



Highly selective and sensitive sensor based on an organic electrochemical transistor for the detection of ascorbic acid

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ABSTRACT

In this study, an organic electrochemical transistor sensor (OECT) with a molecularly imprinted polymer (MIP)-modified gate electrode was prepared for the detection of ascorbic acid (AA). The combination of the amplification function of an OECT and the selective specificity of MIPs afforded a highly sensitive, selective OECT sensor. Cyclic voltammetry and electrochemical impedance spectroscopy measurements were carried out to monitor the stepwise fabrication of the modified electrodes and the adsorption capacity of the MIP/Au electrodes. Atomic force microscopy was employed for examining the surface morphology of the electrodes. Important detection parameters, pH and detection temperature were optimized. With the change in the relative concentration of AA from 1 μM to 100 μM , the MIP-OECT sensor exhibited a low detection limit of 10 nM ($S/N > 3$) and a sensitivity of 75.3 μA channel current change per decade under optimal conditions. In addition, the MIP-OECT sensor exhibited excellent specific recognition ability to AA, which prevented the interference from other structurally similar compounds (e.g., aspartic acid, glucose, uric acid, glycine, glutathione, H_2O_2), and common metal ions (K^+ , Na^+ , Ca^{2+} , Mg^{2+} , and Fe^{2+}). In addition, a series of vitamin C beverages were analyzed to demonstrate the feasibility of the MIP-OECT sensor. Using the proposed principle, several other sensors with improved performance can be constructed via the modification of organic electrochemical transistors with appropriate MIP films.

1. Introduction

Organic electrochemical transistors (OECTs) have demonstrated immense potential in biosensing applications because of their unique properties of biocompatibility, simple structures, easy fabrication, low cost, and their notable low operating voltages of less than 1 V, which ensure their operation in aqueous environments (Bernards and Malliaras, 2007; Tarabella et al., 2012; Liao et al., 2013; Zhang et al., 2016a, 2016b). Various OECT biosensors, including those for glucose (Glu) (Zhu et al., 2004; Macaya et al., 2007; Kim et al., 2010; Liao et al., 2015a), DNA (Lin et al., 2011), uric acid (UA) (Liao et al., 2015b), dopamine (DA) (Tang et al., 2011; Liao et al., 2014; Gualandi et al., 2016), cells (Lin et al., 2010a), and epinephrine (Mak et al., 2015) have been fabricated and investigated. Most of these studies have indicated that the sensitivities of OECT sensors are considerably greater than

those of traditional sensors. For example, Yan's group has reported an OECT sensor with a low detection limit of 10 nM and a change in the effective gate voltage of 370 mV per decade for Glu via the modification of the gate electrode with chitosan–graphene/glucose oxidase (GOx) (Liao et al., 2013).

Selectivity is another important parameter for OECT-based sensors. Generally, specific enzymes or selective membranes are added to the gate or channel of the OECT-based sensors to increase selectivity (Liao et al., 2015; Gualandi et al., 2016; Shim et al., 2009; Xiong et al., 2017). For example, Yan et al. (Liao et al., 2015b) have reported low detection limits and good selectivity for OECT sensors toward UA, Glu, and cholesterol via the modification of the gate electrode with enzymes such as uricase (UOx), GOx, and cholesterol oxidase, respectively. Owens et al. (Braendlein et al., 2017) have fabricated a lactate sensor based on an organic transistor circuit via the immobilization of a

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chitosan-ferrocene/lactate oxidase complex on the gate electrode surface of the OECT sensor and replacement of lactate oxidase with bovine serum albumin as a reference OECT to detect lactate in tumor cell cultures. Owens et al. (Pappa et al., 2016) have immobilized GOx, lactate oxidase, and cholesterol oxidase on the surface of gate electrodes to construct a multi-analyte sensing system for Glu, lactate, and cholesterol. The resulting sensor exhibited excellent sensitivities and low detection limits.

Although enzyme modification endows OECT biosensors with remarkable specificity and selectivity, the immobilized enzymes are limited by several drawbacks, including the limited categories of enzymes that can be immobilized, easy enzyme deactivation, and unsatisfactory selectivity of the OECT sensors for widespread applications. Therefore, it is crucial to explore new methods for preparing OECT sensors with high selectivity, which can overcome these drawbacks.

Meanwhile, molecularly imprinted polymers (MIPs) are fabricated by the molecular imprinting technique (MIT), which creates cavities that exhibit affinity for the selected “template” molecules in the polymer matrix (Rezaei et al., 2016; Zhong et al., 2015; Nezhadali et al., 2012). This method not only affords high selectivity with universal applicability in molecule recognition (Wang et al., 2017), but also provides other advantages such as easy preparation, durability, cost-effectiveness, and robustness under harsh conditions. Hence, MIPs have been applied in sensing devices for the detection of Glu (Cheng et al., 2001; Farid et al., 2016), alkaloids (Liu et al., 2012), and other chemical substances (Xiao et al., 2016; Hong et al., 2016), as well as in separation (Andersson et al., 1990) and electroanalysis (Qin et al., 2011). For example, Deiminiat et al. (Deiminiat et al., 2017) have constructed a highly sensitive, selective electrochemical sensor for the determination of tramadol via the combination of a functionalized multiwalled carbon nanotube layer with a thin MIP film. The integration of MIT in OECTs is a reasonably effective route to improve the selectivity and applicability of OECTs in biosensors. However, MIP-modified OECTs have not yet been explored or published.

In this study, a novel OECT with an MIP-modified gate electrode was successfully prepared and used as a highly selective, sensitive ascorbic acid (AA) sensor. Owing to its importance in water-soluble vitamins, AA has been widely investigated as a target analyte for the prevention and treatment of diseases, such as scurvy, common cold, mental illness, and cancer, related to its antioxidant properties (Fan et al., 2017; Zhao et al., 2016; Zou et al., 2016).

2. Experimental

2.1. Chemicals and reagents

AA, aspartic acid (ASP), Glu, UA, glycine (Gly), sodium dihydrogen phosphate (NaH_2PO_4), disodium hydrogen phosphate (Na_2HPO_4), and dimethyl sulfoxide (DMSO) were purchased from Shanghai Aladdin Biological Technology Co., Ltd. $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$, sodium chloride (NaCl), concentrated sulfuric acid (H_2SO_4), hydrogen peroxide (H_2O_2), o-phenylenediamine (o-PD), acetic acid (HAc), sodium acetate (NaAc), and ethyl alcohol were purchased from Sinopharm Chemical Reagent Co., Ltd. Poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT/PSS) aqueous dispersion was purchased from Sigma-Aldrich Co. and stored at 4 °C. All other reagents were of analytical grade or better. Vitamin C beverage was purchased from Nongfu Spring Co., Ltd. HAc-NaAc (pH 5.2) was prepared using HAc, NaAc, and NaCl, and phosphate buffered solution (PBS) was prepared by NaH_2PO_4 , Na_2HPO_4 , and NaCl. Ultrapure water and a freshly prepared solution were used throughout.

2.2. Device fabrication and characterization

Patterned Au/Ni source and drain electrodes were deposited on

glass slides using a shadow mask by thermal evaporation. After the glass substrates were cleaned by UV/O_3 , and a ~ 60 nm PEDOT:PSS layer was spin-coated on them and patterned on the source and drain electrodes, followed by thermal annealing at 185 °C for 60 min under nitrogen. The ratio of the channel width and length of the devices was 6:0.2 (Lin et al., 2010b).

The Au electrodes modified with the AA MIP film served as gate electrodes for OECT. First, the gold electrode surfaces were polished with 0.3 and 0.05 μm wet alumina powder, followed by sequential cleaning using absolute ethyl alcohol and ultrapure water. Then, a thin film was prepared on the Au electrode surface by cyclic voltammetry (CV) in a 0.2 M HAc-NaAc (pH 5.2) solution, which is mixed with 15 mM of o-PD and 30 mM of AA, at 50 mV s^{-1} using a CHI660D electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd). In the system, the Au electrode, saturated calomel electrode (SCE) (sat. KCl), and a Pt wire served as the working, reference, and counter electrodes, respectively. Fig. 1S shows the electropolymerization curve. After the extraction of templates from the polymer film via the immersion in ultrapure water, the MIP-film-modified electrode (MIP/Au) was obtained. For comparison, the NIP/Au electrodes without templates were also prepared by the same procedure.

The surface morphologies of the bare Au and polymer films were evaluated by tapping-mode atomic force microscopy (AFM, Bruker, Germany). All AFM micrographs were analyzed by NanoScope Analysis. The electrochemical properties of the different electrodes were characterized using a standard three-electrode system, where the modified Au electrode, SCE (sat. KCl), and Pt wire served as the working, reference, and counter electrodes, respectively. The stepwise fabrication of the modified electrodes and the adsorption capacity of the MIP/Au electrodes were investigated by CV and electrochemical impedance spectroscopy (EIS) in 10 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ solutions containing 0.1 M NaCl. For CV measurements, the potential window ranged from 0 to 0.4 V at a scan rate of 0.05 V/s. For EIS measurements, potential was set as 0.175 V, the frequency range was set from 0.1 Hz to 100 kHz, and the alternating potential was 5 mV. The electrodes were washed using ultrapure water after removing them from the solution to eliminate the interference from the other substances. The electrical properties and sensing performance of the OECTs with different electrodes as the gate electrodes were examined using a semiconductor test system (Keithley 4200-SCS) in 10 mL PBS (pH 7.0). Different amounts of the AA solution were added into the beaker every 10 min under a fixed source-drain voltage ($V_{\text{DS}} = 0.02$ V) and a constant gate voltage ($V_{\text{G}} = 0.6$ V). For actual sample analysis, every sample was taken from the same vitamin C beverage (labeled 100 mg of vitamin C per 450 mL): A specific amount of this solution was diluted to the corresponding concentration using PBS (pH 7.0) and used for analysis. All experiments were carried out under ambient conditions.

3. Results and discussion

3.1. Working principle of OECT AA sensors

Fig. 1A shows the structure of the MIP film-modified OECT sensor. Fig. 1B shows the working mechanism of the MIP film-modified electrode. The removal of the AA templates via the immersion of the modified electrodes in ultrapure water leads to the formation of cavities matching the AA size and structure. The cavities recombine with AA molecules after the second immersion of the MIP-modified electrode in the AA solution. After the adsorption of AA and application of the positive gate voltage to the electrodes, the oxidation of AA occurs on the modified gate electrode surface, which permits the transfer of electrons (Faradaic current) near the surface of the gate electrode, affording changes at the gate/electrolyte interface. The latter should decrease the voltage drop at the gate/electrolyte, leading to the increase in the effective gate voltage applied to the transistor (Fig. 1C dashed

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