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Enhancement of electrochemical properties of screen-printed carbon electrodes by oxygen plasma treatment

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ABSTRACT

Plasma treatment is frequently used to clean and modify the surface of materials, including polymers and graphite. However, very limited information has been reported concerning the modification of a matrix, such as a screen-printed carbon electrode (SPCE) which is consisted of a mixture of graphite and pasting binder, using plasma. In this study, the surface characteristics and electrochemical properties of the plasma-treated SPCEs were investigated. The plasma-treated SPCEs performed a good electrochemical response (enhanced about 80-fold compared with those untreated electrode) and exhibited good reproducibility (CV of 4.8%). The response of plasma-treated electrodes was comparable with the electrodes modified with noble metal and superior to those electrode modified with carbon nanotube (CNT) (ca. 20-fold). SEM imaging revealed that an effective decomposition or removal of impurities and pasting binder on the surface of SPCEs during oxygen plasma treatment. The plasma treatment increases the step-like defects on the surfaces of graphite particles resulting in the generation of numerous edge planes. The phenomena could be responsible for the improvement of the electrochemical properties of SPCEs. The results also suggest that the plasma treatment condition is important. Over-erosion on the SPCE surface by high powered plasma may lead to the poor reproducibility of the SPCEs.

1. Introduction

Screen-printed carbon electrodes (SPCEs) are widely used in the fabrication of "one-shot" commercial biosensors for onsite biomedical diagnosis and industrial applications [1–6]. SPCEs, consisting of a matrix of graphite powder and an organic binder, are inexpensive, compact in size and easily prepared [2,7]. Compared with conventional electrodes, SPCEs exhibit higher conductivity and low background current due to their rough and porous structure that generates a large surface area [8,9]. Furthermore, SPCEs can be easily adapted by the process of mass production of simple portable devices [2,7,10,11].

Although SPCEs exhibit many attractive properties, they are insensitive to certain important analytes due to the low rate of electron transfer [12,13]. Thus, electroactive species in the samples can easily interfere with SPCE-based biosensors [14]. Hence, the application of SPCEs in the fabrication of commercial biosensors for analytes in blood other than glucose, such as cholesterol, lactate, urea, creatinine, uric acid, hemoglobin, and aspartate aminotransferase (AST)/alanine aminotransferase (ALT), is often limited. The surface of commercialized SPCEs is largely covered by organic oil, pasting binder and/or other pollutants as revealed by their hydrophobic characteristics. Thus, the access of analytes to an SPCE electrode from a bulk solution can be interfered with by this hydrophobic surface. Several methods are employed to try to improve the electrochemical properties and sensitivity of carbon-based electrodes, including pre-anodization, electrochemical cycling, metal-dispersion and electrochemical metallization [6,15–18]. However, these methods may not be suitable for mass production of biosensors, because a "wet process" or "expensive admixture" is usually involved in their manufacturing. Plasma is a partially ionized gas comprised of electrons, ions and neutral atoms or molecules. Plasma is capable of both mechanical work, through the ablative effect of kinetic transfer of electrons and ions with the surface, and chemical work, through the interaction of reactive radical species with the surface. Hence, plasma treatment may cause physical and/or chemical changes near surface of a material. The properties of the remaining bulk, however, are still maintained during the process of plasma treatment. Plasma treatment has many advantages over other technologies for surface modification, such as requiring few reagents, low environmental pollution, suitability for many materials, and near-ambient procedural temperatures. Plasma treatment is frequently used to clean and modify the surfaces of materials, including polymers [3], platinum [19], graphite

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[20], glassy carbon [21,22], carbon black [23,24] and glass [25]. Recently, inert gas argon plasma was also used to clean the SPCE [26,27]. The electrochemical property of SPCE was reported to be enhanced by the treatment. In this study, the oxygen plasma was used to treat the SPCE. Oxygen plasma can not only to clean the surface of SPCE, but also adding oxygenated functionalities to it surface [23]. The surface characteristics of SPCEs before and after oxygen plasma treatment were studied by light and electron micrography and contact angle measurements. The electrochemical properties and reproducibility of the SPCEs were also investigated. This work shows that plasma treatment is a simple and effective method to substantially improve the sensitivity and electrochemical properties of SPCEs.

2. Materials and methods

2.1. Materials

The SPCEs were obtained from ApexBichem (Hsinchu, Taiwan) which consisting of two carbon strip electrodes. The SPCE has a rectangular form working and counter electrodes with surface diameter of 4.8 mm^2 and both printed using heat curing carbon composite inks. These strips are printed onto a plastic substrate and an insulating layer serves to delimit a working area and electric contacts. Ink formulation and production characteristics of commercial SPCEs are regarded by the manufacturers as proprietary information. The assay buffer was 1× phosphate buffer saline (PBS). Hydrogen peroxide (30%), catechol, dopamine and ferricyanide were obtained from Sigma (St. Louis, MO, USA). Other chemicals used were analytical grade. All of the solutions were prepared with deionized distilled water (d.d. H_2O).

2.2. Oxygen plasma treatment

Oxygen plasma treatment was performed in a 13.56-MHz radio frequency (RF) plasma reactor designed by Branchy Technology Co. Ltd. (Tao-Yuan, Taiwan). The reactor was first evacuated to a base pressure of less than 10^{-3} Pa before the plasma gas was introduced. All of the procedures were performed at room temperature.

The SPCE was placed in the center of the reactor and exposed to O_2 plasma in the RF plasma reactor at a constant system pressure of 13 Pa at a flow rate of 10 m/s. The oxygen plasma treatment of the SPCE was performed at 100, 200 and 300 W of plasma power for a period of 5, 10, 15, 20 and 25 min.

2.3. Apparatus

A video-based optical contact angle measuring device (OAC 15, DataPhysics, GmbH, Germany) was used to measure the contact angle of the SPCE before and after plasma treatment. The static contact angle was determined based on the sessile drop method. A video system with an adaptor and CCD camera was used to capture the side image of the water drops. Signals from the CCD camera were coupled to a personal computer (with a 1.8-GHz Pentium processor) using a high performance video digitizing board. Distilled water droplets were dropped on the surfaces of SPCEs with or without plasma treatment. The images of the water drops were captured by the CCD camera. The contact angle between the tangential line at the surface contacting point of a hemispherical droplet and a line parallel to the surface was determined. Scanning electron micrographs were obtained using a Hitachi S-4200 microscope. The surface characteristics of the SPCEs were also analyzed using an Olympus reflective light microscope. Chemical compositions on the surface of the SPCEs were analyzed by Fourier transform infrared spectroscopy (FTIR).

2.4. Electrochemical measurement

Cyclic voltammetric and amperometric measurements were performed using an electrochemical analyzer (model CHI 440, West Lafayette, IN, USA). All experiments were performed using a conventional three-electrode system, with the enzyme electrode as the working electrode and a standard platinum electrode as the counter electrode. An Ag/AgCl electrode was used as the reference electrode. Input and output signals from the potentiostat were coupled to the personal computer (1.8 GHz Pentium microprocessor). The cyclic voltammetric measurements of electrodes were performed in a phosphate buffer (100 mM, pH 7.0) without stirring. The scan rate for cyclic voltammetry was 50 mV/s. The amperometric measurements were performed by adding 0.1 mL of hydrogen peroxide into a cylindrical cell containing 9.9 mL of PBS buffer (pH 7.0) under a fixed potential of 0.5 V vs. the Ag/AgCl electrode. Unless otherwise stated, all experiments were performed at 37 °C. The baseline current must be achieved prior to injection of the test solution. Magnetic stirring during the operation was used to ensure the homogeneity of the solution. The difference between the baseline and the steady-state current was designated as the response current.

3. Results and discussion

3.1. Effect of oxygen plasma on the properties of SPCE

3.1.1. Enhance the electrochemical response by oxygen plasma

The surface of commercialized SPCEs is known to be largely covered by organic oil and pasting binder or other pollutants. This interferes with, the access of analytes to the electrode from bulk solution. In this study we attempted to improve the electrochemical properties of commercially available SPCEs by oxygen plasma treatment. SPCEs were treated with oxygen plasma at different powers,

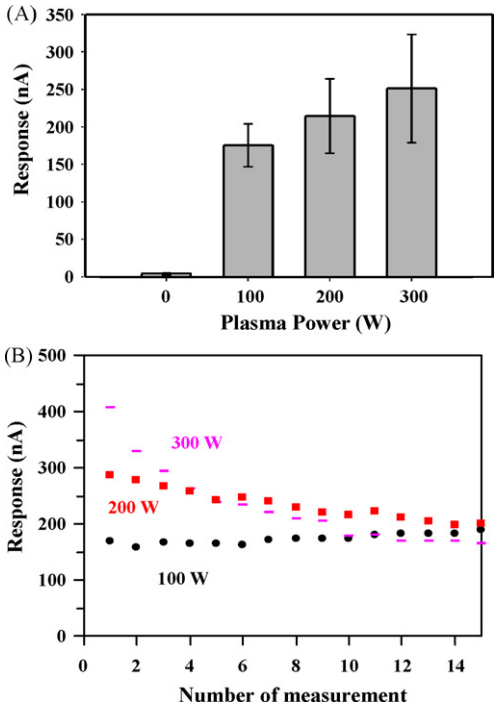

Fig. 1. Effect of oxygen plasma in improving the electrocatalytic activity of SPCE. (A) Effect of the power of plasma to the electrochemical response of SPCE. Each data is presented as the mean ± S.D. (B) Repeated measurements of 1 mM H_2O_2 by SPCEs treated with oxygen plasma of different powers. The treatment of SPCE by oxygen plasma was carried out at the powers of 100, 200 and 300 W for 10 min. The working potential of electrochemical reactions was set at 0.5 V vs. Ag/AgCl.

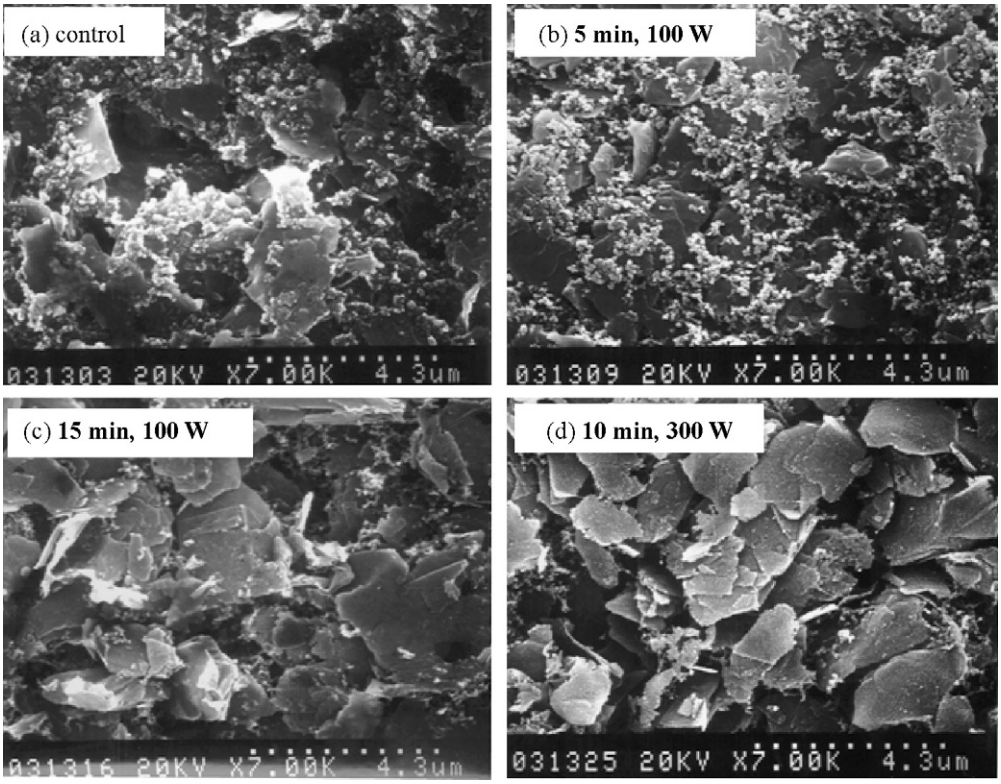

Fig. 2. Scanning electron micrographs of SPCEs. SPCEs were untreated (A), treated with 100 W oxygen plasma-treated SPCE for 5 min (B) and 15 min (C) and treated with 300 W oxygen plasma for 10 min (D) prior to the SEM analysis. Magnification power of images is 7000×.

including 100, 200 and 300 W, at pressures of 13 Pa for 10 min. As shown in Fig. 1A, SPCEs modified with oxygen plasma exhibited 40–57-fold higher electrochemical responses than unmodified SPCEs. Modification of SPCEs with oxygen plasma treatment at powers of 100, 200 and 300 W markedly increased the oxidative current to about 175.5 ± 28.6, 214.5 ± 49.7 and 251.3 ± 72.2 nA/mM of H_2O_2, compared to only 4.4 ± 1.0 nA/mM of H_2O_2 for an untreated SPCE. These results indicate that oxygen plasma improved the electrocatalytic properties of SPCEs. Although oxygen plasma treatment at 200 and 300 W yielded higher electrochemical responses than at 100 W, these high plasma power treated SPCEs had unstable electrochemical responses during repetitive measurements (Fig. 1B) as suggested by a high coefficient of variation (CV) of 16%. This was attributed to over-erosion on the SPCE surface by high powered plasma [28], as was revealed by scanning electronic microscopy (SEM) evidence of a rugged surface (Fig. 2D). By contrast, the responses of SPCEs treated with oxygen plasma at 100 W remained stable throughout testing. The effect of plasma treatment time on the electrocatalytic activity of the SPCEs was further studied by treatment with oxygen plasma at 100 W for various times (0–25 min). The electrochemical response increased sharply after treatment with oxygen plasma for 5–15 min, then reached a plateau after oxygen plasma treatment for 20 min. After oxygen plasma treatment at 100 W for 20 min, the SPCEs exhibited an electrochemical response of 333.7 ± 16 nA/mM H_2O_2. Compared to untreated SPCEs, the electrochemical responses of the plasma-treated SPCEs were enhanced 72.5-fold (Table 1). The long-term stability of this optimized SPCE was also studied. When the sensors were stored in a dry state, no apparent change in the response was found during a storage period of 45 days (data not shown).

3.1.2. Enhance the electron transfer rate by oxygen plasma

Oxygen plasma not only improves the electrocatalytic activity of SPCEs to H_2O_2 as described above but also improves the electrochemical properties of SPCEs. The electron transfer kinetics of the plasma-treated SPCEs were investigated by measuring the cyclic voltammetric behavior of three benchmark redox systems, including ferricyanide, catechol and dopamine. The improvement of the electrochemical properties of SPCEs was justified by reduction

Table 1
Effects of plasma treatment and electrochemical treatment on the electrochemical reactivity of the SPCEs to H_2O_2. The oxygen plasma was carried out under a power of 100 W for various times. The experiment was carried out at room temperature in a phosphate buffer (100 mM, pH 7.0) containing 1 mM H_2O_2. The working potential was 0.5 V vs. Ag/AgCl.

Treating time	Electrochemical[a]			Oxygen plasma[b]		
	Response (nA) (mean ± S.D.)	CV (%)	Folds	Response (nA) (mean ± S.D.)	CV (%)	Folds
Untreated	4.60 ± 1.04	22.6		4.07 ± 0.88	21.62	
5 min	24.94 ± 1.65	6.6	2.4	81.9 ± 16.6	20.3	17.8
10 min	25.56 ± 5.16	20.2	5.6	159.0 ± 29.6	18.6	34.6
15 min	49.81 ± 4.46	8.9	10.8	352.3 ± 10.5	3.0	76.6
20 min	84.98 ± 9.59	11.3	18.5	333.7 ± 16.0	4.8	72.5
25 min	76.74 ± 9.59	8.6	16.7	382.0 ± 54.5	15.8	83.0

[a] The electrochemical pre-treatment was proceeded in the saturated Na_2CO_3 solution at 1.2 V for various times.
[b] The data represent the average valves of three measurements from the same electrode.

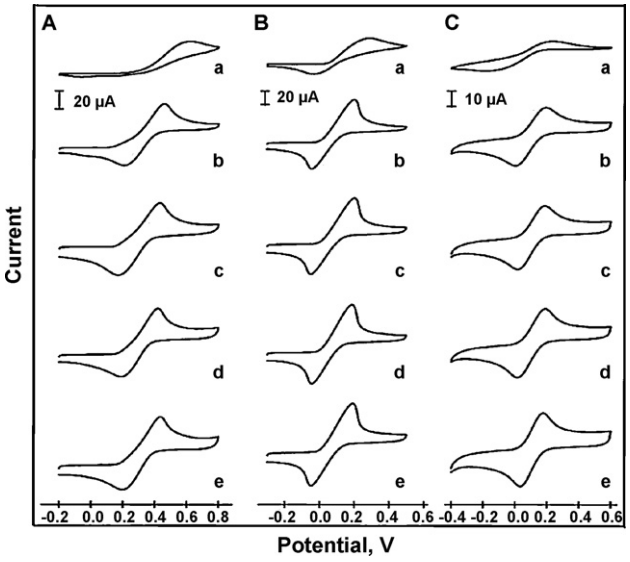

Fig. 3. Cyclic voltammogram of catechol, dopamine and ferricyanide on SPCEs before and after the treatment of oxygen plasma. Cyclic voltammetric behaviors of 4×10^{-4} M catechol (A), 1×10^{-3} M dopamine (B) and 5×10^{-5} M ferricyanide (C) on SPCEs before (a) and after the treatment of oxygen plasma (b–e). The oxygen plasma treatment of the SPCE was performed at 100 W for 0 (a), 5 (b), 10 (c), 15 (d) and 20 min (e). The scan rate of the potential was 50 mV/s; supporting electrolyte, 50 mM phosphate buffer, pH 7.4.

of peak-to-peak potential separation (ΔE_p), separation between oxidative (E_{pa}) and reductive peak potentials (E_{pc}), and approaching the approximate unit of peak currents ($I_{ox}/I_{re} \sim 1$) for redox compounds. As demonstrated in Fig. 3, the plasma-treated and untreated SPCEs exhibited markedly different cyclic voltammograms for the selected benchmark redox compounds. The untreated SPCEs only exhibited clear redox peaks to dopamine and ferricyanide, yielding ΔE_p values of 331 and 440 mV, respectively, at a 50 mV/s scan rate. Interestingly, the ΔE_p of dopamine and ferricyanide on SPCEs was reduced to 232 and 156 mV, respectively, after oxygen plasma treatment. Nonetheless, marked improvements in other parameters of electrochemical kinetics of plasma-treated SPCEs was observed, including larger peak currents and lower anodic peak potentials and approximating unit peak current ratios (I_{ox}/I_{re}) for all three redox compounds. Although catechol also exhibited separated oxidative and reductive peaks, its reductive current (2.93 μA) was unstable, with a RSD of 80%. However, an apparent electrochemically reductive peak of catechol appeared on oxygen plasma-treated SPCEs (Fig. 3). The I_{ox} values of SPCEs before and after treatment with oxygen plasma at 100 W for 0–20 min for catechol, dopamine and ferricyanide increased significantly from 40.4 ± 4.0 to 51.4 ± 2.0 μA for catechol, from 38.5 ± 1.6 to 71.7 ± 2.1 μA for dopamine and from 6.35 ± 0.32 to 22.7 ± 0.8 μA for ferricyanide. The over-potential that triggered the oxidative reactions of the redox compounds to SPCEs treated with oxygen plasma at 100 W for 0–20 min markedly decreased from 618 to 421 mV for catechol, from 274 to 185 mV for dopamine and from 267 to 181 mV for ferricyanide. Therefore, the ΔE_p values for the benchmark redox compounds greatly improved from 665 to 233 mV for catechol, from 331 to 232 mV for dopamine and from 440 to 156 mV for ferricyanide. Moreover, the ratios of peak currents (I_{ox}/I_{re}) for all three benchmark compounds significantly approached 1, a characteristic of a reversible reaction on the surface of the electrode. These results indicate that the rate of electron transfer between the surface of the electrode and the redox couples significantly improved with oxygen plasma treatment at 100 W for 5 min.

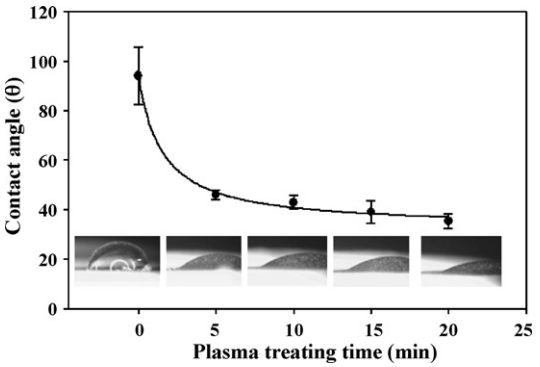

Fig. 4. Effect of oxygen plasma treatment on the surface properties of SPCEs. The water contact angle (θ) of the SPCE after plasma modification was studied. The oxygen plasma treatment of the SPCE was performed at 100 W for 0, 5, 10, 15, 20 and 25 min, respectively.

3.1.3. *The hydrophilicity of SPCE was enhanced by the oxygen plasma*

The surface of commercialized SPCEs is largely covered by organic oil and other pollutants as revealed by its hydrophobic nature. The hydrophobic properties of the pollutants interfere with access of the analytes to the surface of the electrode. The enhancement of electron transfer rates by oxygen plasma treatment of SPCEs is due to the removal of surface contaminants [29,30]. Thus, the hydrophilic surface of an SPCE facilitates the diffusion of analytes to it from a bulk solution [24], thereby improving the electrochemical properties and response. In this study, the contact angle (θ) of a water droplet, which is defined as an angle between the tangential line of a hemispherical droplet at the surface contacting point and a line parallel to the surface, was studied on treated and untreated SPCEs to characterize the effect of plasma treatment on surface hydrophilicity [6]. The shape of a water droplet was round on the untreated SPCE with a contact angle of approximately 90° (Fig. 4). The contact angle was reduced to 43° after treatment of the electrode with oxygen plasma during initial 5 min (CV = 2%, $n = 5$). Afterward, the water contact angle decreased gradually in a time-dependent manner during the treatment period (5–20 min). The water contact angle was 43 (CV = 2.6%, $n = 5$), 39 (CV = 4.6%, $n = 5$) and 35.3 (CV = 2.9%, $n = 5$) at plasma treating of 5, 10 and 15 and 20 min, respectively. Electrochemical treatment also reduced the water contact angle but only to around 65° [6]. Oxygen plasma treatment was superior to electrochemical treatment in improving the hydrophilicity of the electrode. The superior hydrophilic properties provided by plasma treatment compared to electrochemical treatment can be explained by the formation of step-like defect sites on the surface of SPCEs. The effects of oxygen plasma treatment on the surface of SPCEs can lead to cracks and/or the forming of surface roughness of the adherent graphite particles (Fig. 2D), thereby improving the hydrophilicity of the electrode. By contrast, electrochemical treatment only removes contaminants [31] and forms oxygenated functionalities on the electrode surface [6,8,9,20,23,32–34]. Cascarini de Torre, et al. [20] further evidence for the occurrence of cracks on the SPCEs during oxygen plasma treatment which led to the improvement of hydrophilic properties. They applied oxygen plasma to treat carbon black for 30 min. Due to the spherical morphology of carbon black and the lack of pasting binder on the surface of electrode, the oxygen plasma can smoothly peel-off the outer layer of these particles which were shown to have no porosity. The water contact angle of carbon black was reduced to around 60° after treating the electrode with oxygen plasma. The results showed that the contact angle of carbon black was the same as that of electrochemically treated SPCEs but worse than those of plasma-treated SPCEs. These

findings demonstrate that the better hydrophilicity of plasma treated than electrochemically treated SPCEs and carbon black can be explained by the removal of pasting binder and the forming of defect sites on the surface of SPCEs by oxygen plasma.

3.2. Studied on the surface characteristics of the plasma-treated SPCE

Previous studies have shown that some chemical and physical properties of SPCE were improved by oxygen plasma treatment. Hence, the surface characteristics of oxygen plasma-treated SPCE was investigated by both FTIR and SEM. Results show that the exposure of oxygen plasma could induce some chemical and physical change on the surface of SPCE, thereby the electrochemical properties and hydrophilic properties were enhanced. From FTIR (Fig. 5), we believe that some oxygenated functionalities was form after the oxygen plasma treatment. From SEM, some loose lumped particles were removed and some step-like defect was form on the surface of SPCE after exposing to oxygen plasma, thereafter edge planes were exposed.

3.2.1. Formation of oxygenated functionalities on the surface of SPCE

FTIR has been used widely to study the functionalities on the surface of various materials. As shown in Fig. 3, a small band at 1740 cm^{-1} (carbonyl group vibration) was observed for the untreated SPCE, suggesting the existence of small amounts of oxygenated functionalities on the surface of SPCEs before oxygen plasma treatment (Fig. 5). This band was enhanced after exposing the SPCE to oxygen plasma. The oxygen plasma also resulted in the formation of a new band at 865.7 cm^{-1}, a representative of epoxide, on the surface of SPCEs. This result was in agree with previous reported which described that oxygenated functionalities, such as C=O, O–C–O and O–C=O, may form on graphite after treatment with oxygen plasma [20,23,34]. The formation of oxygenated functionalities may contribute to the increase in electrochemical activity of carbon black [6,35,36]. However, the chemical properties of surface of SPCE can be further studied by X-ray photoelectron spectroscopy (XPS), which may help to elucidate the influence of treating time on the chemical composition of the SPCE after oxygen plasma treatment.

3.2.2. Altering of surface topology of SPCE by oxygen plasma

The surface topology of SPCEs before and after oxygen plasma treatment was investigated by SEM. We used SEM analysis to monitor the effect of oxygen plasma on the surface components of an SPCE, including organic oil, plastic binder, graphite particles and other additives. It was postulated that these surface impurities would be trimmed away by oxygen plasma treatment. SEM with a magnification of 7000× was performed on an untreated SPCE, an SPCE treated with oxygen plasma at 100 W for 5 and 15 min and another SPCE treated with oxygen plasma at 300 W for 10 min (Fig. 2). The SEM images showed that the surface of the untreated SPCE was covered with substances which were assumed to comprise the pasting binder, organic oil and other additives (Fig. 2A). However, oxygen plasma treatment at 100 W for 5 or 15 min resulted in visible removal or decomposition of these substances exposing the originally covered graphite particles on the surface (Fig. 2B and C). A similar surface topology of an SPCE treated with oxygen plasma at 300 W for 10 min was also observed (Fig. 2D). During oxygen plasma treatment, the SPCE surface may be bombarded physically and chemically by the ion, oxygen electrons and free radicals in plasma. The bombardment causes decomposing and oxidation of the surface resulting in the formation of oxygen rich functional groups and the generation of heat on the surface. The surface paste binder, organic oil and other impurities may be burned off and expose the original covered graphite particles. The two major microstructures could be clearly seen on the exposed graphite particles of SPCE: the basal plane and the edge plane [37–39]. The basal plane is a hexagonal surface that is parallel to the graphite layer, while the edge plane is the site perpendicular to the graphite layer and shows faster electron transfer kinetics than the basal plane. However, the lumped particle may cover the surface, especially the edge planes, of graphite particles and forms a barrier to electron transfer between the graphite and redox couples. This may partially explain the slow electron transfer kinetics for the untreated SPCEs in this study. It is postulated that the removal of surface covering material on the surface of SPCEs may expose the

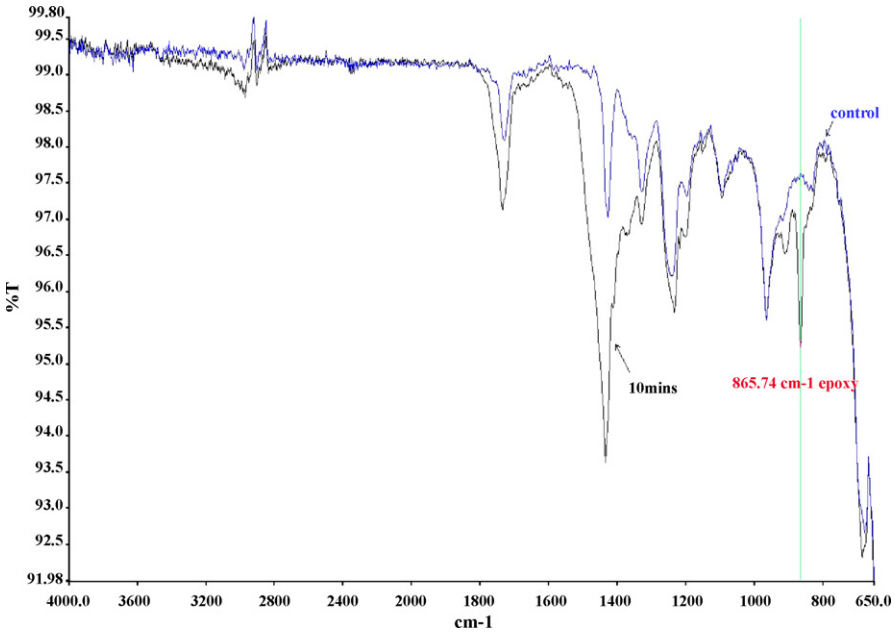

Fig. 5. Effect of oxygen plasma treatment on the formation of oxygenated functionalities of SPCE.

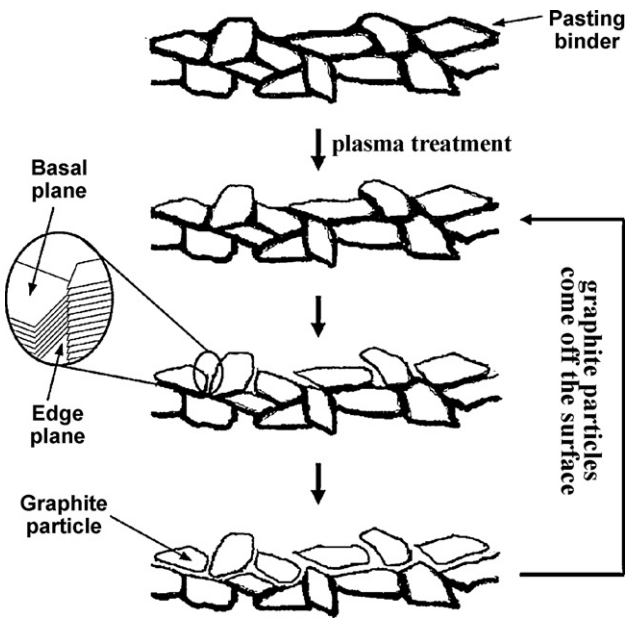

Fig. 6. Hypothetical model for the treatment of SPCEs by oxygen plasma. Plastic binder can be removed by oxygen plasma treatment, exposing the edge planes of the graphite particles. Prolonged oxygen plasma treatment could loosen and released graphite particles on the surface of the SPCE.

graphite particle and hence their edge planes (Fig. 6), thereafter more oxygenated functionalities forming on new exposure edge. A similar result was also observed on the inert argon plasma-treated SPCE [26,27]. Argon plasma was proposed to etch of contaminants without causing the chemical reaction or oxidation on the surface of the electrode. We postulated that the enlargement of surface area and the exposure of the graphite edge due to the oxygen plasma treatment may contribute to the enhancement of the electrochemical response and properties of the oxygen plasma-treated SPCE.

By contrast, over treatment with oxygen plasma may lead to over-etching, causing reduced stability of the thick-film structure (Fig. 2). Accordingly, SPCE may exhibit inconsistency and low reproducibility in electrochemical responses to analyte (Table 1).

In addition to removing surface lumped particle, the presence of step-like defects on the graphite particle were also observed (Fig. 2C and D). The step-like defects were not seen on the graphite particle of the untreated SPCE, suggesting the capability of oxygen plasma in generating surface defect on the exposed graphite particles (Fig. 2B). This result is consistent with the findings of Bourelle and colleagues that oxygen plasma treatment may cause defects in the basal plane of graphite particles [40,41]. The defects on the graphite surface may provide numerous edge planes, which have been suggested to be the electrochemically active sites on the graphite particles [37,38,42,43].

3.3. Comparison of SPCE response with oxygen plasma treatment vs. other modification methods

SPCEs were electrochemically activated in a saturated Na_2CO_3 solution at 1.2 V for various times (5–25 min). The electrochemically treated SPCEs exhibited a time-dependent enhancement of electrochemical responses to H_2O_2 from 4.60 ± 1.04 nA/mM H_2O_2 (untreated electrode) to 84.98 ± 9.59 nA/mM H_2O_2 (electrochemical treatment for 20 min). Under the optimal condition, the electrochemical pre-treatment enhanced the responses of SPCEs by about 20-fold. The enhancement of electrochemical response to H_2O_2 may be due to the enhancement of electron transfer rate of SPCEs [6,35,36]. In comparison, oxygen plasma-treated SPCE exhibits ca. 80-fold enhancement in the response to H_2O_2. Interestingly, the surface defects observed on the graphite particles of the plasma-treated SPCEs were totally absent in the saturated Na_2CO_3-treated SPCE. This finding may explain the much higher enhancement effect of oxygen plasma treatment than that electrochemical activation in saturated Na_2CO_3-treated SPCE.

Surface modification is widely used to improve the electrochemical properties and electrocatalytic activity of SPCEs [6,8,15,31,44–47]. The use of dispersing carbon nanotubes (CNTs) in carbon paste electrode (CPE) has been reported to improve the electrochemical response rate from 5- to 40-fold depending on the relative percentage of CNTs in the carbon paste [45–47]. The edge plane-like properties at the open end of the CNT support its electrochemical property-improving effect [38,39,48]. In this study, we demonstrated for the first time that oxygen plasma treatment has great potential for enhancing the electrochemical properties and electrocatalytic activity of commercial SPCEs. The maximum electrochemical response enhancement is up to 80-fold, with good reproducibility. These findings indicate that plasma treatment is superior to CNT modification for improving the electrochemical characteristics of carbon paste electrodes.

The response of plasma-treated electrode was comparable to those of electrodes modified with noble metal (123-167X) in a previous study [47]. Although electrochemical metallization by noble metals, such as platinum and lead, greatly enhances the electrocatalytic activity of an SPCE, oxygen plasma treatment provides a variety of advantages over conventional electrochemical metallization including: (1) carbon inks are relatively inexpensive compared to noble metal and/or carbon nanotubes. (2) Oxygen plasma treatment is performed in the dry state, without hazardous waste and the need for liquid disposal. (3) The development of continuous plasma equipment has made plasma modification methods more suitable for mass production of electrodes. (4) Plasma can easily penetrate small areas within surfaces. There are no surface tension restrictions that prevent aqueous cleaners from getting into small holes. In this study we found additional advantages of the oxygen plasma-treated SPCEs including good reproducibility (CV of 4.6%) and remarkable long-term stability in storage. By contrast, the response of metallized electrodes decreased by 90% after 4 days storage.

4. Conclusions

We studied a simple and effective method to improve the electrochemical properties and the sensitivity of commercially available SPCEs. The electrochemical responses of SPCEs to H_2O_2 were markedly increased by oxygen plasma treatment in a time-dependent manner. The electrochemical response of SPCEs to H_2O_2 was enhanced up to ca. 80-fold by oxygen plasma treatment. Removal of surface impurities by oxygen plasma, including organic oil and pasting binder or other pollutants, is postulated to improve the surface hydrophilicity and electron transfer rates of SPCEs. SEM images shows that the oxygen plasma treatment not only removed the surface impurities and increased the surface oxygen functionalities, but also caused step-like defects on the basal planes of the graphite particles within it (Fig. 2C and D). The defects on the basal plane of the graphite particles provided numerous edge planes, which exhibit fast electrochemical kinetics. Although the removal of surface impurities and the pasting binder on the surface helps to improve the reproducibility of treated SPCE, optimal conditions for oxygen plasma treatment are required. Under the optimal condition (oxygen plasma; 13 Pa; and 100 W; 20 min), the reproducibility of SPCEs was improved significantly, with a CV of 4.6% for the measurement of 1 mM H_2O_2. Oxygen plasma treatment of SPCEs also greatly improved their surface hydrophilicity, which facilitated the

diffusion of substance to the surface of the SPCE. After oxygen plasma treatment, the electron transfer rates of the SPCEs were also markedly improved, as indicated by the reduction of peak-to-peak potential separation (ΔE_p) of benchmark redox systems, such as ferricyanide and dopamine.

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