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Enhanced electrochemical performance at screen-printed carbon electrodes by a new pretreating procedure

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Abstract

A new method for the pretreatment of screen-printed carbon electrodes (SPCEs) by two successive steps was proposed. In step one, fresh SPCEs were soaked into NaOH with high concentration (e.g. 3 M) for tens to hundreds of minutes, and the resulted electrodes were called as SPCE-I. In step two, SPCE-I were pre-anodized in low concentration of NaOH, which were designated as SPCE-II. The pretreated electrodes showed remarkable enhancement in heterogeneous electron transfer rate constant (k^0) increased from 1.6×10^{-4} cm s^{-1} at the fresh SPCE to 1.1×10^{-2} cm s^{-1} at SPCE-I for $Fe(CN)_6^{3-/4-}$ couple. The peak to peak separation (ΔE_p) in cyclic voltammetry was reduced from ca. 480 to 84 mV, indicating that the electrochemical reversibility was greatly promoted, possibly due to the removing of polymers/oil binder from the electrode surfaces. The electroactive area (A_{ea}) of the electrode was increased by a factor of 17 after pretreatment in step one. Further analysis by the electrochemical impedance method showed that the electron transfer resistance (R_{ct}) decreased from ca. 2100 to 1.4 Ω. These pretreated electrodes, especially SPCE-II, exhibited excellent electrocatalytic behavior for the redox of dopamine (DA). Interference from ascorbic acid (AA) in the detection of DA at SPCE-II could be effectively eliminated due to the anodic peak separation (190 mV) between DA and AA, which resulted from the functionalization of the electrode surface in the pretreatment of step two. Under optimum conditions, current responses to DA were linearly changed in two concentration intervals, one was from 3.0×10^{-7} to 9.8×10^{-6} M, and the other was from 9.8×10^{-6} to 3.3×10^{-4} M. The detection limit for DA was down to 1.0×10^{-7} M.

Keywords: Screen-printed carbon electrodes; Pretreatment; Heterogeneous electron transfer rate constant; Electrochemical impedance; Dopamine

1. Introduction

As the development of point-of-care testing and on-site monitoring in clinical, environmental, biological, food safety and industrial analysis, various kinds of disposable electrochemical sensors based on screen-printed carbon electrodes (SPCEs) have been widely used because of their simplicity, costlessness, versatility and particularly the possibility of mass production [1–6]. Reviews by Hart and Wring [7], Suzuki [8], Alegret and coworkers [9] and Zen et al. [10] on the recent design and application of screen-printed electrochemical sensors have been published.

Compared with solid graphite electrodes the printing inks for SPCEs contain some mineral binders or insulating polymers to improve the adhesion onto the substrate. A certain amount of polymers in the inks might shelter the electrochemically active carbon particles and increase the electron transfer resistance that will result in slower kinetics of heterogeneous reaction, and hence quasi-reversible or irreversible redox processes might occur at SPCEs. It is well known that the pretreatment of carbon electrodes have a dramatic effect on the electron transfer properties of solution substrates [11], thus the development of surface treatment methods to enhance the electrochemical properties of SPCEs have drawn great attentions.

The main purpose of pretreatment on SPCE was to remove organic ink constituents or contaminants and to increase surface roughness or functionalities. For this purpose, Wang et al. [12] proposed a short electrochemical pre-anodization method namely the electrodes were treated in 0.05 M PBS for 30 s–3 min in the potential range between +1.5 and +2.0 V. Other pre-anodization methods were studied by applying various activation

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potentials on the electrodes in four different aqueous solutions (H_2SO_4, KCl, $NaHCO_3$ and Na_2CO_3). It was found that the pretreatment procedure in saturated Na_2CO_3 solution at 1.2 V seems to be mild and effective [13]. Polishing SPCE has shown improved adsorption of immunoglobulin without losing reproducibility [14], but this is a more risky method strongly dependent on the polisher. Osbome et al. [15] activated SPCE by exposure to UV light from an excimer laser source and found that laser treatments selectively etched the organic binding polymer from the composite surface thereby exposing sub-layers of carbon particulates. A contrast of three pretreatment methods was studied [16] including pre-anodization in saturated Na_2CO_3, cyclic voltammetry in 0.5 M H_2SO_4, and polishing with fine emery paper followed by mechanical cleaning in an ultrasonic bath. The results showed that a little more reversible reaction was obtained after pretreatment, e.g. ΔE_p decreased from 147 to 113 mV for $Fe(CN)_6^{3-/4-}$ couple at scan rate 20 mV s^{-1}.

In this work, a two-step pretreated method, combining chemical treatment (soaked in high concentration of NaOH) and electrochemical treatment (anodization in mild NaOH solution), was proposed, which can process as a batch to improve the electrochemical behavior of SPCEs. After pretreatment, the electrochemical and physical properties such as peak to peak separation (ΔE_p), heterogeneous electron transfer rate constant (k^0), electroactive areas of the electrodes (A_{ea}) and electron transfer resistance (R_{ct}), for $Fe(CN)_6^{3-/4-}$ couple were greatly changed. Meanwhile, the electrochemical response to dopamine (DA) has also been dramatically enhanced.

DA is an important neurotransmitter in mammalian central nervous systems. The lack of DA in the brain will cause some serious diseases such as schizophrenia and Parkinson's disease [17]. Recent researches indicated that the level of DA was closely associated with compulsive behaviors such as overeating, hypersexuality and pathological gambling [18]. Therefore, detection of DA is important to the study of physiology mechanism and clinical diagnoses, and has often performed by electrochemical approaches because of its electro-activity [19,20]. Nevertheless, voltammetric response of DA is hindered by ascorbic acid (AA) because of their overlapped oxidation potentials and high concentration ratios of AA to DA in the samples. To resolve this problem, chemically modified electrodes have often been used such as ion-exchange membranes typically as Nafion [21], self-assembled monolayer [22], gold nanoparticles arrays [23] and polymeric films [24], demonstrating very potential for improving the selectivity against AA. Other attempts on carbon nanotube (CNT) have revealed that CNT modified electrodes could be successfully used in the detection of dopamine [25–27]. However, those methods have some disadvantages such as special reagents are required and heavy and complicated modified steps are needed. In addition, these modified electrodes showed a slow electron transfer rate during the electrochemical detection of DA.

The pretreated SPCEs in this work, can substantially lower the over potentials for the oxidation of DA and AA and exhibited an excellent high sensitivity and selectivity to the detection of DA. The interference of high concentration of AA also can be eliminated by a large anodic peak separation (ca. 190 mV) between DA and AA at SPCEs with a two-step pretreatment.

2. Experimental

2.1. Chemicals and reagents

Carbon ink No. CH-1 was obtained from Jujo Chemical Co., Ltd., Tokyo, Japan. Silver conductive ink (product: BY9700H) was purchased from Shanghai Baoyin Electronic Materials Ltd., Shanghai, China. Dopamine and ascorbic acid were purchased from Fluka. All the other compounds from Sinopharm chemical Reagent Co. Ltd. were at least of analytical reagent grade without further purification. The supporting electrolyte phosphate buffer solutions (PBS) were prepared by mixing the stock solutions of 0.2 M KH_2PO_4–Na_2HPO_4, and then adjusting the pH with 0.2 M H_3PO_4 and 0.2 M NaOH. Electrochemical characterization was performed in 5 mM potassium hexacyanoferrate and 5 mM potassium ferrocyanide trihydrate dissolved in 0.5 M potassium chloride solution. Aqueous solutions were prepared with deionized water (Millipore-Q purification system).

2.2. Apparatus

Electrochemical experiments were carried out using CHI 832 or CHI 604B (ChenHua Instrument, Shanghai, China). A conventional three-electrode system was employed with a pretreated or not pretreated SPCE as the working electrode, a platinum wire as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode. All experiments were performed at room temperature.

2.3. Fabrication of screen-printed carbon electrodes

SPCEs were prepared by using a silk printing technique according to Wring and Hart [28], coated polyester films with silver and carbon inks successively. First, silver ink was printed onto the polyester and supported as conductor, and then carbon ink was printed on the silver layer. The film was heated at 60 °C for ca. 5 h after each of the above step to drive off the solvents from the applied paste and to cure the patterned paste. The resulted electrodes had a resistance of around 8 Ω between the electrical contact and the graphite pad (3 cm) with a 3 mm × 5 mm working area.

2.4. Two-step pretreatment of SPCEs and analytical procedures

In this work, a two-step procedure was employed to pretreat fresh SPCEs (Scheme 1). In the first step, the fresh SPCEs were soaked into NaOH solutions with a series of concentration (1–8 M) for tens to hundreds of minutes. The resulted electrodes were named as SPCE-I. After rinsed with deionized water, SPCE-I were placed in an electrochemical cell for the voltammetric or ac impedance measurement of $Fe(CN)_6^{3-/4-}$ couple.