Talanta 192 (2019) 40–45

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Improvement of electrochemical performance of screen-printed carbon electrodes by UV/ozone modification

Jing Wang[a], Zheng Xu[a,*], Mengqi Zhang[a], Junshan Liu[a], Hongqun Zou[b], Liding Wang[b]

[a] Dalian University of Technology, Key Laboratory for Micro/Nano Technology and System of Liaoning Province, Dalian 116085, China
[b] Dalian University of Technology, Key Laboratory for Precision and Non-traditional Machining Technology of Ministry of Education, Dalian 116085, China

ARTICLE INFO

Keywords:
Screen-printed carbon electrode
UV/ozone
Electron transfer

ABSTRACT

Screen-printed carbon electrode (SPCE) has been widely used in electrochemical (EC) field. Nevertheless, compared with some metal electrodes, SPCE is not sensitive to small amounts of reagent owing to its relatively low electron transfer rate. In this paper, the UV/ozone modification was proposed to treat SPCE to improve its electron transfer rate and EC performance. The changes of SPCE morphology and composition induced by UV/ozone modification were investigated in detail. The results show that the improved electron transfer rate can be mainly attributed to the increase of oxygen functional groups. To clarify the essential EC characterization, potentiodynamic polarization and electrochemical impedance spectroscopy of $K_3[Fe(CN)_6]$ was studied. Furthermore, to demonstrate the improved EC effect, two typical samples: small-molecule $K_3[Fe(CN)_6]$ and macro-molecule nicotinamide adenine dinucleotide (NADH), were measured by cyclic voltammetry. After UV/ozone modification, the oxidation potential and peak current responses to $K_3[Fe(CN)_6]$ and NADH were obviously improved in both original and CNT-modified SPCEs. Whereas, the original SPCE is more suitable to measure macromolecule NADH rather than CNT-modified one as the oxidative products of NADH are more likely to adsorb on rough surface.

1. Introduction

Screen-printed carbon electrode (SPCE) has been widely used in electrochemical (EC) field, owing to its excellent properties, such as low background current, wide potential window, high chemical stability etc [1–5]. Furthermore, SPCE is inexpensive as disposable unit [6]. However, compared with platinum electrode etc, SPCE is not sensitive to small amounts of reagent due to its relatively low electron transfer rate which limits its application [7,8].

In order to improve the EC performance of SPCE, several methods had been employed, including chemical treatment [9–11], EC activation [12,13], plasma treatment [14,15], surface modification with various catalysts [16,17] and nanomaterials [18–21]. For example, Wei et al. [9] modified SPCE by chemical treatment. SPCE was soaked into 3 M NaOH solution for 1 h, and then was anodized at 1.2 V in 0.5 M NaOH solution for 20 s. The peak to peak separation of modified SPCE for $Fe(CN)_6^{3-/4-}$ couple was reduced from 480 to 84 mV. Cui et al. [12] activated SPCE in saturated Na_2CO_3 solution at 1.2 V for 5 min, the peak to peak separation of activated SPCE for $Fe(CN)_6^{3-/4-}$ couple was reduced from 122 to 72 mV. Generally, chemical or EC activation of SPCE utilizes anodization to increase the EC activity of SPCE through the increase of surface functionalities and roughness. However, these chemical methods are not fully suitable for SPCEs that are composed of counter/reference electrode made of silver or copper since these metals are more likely to be corroded by alkaline solution. On the other hand, the oxygen plasma treatment of SPCE can etch SPCE, and both vacuum pump and gas resource are indispensable to produce plasma too [22,23].

Herein, the method of UV/ozone modification is presented to improve electron transfer rate and EC performance of SPCE. Both original and carbon nanotubes (CNT) modified SPCEs were treated with UV/ozone. The changes of SPCE morphology and composition induced by UV/ozone modification were investigated. The improved EC responses of modified SPCEs were evaluated by the measurement of two typical electroactive samples: small-molecule $K_3[Fe(CN)_6]$ and macro-molecule nicotinamide adenine dinucleotide (NADH). The results show that UV/ozone modification is helpful to improve the EC performance of SPCEs. Compared with other methods, UV/ozone modification is cost-effective since it doesn't require both extra reagents and external gas source. In addition, the price of UV/ozone cleaner is acceptable.

* Correspondence to: Dalian University of Technology, School of Mechanical Engineering, Key Laboratory for Micro/Nano Technology, No.2 Linggong Road, Dalian City, Liaoning Province, China.
E-mail address: xuzheng@dlut.edu.cn (Z. Xu).

https://doi.org/10.1016/j.talanta.2018.08.065
Received 18 May 2018; Received in revised form 19 August 2018; Accepted 27 August 2018

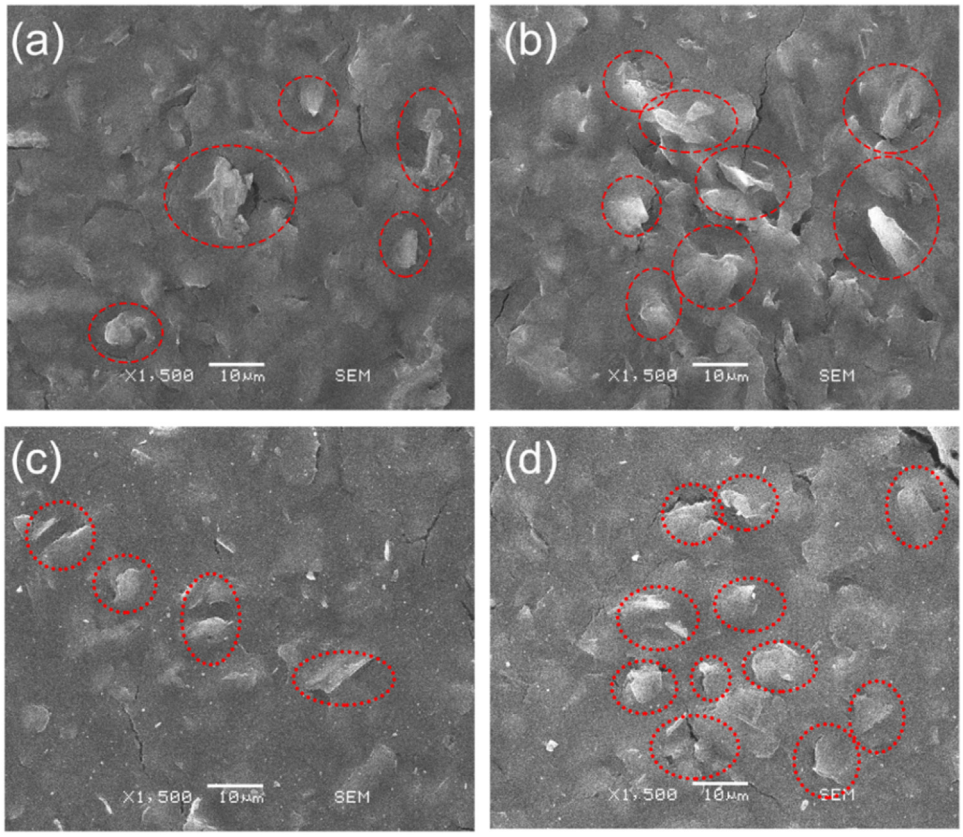

Fig. 1. Scanning electron micrographs of original SPCE (a) before and (b) after UV/ozone modification. Scanning electron micrographs of CNT-modified SPCE (c) before and (d) after UV/ozone modification. The red circles are for step-like carbon sheets.

2. Experimental section

2.1. Materials

Two kinds of SPCE strips: SPCE modified with CNT and original SPCE without CNT, were purchased from Dropsens. Both SPCE strips consist of a carbon electrode as working electrode, silver electrode as reference electrode, and another carbon electrode as counter electrode. NADH was purchased from Roche. NAD^+ was purchased from Sigma-Aldrich. $K_3[Fe(CN)_6]$ was purchased from Dalian Meilun. NADH and $K_3[Fe(CN)_6]$ samples were freshly prepared in PBS (0.1 M, pH 7.4) and KCL (0.1 M) solutions respectively.

2.2. Apparatus

A UV/ozone cleaner (144AX-220, JELIGHT Co., Ltd., USA) was used to modify SPCEs, in which a 10 mW/cm^2 Hg lamp provided 185 and 254 nm UV light. The lamp was warmed for 15 min, and then SPCE strips were placed in chamber and modified at 6 cm distance from the Hg lamp for 5 min. In the process, oxygen molecules (O_2) absorbed 185 nm UV light and formed ozone, then ozone molecules (O_3) absorbed 254 nm UV light and broke into atomic oxygen (O).

The electrochemical impedance spectroscopy (EIS) of SPCE was determinated with an impedance analyzer (E4990A, Keysight Co., USA). The surface morphology of SPCE was characterized by a scanning electron microscope (SEM, JSM-6360, LV JEOL Co., Japan). Chemical compositions of SPCE were analyzed by an X-ray photoelectron spectroscope (ESCALAB 250Xi, ThermoFisher Co., USA). All EC experiments were carried out with an electrochemical workstation (Reference 600 +, Gamry Co., USA).

3. Results and discussion

3.1. Investigation on the surface characteristics of SPCEs

Surface morphology of original and CNT-modified SPCEs was investigated by SEM. A series of images were analyzed for each surface morphology (40 images). One image selected for each type of surface morphology is shown in Fig. 1. It can be seen that the step-like carbon sheets increase after UV/ozone modification of both original and CNT-modified SPCEs. This is because ozone or single oxygen molecules could slowly etch the carbon surface to form oxygen-containing groups which would let the carbon surface become rough [24]. Besides, some organic binders existed on the electrode surface can be removed *via* UV/ozone modification [25]. Therefore, the morphology of both original and CNT-modified SPCEs becomes rougher after modification.

The change of chemical composition of original and CNT-modified SPCEs was investigated by XPS. As shown in Fig. 2, O_{1s} peak intensity obviously increases for both original and CNT-modified SPCEs after UV/ozone modification. The ratio of O_{1s} increases from 0.04 to 0.13 for original SPCE and from 0.06 to 0.12 for CNT-modified one. The reason is that oxygen-containing functional groups were generated on SPCE surface [24].

Since the oxygen-containing groups on the SPCE surface can improve the wettability which could promote the diffusion-controlled process and thus enhance the electron transfer rate of SPCE [26]. The detailed change of oxygen atoms was further studied through Gaussian decompositions of O_{1s} spectra as follows. For original SPCE, there is only one C-O bond peak before UV/ozone modification. It becomes the mixture of C-O and C=O bonds *via* UV/ozone modification, and the ratio of C-O and C=O bonds are 37.8% and 62.2% respectively. For CNT-modified SPCE, the ratio of C-O and C=O bonds are 45.9% and 54.1% before UV/ozone modification, and the ratio of C-O and C=O bonds become to 53.7% and 46.3% *via* UV/ozone modification.