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Original article

Detection of dopamine using self-assembled diazoresin/single-walled carbon nanotube modified electrodes

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ABSTRACT

Ultrathin films of diazoresin (DR)/single-walled carbon nanotube (SWNT) were fabricated on thioglycollic acid (TGA) decorated gold (Au) electrodes by the self-assembly method combined with the photocrosslinking technique. The electrochemical behavior of dopamine (DA) at the DR/SWNT modified electrodes was studied using the cyclic voltammetry (CV) and differential pulse voltammetry (DPV) methods. Under the optimal conditions, a linear CV response to DA concentration from 1 μmol/L to 40 μmol/L was observed, and the detection limit of DA was 2.1×10^{-3} μmol/L *via* the DPV method in the presence of 10 μmol/L of uric acid (UA) or 2.5×10^{-3} μmol/L *via* the DPV method in the presence of 10 μmol/L of ascorbic acid (AA). Moreover, the modified electrodes exhibited good reproducibility and sensitivity, demonstrating its feasibility for analytical purposes.

1. Introduction

Dopamine (DA) is a natural catecholamine formed by the decarboxylation of 3,4-dihydroxyphenylalanine and belongs to the family of excitatory chemical neurotransmitters [1]. DA is one of the important neurotransmitters and is widely distributed in the mammalian central nervous system for signaling. It is mainly responsible for the reward sensation, and transmits the information of excitement and fun, but at the same time, is related to the addiction [2]. It is of great clinical importance to measure the DA level in extracellular fluids to monitor neurotransmission processes and diagnose Parkinson's disease [3]. Therefore, it is of great importance to sensitively and selectively monitor DA not only for biomedical chemistry and neurochemistry research but also for diagnostic and pathological purposes. To date, several impressive techniques have demonstrated the feasibility for the assay of DA, including electrochemical [4–9], colorimetric [10–13], fluorescence spectrometry [14], liquid chromatography/electrospray tandem mass spectrometry [15], and high performance liquid chromatography methods [16]. Among these, electrochemical approaches have attracted most attention because of their simplicity, low instrumental cost, and capability in real-time and even in vivo measurements. Although the electrochemical responses have been continuously improved, the development of more reliable and efficient sensors for sensitive analysis of DA still remains very challenging. Therefore, the choice of material is essential and important to construct sensors with excellent performance.

In recent years, various self-assembly methodologies have achieved great diversity [17–19]. Diazoresin (DR), as a photosensitive polyelectrolyte, has been massively utilized in self-assembly systems to improve the stability of the self-assembled multilayer films via the photocrosslinking technique [20–24]. For example, the unstable ionic linkages involved in the multilayers will convert to stable covalent bonds with exposure of the DR containing films to UV light. In this article, we applied the self-assembly method combined with the photocrosslinking technique to the preparation of DR/SWNT modified Au electrodes, and investigated the electrochemical behavior of DA on the electrodes by the methods of cyclic voltammeter (CV) and differential pulse voltammeter (DPV).

2. Experimental

2.1. Materials

Dopamine (DA), uric acid (UA) and ascorbic acid (AA) were purchased from Sigma. Single-walled carbon nanotubes (SWNTs,

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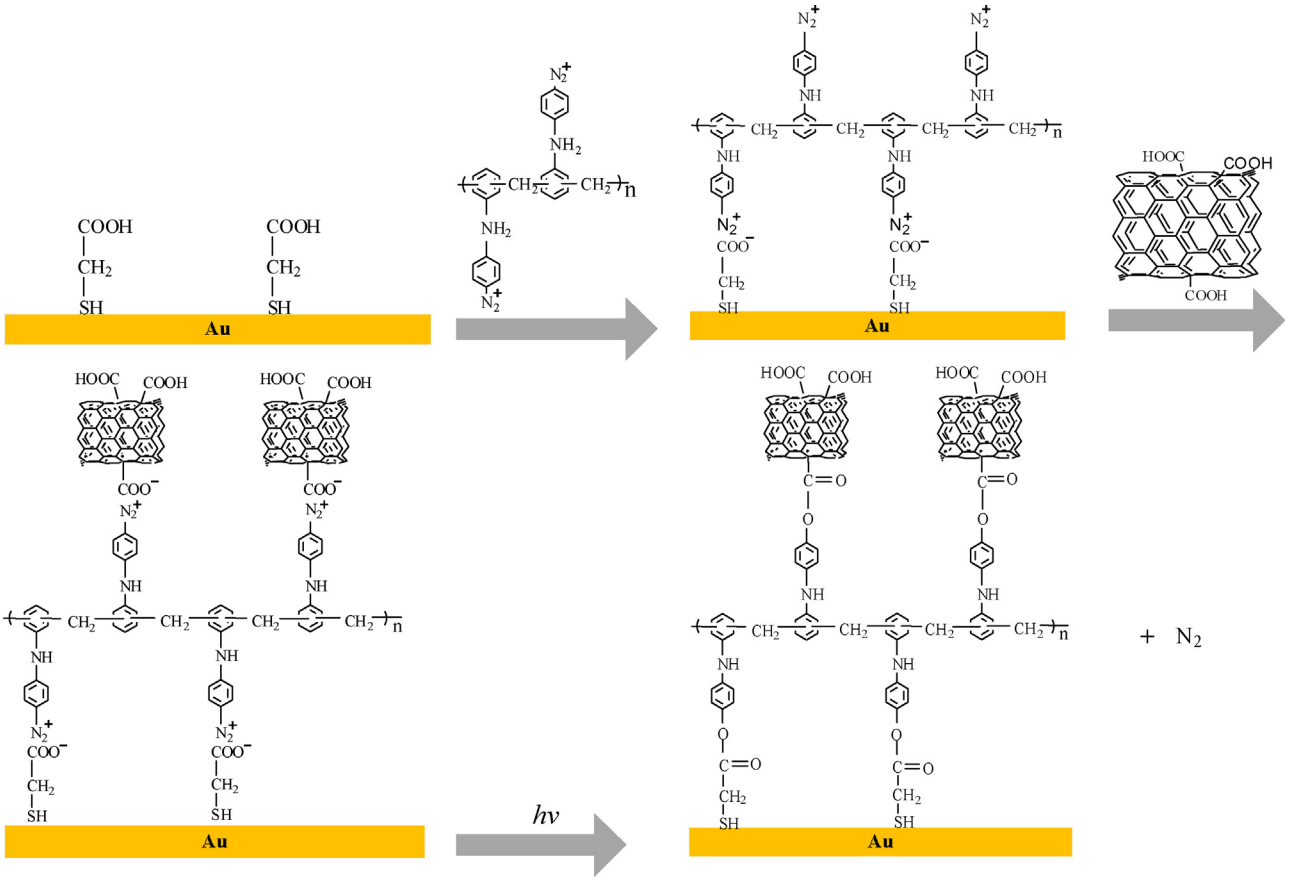

Fig. 1. Illustration of self-assembly process of DR/SWNT modified electrodes.

95% purity, diameter 10–20 nm, length 1–5 μm) were purchased from Nanoport Company (Shenzhen, China). Dopamine hydrochloride injection (DHI) was purchased from Shandong provincial hospital (Jinan, China). All other chemicals were of analytical grade and used as obtained without further purification. Phosphate buffer solutions (PBS, 100 mmol/L) of pH 5–8 were used as a supporting electrolyte. The preparation of aqueous solution was done with deionized water. Solutions were deoxygenated by purging with prepurified nitrogen gas. DR was synthesized according to the method described elsewhere [20]. Carboxylic acid modified SWNT (COOH-SWNT) was prepared according to a reported method [22]

2.2. Apparatus

Electrochemical measurements were carried out on a CHI-832C electrochemical analyzer (CH Instruments, China). A three-electrode cell was used with a Ag/AgCl electrode (KCl electrolyte concentration: C_{KCl} = 3.0 mol/L) as a reference electrode, a Pt wire as a counter electrode and a bare gold electrode with a diameter of 3 mm (modified and unmodified) as a working electrode, respectively. All the electrodes were purchased from CH Instruments. The pH values of solutions were measured with a PB-10 pH meter (Renhe Instruments, China). All the measurements were performed at room temperature.

2.3. Fabrication of DR/SWNT modified electrodes

The schematic fabrication process was illustrated in Fig. 1. Prior to the self-assembly process, the bare gold electrode was polished to a mirror finish using aqueous alumina (particle size 0.05 μm) slurry, and rinsed with deionized water. The treated gold electrode was immersed in an aqueous solution of 0.1 mol/L thioglycollic acid (TGA) at room temperature for 3 h. And then, the electrode was rinsed by anhydrous alcohol and deionized water to remove non-specifically adsorbed TGA. After N_2 drying, the electrode was alternately immersed in an aqueous polycation DR solution (0.05 mol/L) and an aqueous COOH-SWNT dispersion (0.05 mol/L) for 5 min and 10 min, respectively. The electrode was then rinsed thoroughly with deionized water and dried with N_2 to complete the assembly process. Finally, the modified electrode was exposed to UV light from a medium-pressure mercury lamp with an intensity of 12 mW/cm^2 at 365 nm for 30 s to finish the whole fabrication process.

3. Results and discussion

3.1. Electrochemical oxidation of dopamine at modified electrodes

The electrocatalytic activity of the DR/SWNT modified electrodes toward the oxidation of DA is characterized by cyclic voltammetry (CV) ranging from −0.1 V to 0.6 V. The CV responses of 2 μmol/L DA in 0.1 mol/L PBS (pH 6.0) at the bare and DR/SWNT modified electrodes are shown in Fig. 2. Compared to bare Au electrodes, the DR/SWNT modified electrodes show well-defined and resolved voltammetric responses for the direct oxidation of DA. The oxidation peak current at the modified electrode is much higher than that of the bare electrode, which indicates that the DR/SWNT modified electrode is an effective electrocatalyst for the oxidation of DA.