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High performance electrochemical electrode based on polymeric composite film for sensing of dopamine and catechol

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ABSTRACT

A highly conductive and electrochemically active film has been successfully fabricated by combining beta-cyclodextrin with acid-treated poly(3, 4-ethylenedioxythiophene):polystyrene (denoted as CD-f-PEDOT:PSS). The unique properties of the high performance CD-f-PEDOT: PSS sensor was investigated by utilizing X-ray photoelectron spectroscopy, atomic force microscope, cyclic voltammetry and amperometric *i-t*, etc. The CD-f-PEDOT:PSS film exhibits high-sensitivity towards dopamine (DA) and catechol (CT) without employing expensive noble metal or indium tin oxide (ITO) substrate and consuming much more time to polish the surface of traditional electrodes. The detection limits (S/N = 3) for DA and CT in phosphate buffer solutions (PBS, pH = 7.4) are 9.596 nM and 0.0275 μM, respectively. Furthermore, the CD-f-PEDOT: PSS film sensor exhibits good anti-interference and reproducibility. The encouraging results as well as facile preparation method suggest the CD-f-PEDOT: PSS film sensor is a promising alternative electrode to traditional ones such as ITO, gold or glassy carbon electrodes.

1. Introduction

Electrochemical detection is fast, sensitive, clean and accurate compared to many other detection methods, thus it has been applied to many aspects of our life [1]. Glassy carbon electrode (GCE) is the most popular electrode due to its good electrical conductivity, high chemical stability, and wide potential range [2]. However, the pre-treatment of GCE can be tedious and time-consuming. Subsequently, indium tin oxide (ITO) glass electrode and carbon paper electrode have been developed as two important alternatives to GCE. The ITO electrode exhibits excellent opto-electronic properties, and finds applications in solar cells, light-emitting diodes, touch panel displays and biosensors [3]. But ITO is expensive due to limited indium source on earth [4]. More importantly, the electroanalytical activity of ITO is relatively low, thus surface modification is commonly required. Up to date, metal nanoparticles, metal oxide, conducting polymers, carbon materials and composites have been introduced for ITO surface modification [5]. For example, Fu used ion implantation technique to deposit gold nanoparticles (Au NPs) on ITO, allowing for the detection of glucose [6]; Ding realized the sensitive detection of copper ions with the ITO/Au NPs electrode [7]; in-situ growth of microporous ZnO nanorods on ITO also enhanced the electrochemical behavior [8]. However, there are concerns about the interface stability and brittleness of ITO, which might hinder practical applications [9]. The carbon paper electrodes that mainly constitute of graphene and/or carbon nanotubes can be free-standing and flexible [10]. But the carbon paper electrodes suffer from low conductivity and low density of active sites for catalysis [11],thus reduction or selectively chemical doping were explored [12,13]. For example, KaderDagcĭ prepared graphene/Ag nanoparticles/poly(pyronin Y) hybrid paper electrode for effective nitrite detection [14]; Sun prepared graphene paper electrode decorated with Pt/Pd alloy nanoparticles for electrochemical catalysis and sensing [8].

It is clear from the above-mentioned examples, ITO or carbon paper mainly acts as a conducting substrate, surface modification or decoration are often required for the application of electrochemical detection [15]. It is significant to develop new electrode materials that are both highly conductive and highly active in catalysis, and preferably stable and flexible to suit wider appli-

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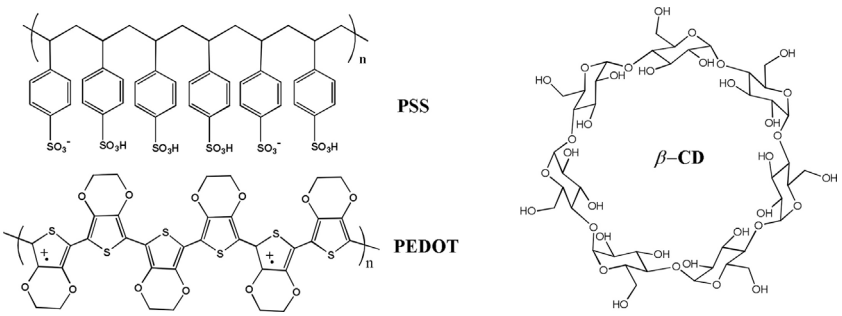


Fig. 1. Chemical structures of PEDOT:PSS and β-cyclodextrin.

cations. Poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS, chemical structure is shown in Fig. 1) is a conducting polymer that is cheap, solution processible, chemically stable, conductive, flexible and transparent [13,16,17]. These brilliant properties provide it great potential in electrochemical devices [18]. Though GCE coated with PEDOT: PSS film realized the detection of hydrazide, nitrite, and salicylic acid [19], it is still challenging to utilize neat PEDOT:PSS films without any conducting substrate or plasticizer, as the film can be dissolved in water after certain time duration. Furthermore, the inherent electrochemical property is poor for the PEDOT: PSS [20].

Here we introduce neat PEDOT:PSS film coated on glass substrate as an alternative electrode for electrochemical detection. After post-treatment of concentrated H_2SO_4 (CSA), the PEDOT: PSS film became more conductive and hydrophobic due to the partial removal of the insulting and hydrophilic PSS component [21,22]. The resultant film, which is denoted as CSA-t-PEDOT:PSS was subsequently immersed in β-cyclodextrin (CD, chemical structure is shown in Fig. 1) solution to create more electrochemically active sites by supramolecular self-assembly. The CD functionalized PEDOT:PSS film (CD-f-PEDOT:PSS) could realize ultrasensitive detection of dopamine (DA) and catechol (CT). To the best of our knowledge, this is the first time we demonstrate a functionalized PEDOT:PSS film can realize highly sensitive and selective determination without employing any expensive ITO glass and noble metals and consuming much more time to polish the surface of traditional electrodes.

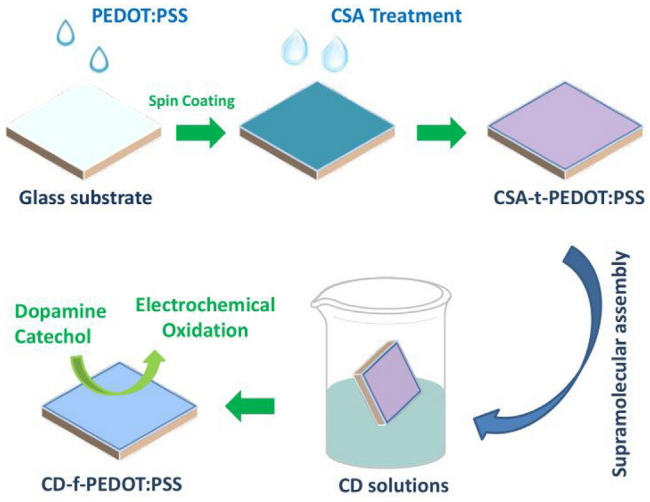
2. Experimental

2.1. Chemicals and materials

PEDOT:PSS aqueous solution was purchased from Sigma Aldrich (Conductive grade, Lot No. WXBB6393 V). The concentration of PEDOT:PSS was 1.3% by weight, and the weight ratio of PSS to PEDOT was 8:5 in solution. β-cyclodextrin (CD) was purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China). Concentrated sulfuric acid (H_2SO_4, CSA)was purchased from Nanjing Chemical Company. NaH_2PO_4 (≥99.0%), Na_2HPO_4 (99%), $K_3Fe(CN)_6$ (≥99.5%), $K_4Fe(CN)_6$ (99%), KCl (99.5%) and dopamine (DA, 98%) and catechol (CT) were purchased from Aladdin Chemistry Co., Ltd (Shanghai, China). DA and CT solutions were prepared fresh prior to use. Phosphate buffer solutions (PBS) (0.1 M, pH 7.4) were prepared using 0.1 M Na_2HPO_4 and 0.1 M NaH_2PO_4. And doubly distilled water was used throughout. All the materials were used as received.

2.2. Treatment of PEDOT:PSS films

PEDOT:PSS films were prepared by spin coating the PEDOT:PSS aqueous solution (3000 rpm/min) on 1.2 × 1.2 cm^2 glass substrate, which were pre-cleaned successively with detergent, de-ionized (DI) water, acetone for three times before use. The PEDOT:PSS films were dried at room temperature for about 5 min. Then The CSA treatment was performed by dropping 100 μL concentrated H_2SO_4 on a PEDOT:PSS film on a hot plate at 120 °C. The film lasted for about 15 min, and then they were rinsed with DI water twice to practically remove the PSS and dried at 120 °C again. Finally, CSA-treated film (CSA-t-PEDOT:PSS) can be achieved.



Scheme 1. The fabrication process of the CD-f-PEDOT:PSS.

2.3. Preparation of CD-functionalized PEDOT:PSS films

The obtained CSA-treated PEDOT:PSS film was immersed in β-CD aqueous solutions with various concentrations for about 40 s. The CD-functionalized PEDOT:PSS films (CD-f-PEDOT:PSS) were dried at 120 °C. The detailed fabrication process of the CD-f-PEDOT:PSS is shown in Scheme 1.

2.4. Characterization of PEDOT:PSS films

The AFM images of the polymer films were obtained using a VeecoNanoScope IV Multi-Mode AFM (Bruker, German) with the tapping mode. X-ray photoelectron spectroscopy (XPS) analysis was obtained using PHIQuantera II with C60 high resolution spectrometer with a monochromatized Al Ka X-ray source (1486.71 eV photons) to analyze the chemical composition of the materials. Sheet resistances were measured by the van der Pauw four-point probe method with a Keithley 2400 source/meter. The electrical contacts were made by pressing indium on the four corners of each PEDOT:PSS film on a glass substrate.

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