{II}-nta-functionalized electrode of the OFET was immersed in individual aqueous solutions containing proteins such as immunoglobulin G (IgG), immunoglobulin A (IgA), trypsin, and hemoglobin. These are often employed as analytes in studies for albumin sensor systems.[23] Figure 4 shows the current responses of the OFET when adding proteins. The response of the OFET to BSA was obviously high, whereas those for IgG, IgA, trypsin, and hemoglobin were very weak. Control analytes have no consecutive histidine residues. Thus, the observed differential responses to proteins indicate that the binding affinity between the Ni^{II}-nta on the extended-gate electrode and the histidine residue sites of BSA is the prime influence for the changes in the drain current. With these results, we have successfully demonstrated that the fabricated device could selectively recognize histidine-residual sites of the protein.

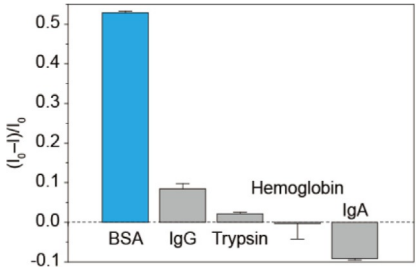

Figure 4. Changes in the output current ($n = 3$) of the OFET sensor by proteins at various concentrations in a HEPES buffer (10 mM) with NaCl (100 mM) at pH 7.0 at 25 °C. [Protein] = 10 ng mL^{-1}.

In summary, a highly sensitive electrical detection system for histidine-rich protein was achieved by combining the Ni^{II}-nta-functionalized electrode and the low-voltage-operated OFET. Specific changes in the drain current of the OFET for the addition of BSA were observed, which were derived from the recognition ability of the Ni^{II}-nta for the histidine-rich protein. As the fabricated sensor sensitively responded to the protein analyte ($LOD = 6.0 \times 10^{-13}$ M), we propose that an artificial receptor-modified OFET is an ideal candidate for protein sensing platforms. Importantly, the described label-free bioassay for BSA is much easier to operate and quicker than conventional immunoassays[3] (assay time in this study: < 15 min). Moreover, the described approach combined with an artificial receptor and an OFET can be popularized toward the simple and fast detection of many types of biomarkers. Thus, our preliminary results indicate that the OFET-based sensors could open up new opportunities for developing diverse sensing platforms for protein analyses. Further developments toward the sensing of various biomarkers using an artificial receptor-functionalized OFET are underway in our group.

Experimental Section

Modification of the Extended-Gate Electrode[10a]

A gold extended-gate electrode (50 nm in thickness, sensing area: 15 mm^2) was prepared on a 125 μm-thick polyethylene naphthalate (PEN) film through vacuum vapor deposition. The deposited electrode was immersed in the solution of nta (1 mM in an ethanol solution) for 12 h at 25 °C. Then, the electrode was rinsed with ethanol and pure water. To form a metal–ligand complex on the electrode, the nta-modified electrode was treated with NaOH (1 mM) for 5 min and subsequently immersed in pure water containing $NiSO_4$ (40 mM) for 1 h at 25 °C. Finally, the extended-gate electrode was rinsed with a HEPES buffer (10 mM) with NaCl (100 mM) at pH 7.0 and pure water.

Electrical Detection of Proteins

All electrical measurements in titration experiments of proteins were performed by using a source meter (Keithley 2636B) in ambient conditions, and the gate voltage (V_{GS}) was applied through a Ag/AgCl (3 M NaCl) reference electrode (BAS RE-1S). The detection signal of proteins was quantified from changes in the drain current in the output characteristics ($I_{DS}-V_{DS}$). The drain current in the saturation region of the OFET is generally provided by the following equation [Eq. (1)]: [24]

$$I_{DS} = (W/2L)\mu C(V_{GS} - V_{TH})^2 \quad (1)$$

where I_{DS} is the drain current, W the channel width (1000 μm), L the channel length (50 μm), μ the field-effect mobility, C the capacitance of the gate dielectric (ca. 0.8 μF cm^{-2}), V_{GS} the gate voltage, and V_{TH} the threshold voltage. The intersection of the minimum signal (Y) and the regression line obtained from the value of current changes in the dynamic range of the titration curve allowed us to estimate the limit of detection (LOD)[16] for BSA. The value of Y is estimated by using the following equation [Eq. (2)]:

$$Y = I_0 + 3\sigma \quad (2)$$

where I_0 is the average value in the absence of BSA ($n=3$) and σ the standard deviation of I_0.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: molecular recognition · organic transistors · self-assembled monolayers · sensors · serum albumin

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