

A novel procedure for fabricating flexible screen-printed electrodes with improved electrochemical performance

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Abstract. Screen-printed electrodes (SPEs) with improved electrochemical performance were fabricated in this study. The SPEs on hydrophilic surface of polyethylene ethylene terephthalate (PET) film showed better electrochemical behaviour than that on hydrophobic surface. The optimal condition of pretreating fresh SPEs was that alternately dealt with chemical treatment (soaked in 3M NaOH solutions for 1h) and high temperature curing (heated at 120 °C for 15 min) for two times. After chemical treatment, the electrochemical performance of self-made SPEs was better than the commercial three electrodes system. By analyzing cyclic voltammetry (CV) curves, we found that the oxidation peak currents and peak to peak separation reached 407.65 μ A and 111.16 mV, which mean the sensitivity and electron transfer rate improved 1.9 times and 3.8 times compared with fresh SPEs, and 2 times and 3 times compared with commercial DropSens (DS) electrodes. The obtained SPEs were stable, convenient and inexpensive, which could be extensively applied for developing novel electrochemical sensors.

1. Introduction

Electrochemical sensors behave as a crucial analytical tool to detect a variety of analytes including antigens [1], enzymes [2, 3] and heavy metal ions [4], have received great interests due to their high efficiency and sensitivity [5]. Sensitive membranes and substrate electrodes are the core components of electrochemical sensors. Two categories of substrate electrodes are usually employed, namely, solid electrodes and screen-printed electrodes (SPEs). In contrast to solid electrodes, SPEs demonstrated more advantages in developing disposable electrochemical sensors due to its low cost, easy to manufacture and mass production [6-8].

However, in China, SPEs with excellent performance mainly relied on import from Spain and other countries, which leads to the higher prices of electrochemical sensors. Moreover, most of commercialized SPEs in the Chinese market are printed onto hard substrates, such as ceramics [9], glasses and so on, which limited its application in portable or reliable electronic devices.

Considering the above-mentioned problems, in this work, a screen printing three-electrodes system containing working electrode, auxiliary electrode (counter electrode) and reference electrode was printed on a flexible PET film as substrates. We thoroughly evaluated the effects of surface hydrophilicity or hydrophobicity of PET substrates on electrochemical performance of SPEs.



Additionally, the pre-treating methods including chemical treatment and anodizing processing for working electrodes of SPEs were studied by assessing the electrochemical behaviors of the screen printing three-electrodes system. Thus, the obtained SPEs could be extensively applied for developing novel electrochemical sensors.

2. Experimental section

2.1. Materials and reagents

Carbon ink (No.CH-8) and insulating ink (No.AC-3G) was obtained from Jujo Chemical Co., Ltd., Tokyo, Japan. Silver conductive ink (No.BY-2100) was purchased from Shanghai Baoyin Electronic Materials Ltd., Shanghai, China. PET films (100 μ m) were gained from Baoding Lucky Innovative Materials Co., Ltd., Hebei, China. Potassium hexacyanoferrate (III) and potassium hexacyanoferrate (II) trihydrate were purchased from Sigma–Aldrich (St. Louis, MO, USA). Sodium hydroxide was analytical reagents and purchased from Beijing Chemical Works. Ultrapure water obtained from a Millipore water purification system was used in all assays.

2.2. Fabrication and pretreatment of SPEs

High precision manual screen printing machine (Shanghai HOTING screen printing equipment Co. Ltd. Model: PHM Series) was used to fabricate SPEs. The process was shown in Figure 1. First, silver ink (a) was printed onto the PET films and supported as conductor and reference electrode, and then carbon ink (b) was printed on the silver layer and supported as working and auxiliary electrode. After each step, the film was heated at 120 °C for 1 h to cure the patterned paste. Finally, insulating ink (c) was printed on the carbon layer and then heated the film at 120 °C for 15 min to cure the insulating layer.

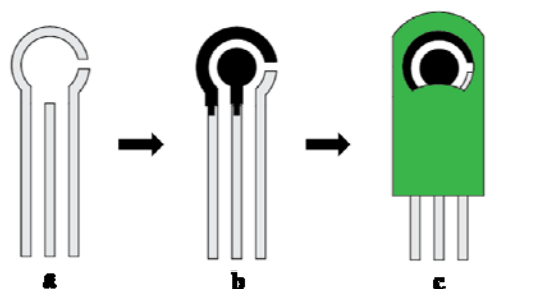


Figure 1. The schematic diagram of the process of printing SPEs.

In the procedure of pretreating fresh SPEs, we adopt two different approaches. In the first approach, the fresh SPEs were soaked into 3M NaOH solutions for 1 h as chemical treatment and then anodized in 0.5M NaOH solutions by applying 1.2V anodic potentials for 20s as electrochemical treatment. In the second approach, the fresh SPEs were alternately treated with chemical treatment and curing at 120 °C for 15 min for several times. After each alkaline solution treatment step, SPEs were rinsed using deionized water and then electrochemical testing was conducted.

2.3. Characterization

The contact angle of water on PET substrate was investigated by a video contact angle meter (Kruss, DSA100, Germany). Four-probe tester (Four probes tech, RTS-8, China) was used to detect the square resistance of SPEs. Electrochemical measurement was carried out using electrochemical workstation (Voltalab, PGZ402, France). The CV measurement of all SPEs samples were performed in a solution containing 1 mM $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ with the scan rate of 100 mV/s, and the performance of our SPEs were compared with import three electrodes systems (DropSens, DRP110, Spain). The surface morphology of SPEs was observed by D laser confocal topography measurement microscope (Keyence, VK-S105, Japan) and Scanning Electron Microscopy (SEM, Quanta 400, FEI) for different purposes.

3. Results and Discussion

3.1. Effect of hydrophilicity of PET substrate on electrochemical performance of SPEs

In order to ensure printing precision and quality, thermal stability and surface affinity of PET substrates are two crucial factors that we should consider seriously. After the cleaning of PET film, we heated it at 120 °C for 15 min. Considering ink adhesion can be seriously influenced by the hydrophilicity or hydrophobicity of substrates, the contact angle (θ) of water on both sides of PET film (denoting as PET-A and PET-B) was detected. In order to further improve the hydrophilicity of PET, O₂ plasma technique was employed to treat PET for 1 min. As shown in Figure 2, θ values of water on PET-A and PET-B are 52.5° and 75.7°, respectively, indicating PET-A surface displayed better hydrophilicity than PET-B. After O₂ plasma treatment, θ value of water decreased to 10.2°.

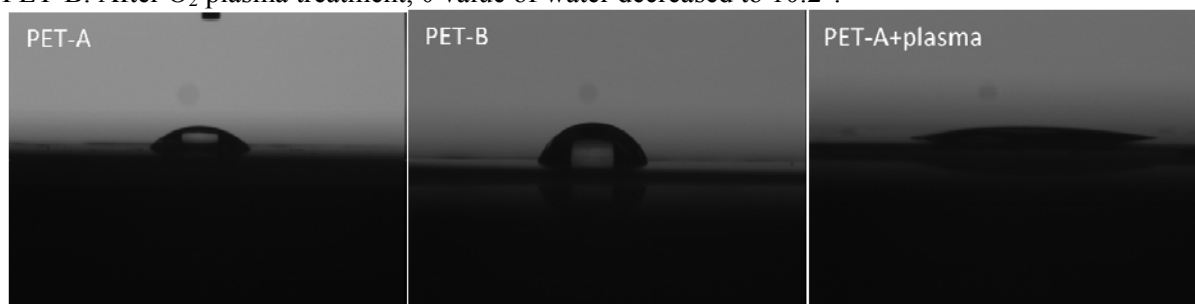


Figure 2. The contact angle of water on both sides of PET film and O₂ plasma treated PET-A surface.

The electrochemical behaviors of SPEs on PET-A, PET-B and plasma treated PET-A were thoroughly evaluated using commercial SPEs (DropSens, DRP110, Spain) as a control. As illustrated in Figure 3A, the electrochemical properties of self-made SPEs were inferior to DS electrodes. However, compared with SPEs on PET-B, SPEs screen-printed on PET-A and plasma treated PET-A possessed better performance, as shown in Figure 3B-C. Additionally, in terms of the oxidation peak current density and peak to peak separation, there was no significant difference between SPEs printed on PET-A and PET-A+plasma, elucidating that plasma treatment could not obviously improve the electrochemical performance of SPEs on PET-A. In order to further investigate the attachment results of carbon pastes on PET films, the morphology of the edges and surface planeness of carbon electrodes and were observed. As displayed in Figure 3D, an enlargement at the edge of SPEs on PET-A occurred more obviously than that of SPEs on PET-B. Moreover, there was a better surface planeness for SPEs on PET-A compared to that on PET-B, further demonstrating that the suitable hydrophilicity of substrates was propitious to the adhesion of carbon pastes, leading to their excellent electrochemical performance. Therefore, it was concluded that PET-A with contact angle of 52.5° was chosen as printing substrate and SPEs printed on PET-A were provided with better electrochemical performance ($I_o=216.97\mu A$, $\Delta E_p=423.32mV$).

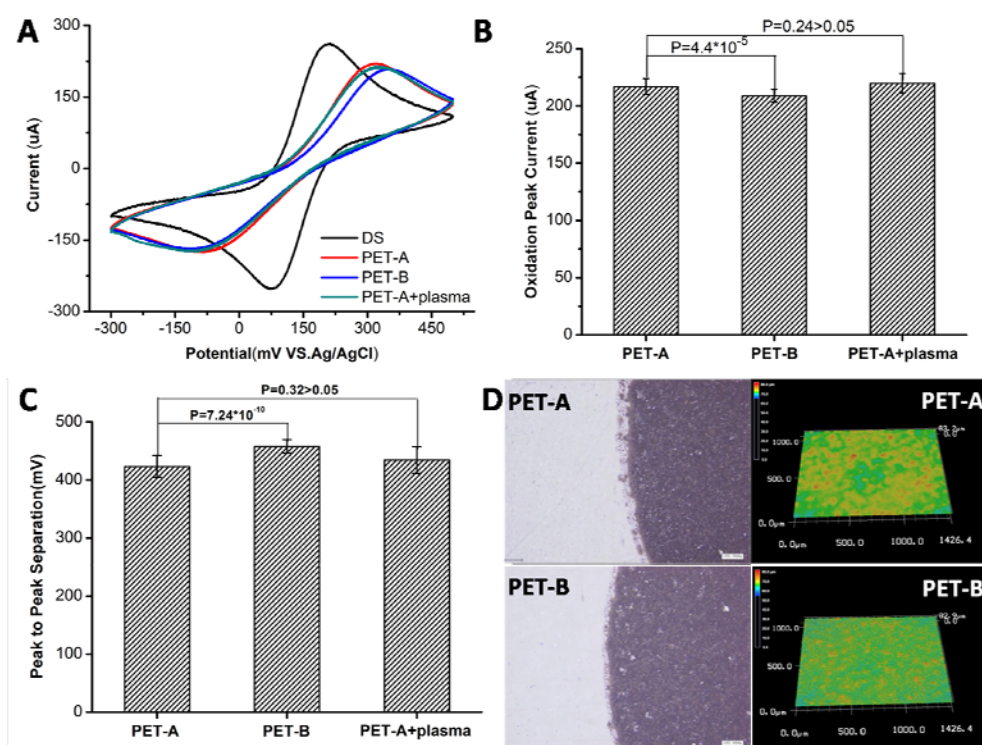


Figure 3. (A) Representative CVs of SPEs on PET-A, PET-B and plasma treated PET-A with comparison of DS electrodes; (B) oxidation peak current and (C) peak to peak separation of self-made SPEs (P is the probability value of F test statistics when significance level is $\alpha=0.05$); (D) surface flatness of carbon working electrode on PET-A and PET-B.

3.2. Effect of pretreating procedures to SPEs

In order to improve the adhesion ability of carbon inks on substrates, insulating polymers were usually added, which might increase the electron transfer resistance [10, 11]. The main purpose of pretreatment on SPEs was to remove insulating polymers and to increase surface roughness. It can be seen from Figure 4A, before chemical treatment, the electrochemical performance of self-made SPE was inferior to DS electrode ($I_o=199.01\mu A$, $\Delta E_p=341.40mV$). However, it was significantly improved after chemical treatment and superior to DS electrodes. Fresh SPEs were then treated with NaOH solution, denoting as SPE-A. Similarly, fresh SPEs were treated not only with NaOH solution but also with anodizing treatment, denoting as SPE-B. The CV curves of SPE-A and SPE-B were plotted in Figure 4B. Compared with non-treated SPE, the electrochemical response of SPE-A and SPE-B was dramatically enhanced. As shown in Figure 4C and 4D, the oxidation peak current of SPE-A and SPE-B was remarkably higher than that of fresh SPE. Additionally, the peak to peak separation of SPE-A and SPE-B was evidently lower than that of fresh SPE. The superior electrochemical behaviors of SPE-A and SPE-B may be ascribed to the removal of insulating organic binders on surfaces of working electrodes. However, after further anodization treatment, the performance of SPE-B was inferior to SPE-A with largest oxidation peak currents ($I_o=324.79\mu A$) and smallest peak to peak separation ($\Delta E_p=140.68mV$), which was contrary to the reported results [12]. It may be owing to the difference in carbon ink composition and in printing and curing conditions. Finally, the surfaces of working electrodes on SPE, SPE-A and SPE-B were observed by SEM (Figure 5), illustrating that the rough surface exposed more carbon particulates which improved the electrochemical performance of SPEs. It was concluded that alkaline treatment on working electrodes of SPEs could significantly increase the electron transfer and then enhance the sensitivity of SPE, without the need of anodization treatment.

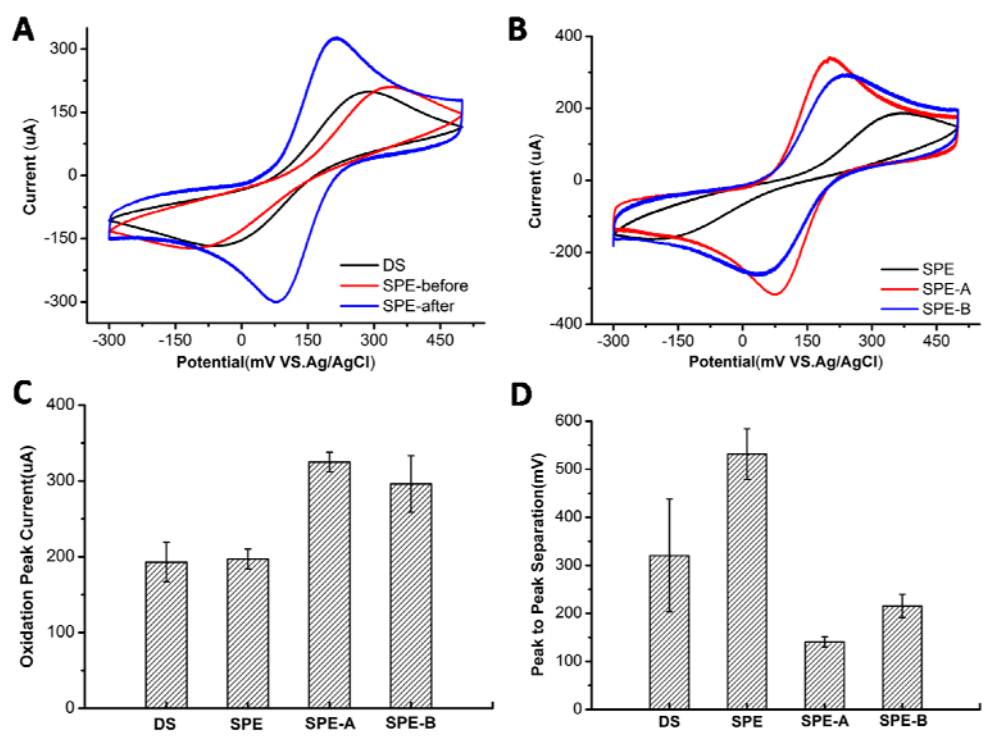


Figure 4. (A) Representative CVs of SPEs before and after chemical treatment with comparison of DS electrodes; (B) Representative CVs of fresh SPEs and SPEs suffering from different pretreating methods; (C) Oxidation peak current and (D) peak to peak separation of DS electrode, fresh SPEs and SPEs after pretreating with NaOH solution and/or anodizing treatment.

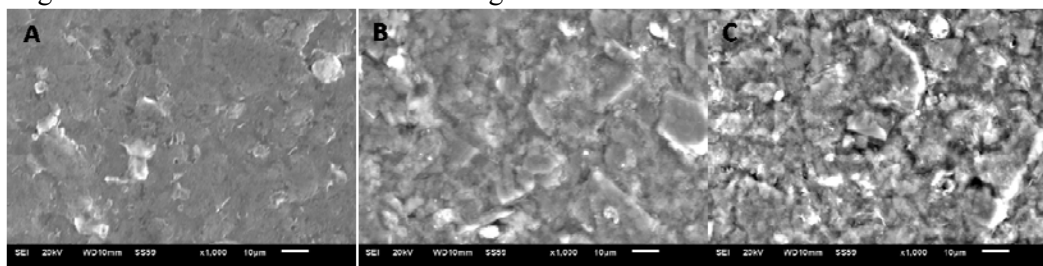


Figure 5. SEM images of working electrode surfaces of SPE (A), SPE-A (B) and SPE-B (C).

Whether increasing the times of alkaline treatment could further enhance the electrochemical performance of SPEs, the CVs of fresh SPEs and SPEs treated with different times were measured and illustrated in Figure 6A. It was demonstrated that, the peak current of treated SPEs increased obviously and the peak potential difference decreased slightly with increasing the corrosion times by 3M NaOH. Moreover, the square resistance of working electrodes exposed to alkaline solution for two times and three times decreased to $123.17 \Omega/\square$ and $95.67 \Omega/\square$, respectively, as shown in Figure 6B, which further confirm the results of CV curves in Figure 6A. However, we can observed from Figure 6C that there was a decline for carbon ink adhesion when the working electrode was treated by NaOH solution at the third time. Therefore, the optimal condition of pretreating procedure is that, fresh SPEs were alternately treated with chemical treatment and high temperature curing for two times, the oxidation peak currents of which is $407.65 \mu\text{A}$ and peak potential difference of which is 111.16 mV .

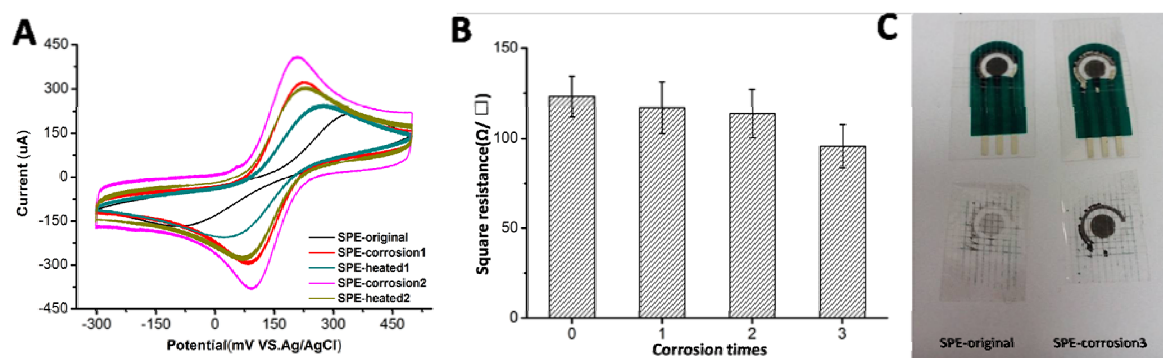


Figure 6. (A) CVs, (B) square resistance and (C) the result of 3M tape adhesion test of fresh SPEs and SPEs treated by alkaline solution for different times.

4. Conclusion

A new procedure for fabricating SPEs with excellent electrochemical behaviors was presented in this study. The SPEs printed on PET-A showed better performance than that on PET-B owing to the better hydrophilicity of PET-A than PET-B. When the SPEs were treated via the best condition, that is alternately treated with chemical treatment and high temperature curing for two times, the oxidation peak currents and peak potential difference of treated SPEs reached 407.65 μA and 111.16 mV, implying that the sensitivity and electron transfer rate improved 1.9 times and 3.8 times compared with fresh SPEs, and 2 times and 3 times compared with DS electrodes. Thus the obtained SPEs were stable, convenient and inexpensive, which could be extensively applied for developing novel electrochemical sensors.

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