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Organic electrochemical transistor based biosensor for detecting marine diatoms in seawater medium

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ABSTRACT

Organic electrochemical transistors (OECTs) based on poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS) have been successfully used for the detection of marine diatoms in the seawater medium for the first time. OECTs showed stable performance and excellent biocompatibility in seawater medium. Two species of common benthic fouling diatoms were used as samples to investigate the performance of OECT-sensor platform. Maximum gate offset voltages, about 60 mV for *Navicula* sp. and 28 mV for *Amphiprore* sp., were observed after the attachment of diatoms. The transfer curves of OECT device shifted to higher gate voltage after the capture of diatoms, which can be attributed to the electrostatic interaction between diatoms and the PEDOT:PSS layer. The devices can detect *Navicula* sp. and *Amphiprore* sp. concentrations down to 100 cell/mL and 400 cell/mL, respectively. It is expected that such organic transistors may pave the way for the chemical and biochemical sensing in marine environment.

1. Introduction

Because of their potential as disposable sensors in health care and food monitoring applications, organic thin-film transistors have recently been studied as the active candidate in chemical and biological sensors [1–5]. Among these transistor-based sensors, organic electrochemical transistors (OECTs), a type of organic thin-film transistors, have been extensively studied for their particular advantages, including easy fabrication, low operational voltage (∼1 V), good biocompatibility, low-cost and mechanical flexibility [6–11]. The first OECT based on polypyrrole was reported by Wrighton et al. in 1984 [12]. Then OECT devices rapidly found applications in ion [13], humidity [14], glucose [6,9,11], protein [15], DNA detection [16], as well as recording transepithelial ion transport [17]. Therefore, we consider that OECTs can be used as disposable sensors for the detection of marine diatoms in the seawater medium, which have not been reported before to the best of our knowledge.

Diatoms are usually the first eukaryotic microalgae which colonize and dominate microcommunities in marine fouling [18,19]. Once diatoms attach on the solid surface, they form diatom biofilms then cause the subsequent adhesion of many other fouling organisms. Adhesion of marine fouling organisms on artificial surfaces such as ship hulls will cause many problems, including extra energy consumption, high maintenance costs, and increased corrosion [20]. It has been reported that microfouling alone can increase fuel consumption by up to 18%, and reduce the sailing speed by at least 20% [21]. Therefore, marine antifouling is a relevant problem. Considering this, it is crucial to develop an efficient sensor for the detection of marine diatoms.

In this work, we studied the application of OECTs in the detection of two species of common benthic fouling diatoms in the seawater medium for the first time. OECTs showed a good response to the attachment of marine diatoms. Also, the possible sensing mechanism of OECTs was discussed in detail in this paper. Such organic transistors may pave the way for the chemical and biochemical sensing in marine environment.

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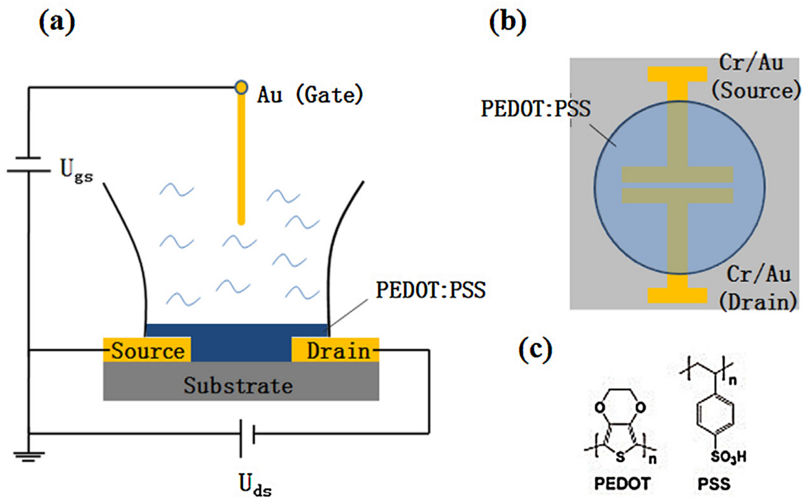

Fig. 1. Schematic diagram of the PEDOT:PSS-based OECT device structure. (a) Side view; (b) top view; and (c) chemical structures of PEDOT and PSS.

2. Experimental

2.1. Device fabrication

Fig. 1 shows the schematic diagram of an OECT device structure. The OECT device was fabricated on a glass substrate. Cr/Au source/drain electrodes were deposited on the top of the glass substrate through a shadow mask. The channel length and width of the device were 0.2 and 6 mm, respectively. After the glass slide was cleaned with deionized (DI) water, a PEDOT:PSS solution (Clevios PH500) was spin coated at 3000 rpm onto the patterned substrate. Then the devices were annealed at 200 °C for 60 min in high purity N_2 (the optimal annealing condition was determined by AFM morphologies, see Fig. S1). The thickness of the PEDOT:PSS was about 80 nm. Finally, a silicone tube (2 cm diameter) was glued on the top of the device to serve as a reservoir for the electrolyte, and an Au electrode was immersed into the electrolyte as the gate electrode.

2.2. Marine diatoms culture

The diatoms were cultured according to the literature reported before [22]. Briefly, diatom sampling was carried out in Sanya Yalong Bay of South China Sea (18°23 N, 109°65 E). This coastal area has a typical tropical oceanic climate. Two species of common benthic fouling diatoms (*Navicula* sp. and *Amphiprore* sp.) were selected and separated for further cultivation. Cultures were incubated at an incident light intensity of 2000 ± 100 lux in a 12 h light/12 h dark photoperiod at 25 ± 1 °C. After two weeks of the enrichment cultures, the diatom samples grew stably, then were used for the next sensing measurements.

2.3. Electrical measurements

The OECTs were characterized with a semiconductor parameter analyzer (Keithley 4200). All OECTs and the Au gate electrodes were sterilized with UV radiation for about 30 min before electrical characteristics. The seawater medium was prepared by dissolving artificial sea salt (Asian Marine Fantastic) with DI water, and then sterilized with boiling method. The seawater composition is listed as follows: 21 g/L NaCl, 2.54 g/L $MgCl_2$, 1.54 g/L $MgSO_4{\cdot}7H_2O$, 2.43 g/L $CaSO_4{\cdot}2H_2O$, 0.1 g/L $CaCO_3$. The channel current I_{ds} between source and drain electrodes of each device was measured as a function of gate voltage V_g under a constant drain voltage (V_{ds} = −0.1 V). To obtain stable curves, the channel currents were measured at a speed of 10 s for one point.

The diatom morphologies were imaged using a Hitachi S-4800 field emission scanning electron microscope (FESEM) operated at an acceleration voltage of 0.8–1.0 kV and current of 10.0 μA. The impedance of the diatom/Au electrode in the seawater medium was characterized by using an electrochemical workstation (Zanher Zennium) in a three-electrode configuration with a Pt foil counter electrode and a saturated calomel reference electrode. The amplitude of the applied ac signal is 10 mV.

3. Results and discussion

To be used as a marine diatom sensor, the OECT device should be very stable in the seawater medium. All the OECT devices and the Au gate electrodes were sterilized by UV radiation for about 30 min before electrical measurements. The transfer characteristics ($I_{ds} \sim V_g$, V_{ds} = −0.1 V) measured in sterile seawater are shown in Fig. 2a. We found that the device showed stable performance during the measurements for 6 days.

The output characteristics ($I_{ds} \sim V_{ds}$, at different V_g) of the OECT device are shown in Fig. 2b. The results confirm that the device behaves as a p-type field effect transistor [23]. When no gate voltage is applied, the presence of PSS makes PEDOT conducting. The device is in its "on" state, and I_{ds} is relatively large. As V_g increases, I_{ds} decreases and the device turns "off". The mechanism is proposed as following: upon application of a gate bias, cations in the electrolyte penetrate the polymer bulk to compensate the negatively charged sulfonate moieties on the PSS backbone ($PEDOT^+{:}PSS^- + M^+(aq) + e^- \leftrightarrow PEDOT^0 + M+{:}PSS^-$). As a consequence, the hole density reduces, resulting in a decrease in polymer conductivity, thus a lower current through the channel [7].

The OECTs also showed excellent biocompatibility with the marine diatoms (see Fig. 3). *Navicula* sp. were cultivated on glass slide and PEDOT:PSS surface at the same condition. It was found that the cell densities on PEDOT:PSS were much higher than that on glass slide. Excellent biocompatibility of PEDOT:PSS for *Amphiprore* sp. has also been observed.

Before we used the OECT to detect the diatoms, the stability of the device in the seawater medium was tested for at least two days to make sure that the changes of transfer characteristics of the device can only be caused by diatoms. Then the OECT device was sterilized with UV radiation for about 30 min. Next, the marine diatoms *Navicula* sp. with a concentration of 10^3 cell/mL in seawater solution was injected into the silicone tube, 2 h later the diatoms began to attach onto the PEDOT:PSS film. As shown in