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Highly sensitive real-time detection of tyrosine based on organic electrochemical transistors with poly-(diallyldimethylammonium chloride), gold nanoparticles and multi-walled carbon nanotubes

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ABSTRACT

A novel electrochemical sensor based on poly-(diallyldimethylammonium chloride) (PDDA), gold nanoparticles (AuNPs) and multi-walled carbon nanotubes (MWCNTs) modified organic electrochemical transistors (OECTs) was successfully fabricated and applied to determination of Tyrosine (Tyr). The as-prepared device was characterized by field emission scanning electron microscopy (FE-SEM) and electrochemical workstation. Electrochemical performance of the modified OECT for detection of Tyr was investigated by cyclic voltammetry (CV) and chronoamperometry methods. Compared with the OECTs with the bare and the MWCNTs/PDDA modified OECTs Au gate electrode, the ultimate OECT with the MWCNTs/PDDA/AuNPs modified Au gate electrode displayed higher catalytic activity toward the oxidation of Tyr. The MWCNTs/PDDA/AuNPs modified OECT exhibited a linear response to Tyr over a wide concentration range of 0.3 μM to 10 μM with a detection limit of 10 nM in PBS solution (pH = 7.4), suitable for Tyr detection in human body fluids. Considering the main advantages of OECT such as low cost, no need for pre-treatment, easy to use and real-time detecting capability, we believe that the MWCNTs/PDDA/AuNPs modified OECT can potentially be employed as a highly-sensitive, real-time, portable and disposable sensor for practical detection of Tyr in real sample.

1. Introduction

Tyrosine (4-hydroxyphenylalanine, Tyr) is an essential amino acid and vital constituent of proteins. Tyr comprises 1 to 6% by weight of most proteins, and thus is indispensable in human nutrition for establishing and maintaining a positive nitrogen balance [1]. Tyr is also a biochemical compound that plays important roles in various biological processes. For example, it is a co-existing substance in many biological matrices. It has also been reported that Tyr is also the precursor of many neurotransmitters such as dopa, dopamine, thyroxin, and epinephrine hormone. The absence of Tyr would induce albinism, alkaptonuria, hypochondria and other psychological diseases [2,3]. On the other hand, a high Tyr concentration in culture medium increases sister chromatid exchange [4]. Tyr and other amino acids play roles in Alzheimer's or Parkinson's disease [5]. Besides, it has been discovered that alteration of Tyr concentration is also highly related to atherosclerosis and lung diseases [6,7]. To sum up, Tyr concentration changes have an impact on human health, and therefore the determination of Tyr has been of great interest.

Up to date, various analytical techniques for determination of Tyr have been reported such as liquid chromatography [8], spectrophotometry [9], chromatography [10] and capillary zone electrophoresis [11,12]. However, these detection methods not only consume a lot of time, but also need cumbersome sample pretreatment. To address these problems, electrochemical detection methods have been developed [13] and extensively used due to their outstanding features including high sensitivity, low cost and feasibility of miniaturization [14].

Yet the accuracy and sensitivity of traditional electrochemical sensors have certain limitations. In this regards, organic thin-film transistors (OTFTs) have emerged as state-of-the-art potential measurement sensing platform due to its flexible, versatile, real-time and disposable properties and features [15–19]. Nowadays, OTFT-based sensors has

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been successfully prepared and applied to detect substances in special environments as well as real physiological samples [20]. Organic electrochemical transistors (OECTs) are a simple structure of OTFTs, in which a thin layer of organic semiconductor is deposited on the channel area between the source and drain electrodes and exposed to an electrolyte together with the gate electrode. Nevertheless, the traditional OECTs with bare electrodes for detection of Tyr usually do not exhibit obvious voltammetric response due to their low electrocatalytic activity. Thus, it is a difficult task to detect trace amount Tyr by traditional OECTs with bare electrodes. To solve this problem, it is necessary to carry out electrochemical modification on the bare electrodes of OECTs [21–24].

For better sensitivity, many studies have reported on different methods for modifying the bare electrode of OECTs for Tyr detection, such as electrochemically reduced grapheme oxide (ERGO), nafion/TiO2-Graphene, Fe-doped hydroxyapatite (Fe-HA) nanoparticles and tyrosinase, single-walled carbon nanohorns (SWCNH), MWCNT-graphene nanosheet nanocomposite (MWCNT-GNS) and AuNPs/MWCNTs [4,23,25–30]. However, these methods generally require complicated procedures of modification. Hence, a simple, rapid and cost effective method for electrode modification is urgently needed.

In this paper, we report the development of efficient and low consumption sensors for Tyr detection based on OECT. The bare electrode was further modified by nanocomposite of gold nanoparticles (AuNPs), poly-(diallyldimethylammonium chloride) (PDDA) and multi-walled carbon nanotubes (MWCNTs). AuNPs have been shown to exhibit good catalytic ability, large aspect ratio, high electrical conductivity and biocompatibility [31] in electrochemical modification analysis of various species. PDDA plays an important role in dispersing carbon nanotubes and nanoparticles, and can also be used as a combination agent [32]. MWCNTs have excellent properties such as good chemical stability, high electrical conductivity, and extreme mechanical strength [33,34]. Compared with the sensor with bare electrodes, the sensor with AuNPs, PDDA and MWCNTs modified electrode shows a significantly enhanced response, sensitivity and biocompatibility for the detection of Tyr. More importantly, the modified OECT-based sensor can be easily fabricated with flexible electrodes for dynamic and real-time detection on human bodies.

2. Experimental

2.1. Materials

L-Tyrosine (Tyr, 98%), poly (diallyldimethylammonium chloride) (PDDA, 20%, w/w in water) reagent were purchased from Sigma-Aldrich and stored at 4 °C. Phosphate buffered saline (10 × PBS) solution (pH = 7.4) was purchased from Sangon (Shanghai, China). Sodium chloride (NaCl), chloroauric acid ($HAuCl_4{\cdot}4H_2O$), sodium citrate, methanol, acetone, isopropanol and ethanol were purchased from Sinopharm (Shanghai, China). Dimethyl sulphoxide (DMSO) was purchased from Sigma-Aldrich. All the above reagents were of analytical grade. PEDOT: PSS aqueous solutions (Clevios™ PH 1000) were purchased from Heraeus and stored at 4 °C. MWCNTs (purity > 95%) were purchased from Nanjing XFNano Material Tech Co., Ltd. (China). MWCNTs were treated for multiple carboxyl groups. Deionized ultrapure water was produced by a Milli-Q system (18.2 MΩ, Millipore, Bedford, MA, USA).

2.2. Apparatus

Electrochemical workstation (CHI660D) was purchased from Shanghai Chen Hua. A conventional three-electrode system was used for electrochemical experiments, which consisted of an Ag/AgCl (sat. KCl) as reference electrode, a platinum wire as auxiliary electrode, a bare or modified Au gate electrode as working electrode. The prepared OECT has a three-electrode structure. Magnetics stirrer (C-MAG HS4 digital) was purchased from IKA. Magnetic stir bar and beaker were purchased from Sinopharm (Shanghai, China).

All experiments were carried out at room temperature. PEDOT: PSS was used as the active material of OECT source and drain levels. The other electrode is modified by MWCNTs/PDDA/AuNPs. However, the last one electrode holds the post of gate of OECT for electrochemical measurements. Cyclic voltammetry (CV) and chronoamperometry were used for the electrochemical detection of Tyr.

2.3. Sensor fabrication

OECT-based Tyr sensor was fabricated according to the schematic diagram shown in Fig. 2a. A clean glass slide (size: 1 cm × 1 cm) was used as the substrate for the sensor. A sensor mask was designed that the patterned Cr/Au source, drain and gate electrodes. Then, Cr/Au was plated onto the sensor substrate (thickness: 10 nm/80 nm) by radio frequency magnetron sputtering. Dimethyl sulphoxide (DMSO) was added into PEDOT: PSS solution to improve the conductivity and stability performance of the PEDOT: PSS films. After UV-ozone cleaning on the surface of the samples several times, the PEDOT: PSS solution was spin-coated (600 rpm, 9 s; 3500 rpm, 30 s) on the OECT source and drain levels channel (length, 6 mm; width, 0.2 mm) area. Finally, the OECT sensors were moved to a glove box filled with high purity N_2 and annealed at 185 °C for 1 h.

2.4. Synthesis and characterization of AuNPs and MWCNTs/PDDA

The AuNPs were synthesized according to previous literature [35] with subtle modifications. In this article, 850 μL of $HAuCl_4{\cdot}4H_2O$ solution (5 g/L) was added to 50 mL of ultra-pure water and was kept on ultrasonic. Afterwards, the diluent solution was heated to boil with magnetic stirring. Hereafter, 960 μL of 1% trisodium citrate dehydrate was added dropwise to the boiled solution. By sodium citrate reduction, $HAuCl_4{\cdot}4H_2O$ was gradually poured into AuNPs suspension solution. When the color of the solution changed from black to wine red, AuNPs were formed. The AuNPs suspension solution were then stored in dark bottles at 4 °C after cooling. ~~The morphological characterization of the AuNPs was carried out by a field emission scanning electron microscopy (FE-SEM).~~

MWCNTs powders (10 mg) were dispersed into 10 mL double distilled aqueous solution by ultrasonic vibration for 30 min. Then, we added 125 μL PDDA and 0.5 M NaCl to MWCNTs suspension solution and stirred for 8 h to obtain a homogeneous black suspension. To remove excess PDDA and NaCl, we centrifuged the suspension washed the residue for three times. The mixture was sonicated for 5 min immediately before preparing the films. The morphological characterization of the MWCNTs/PDDA/AuNPs was investigated by FE - SEM.

2.5. Preparation of MWCNTs/PDDA/AuNPs modified au gate electrodes

A certain size of the clean glass slide was used as the substrate material of OECT-based Tyr sensor. Prior to use, OECT-based sensor was rinsed, followed by sonication in acetone and distilled water, thoroughly to remove thoroughly the impurities on the channel and gate electrode. Before electrode modification, the composite material and gold nanoparticles were sonicated for 5 min. First, 10 μL of the MWCNTs/PDDA suspension was dropped onto the surface of the gate electrode. Simultaneously, the electrode was placed in a dry place to dry naturally. Hereafter,the gate electrode with the composite treatment was immersed in the AuNPs suspension solution for 10 h. Finally, the electrode after soaking was dipping washed 3 times in ultrapure water and blow-dried.

2.6. Sensor characterization and electrochemical measurements methods

Cyclic voltammetry (CV) was performed on a CHI660D