Fabrication and electrochemical properties of free-standing single-walled carbon nanotube film electrodes*

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An easily manipulative approach was presented to fabricate electrodes using free-standing single-walled carbon nanotube (SWCNT) films grown directly by chemical vapor deposition. Electrochemical properties of the electrodes were investigated. In comparison with the post-deposited SWCNT papers, the directly grown SWCNT film electrodes manifested enhanced electrochemical properties and sensitivity of sensors as well as excellent electrocatalytic activities. A transition from macroelectrode to nanoelectrode behaviours was observed with the increase of scan rate. The heat treatment of the SWCNT film electrodes increased the current signals of electrochemical analyser and background current, because the heat-treatment of the SWCNTs in air could create more oxide defects on the walls of the SWCNTs and make the surfaces of SWCNTs more hydrophilic. The excellent electrochemical properties of the directly grown and heat-treated free-standing SWCNT film electrodes show the potentials in biological and electrocatalytic applications.

Keywords: single-walled carbon nanotube, electrode, electrochemical properties, electrocatalytic activities

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1. Introduction

As a new kind of carbon materials, single-walled carbon nanotubes (SWCNTs) are different from other kinds of carbon-based materials frequently used in electrochemistry.[1,2] Due to their unique structure and electronic properties, SWCNTs are expected to manifest distinct electrochemical properties and to be of great potential for electrochemical and bioelectrochemical applications. Therefore, there has been increasing interest in using SWCNTs as electrodes and much attention has been paid to fabricating SWCNT-modified film electrodes.[3−7]

Most of SWCNT-modified film electrodes were prepared by depositing SWCNTs dispersed in solvents onto conducting solid substrates. A variety of methods have been proposed, such as layer-by-layer assembling,[8,9] electric-field-enhanced assembly,[10] magnetic-field enhanced assembly[11] and drop-drying method.[12−16] By these methods, however, uniform SWCNT films with high conductivity are not easy to be realized because of the aggregation among SWCNTs. Besides, the interferences from conducting substrates and the extra molecules used for suspending SWCNTs cannot be neglected in the electrochemical measurements. These interferences affect the investigation of the inherent electrochemical process and mechanism of SWCNT film electrodes.

Recently, a breakthrough in fabricating free-standing and highly conducting SWCNT films was made in our group by a floating chemical vapour deposition (F-CVD) method.[17] In this paper, we report an easily manipulative approach of processing the free-standing SWCNT films grown directly by F-CVD (denoted as d-SWCNT films hereafter), resolving the stickiness problem for fabricating electrochemical electrodes. The d-SWCNT film electrodes provide a possibility of investigating the inherent electrochemical properties of SWCNT film, since the aggregation of SWCNTs in solution and contamination of solvents such as surfactant used to obtain stable colloidal

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solutions are avoided. The electrochemical properties of d-SWCNT films, post-deposited SWCNT papers and heat-treated SWCNT films were investigated and compared. The electrodes based on free-standing SWCNT films are believed to be attractive for biological and electrocatalytic applications.

2. Experimental details

The free-standing SWCNT films were prepared by F-CVD method as reported previously.[17] Briefly, ferrocene/sulfur powder as catalyst source with a molar ratio of 16:1 was heated to 70 °C–80 °C, then the sublimed catalyst was carried by a mixture of flowing argon (1000 sccm) and methane (8 sccm) to the reaction zone in a quartz tube. The growth rate of the films was basically determined by the sublimation rate of the catalyst. The temperature of the quartz tube was set at 1100 °C. After 3 h, the quartz tube was cooled to room temperature in 50-sccm Ar atmosphere, and the SWCNT films were carefully peeled off from the wall of the quartz tube.

Heat-treatment of the d-SWCNT films was carried out in air at 420 °C for 3 h. The SWCNT papers were prepared by vacuum filtration method.[18] The SWCNTs used to prepare the SWCNT papers were synthesized by chemical vapour deposition (CVD), and CH_4 and Mo–Fe–MgO catalyst were used as carbon source and catalyst, respectively.

Cyclic voltammetry (CV) was performed on CHI 660C instrument (CHI Instruments) in phosphate-buffered solution (PBS, pH = 6.8±0.2) with potassium ferricyanide ($K_4[Fe(CN)_6]$). The d-SWCNT films, heat-treated SWCNT films and SWCNT papers were used as the working electrodes, respectively, and a Pt coil was used as the counter electrode. The potential was biased versus an Ag/AgCl electrode. The morphology and microstructures of SWCNT films were characterized by scanning electron microscopy (SEM, Hitachi S-5200) and transmission electron microscopy (TEM, JEOL JEM-2010).

3. Results and discussion

Figure 1(a) shows the optical image of a free-standing d-SWCNT film, the area of which reaches about 50 cm^2. The d-SWCNT film is porous as revealed by the SEM image (Fig. 1(b)), which is beneficial to the electrochemical performance of the SWCNT film electrodes. Figures 1(c) and 1(d) display the TEM images of the directly grown and the heat-treated d-SWCNTs films, respectively. As shown in Fig. 1(c), the walls of d-SWCNTs are clean and almost amorphous carbon free, which is also of benefit to improving the electrochemical properties of the SWCNT film electrodes.[19] Heat-treatment resulted in partial etching of the walls of the SWCNTs (Fig. 1(d)).

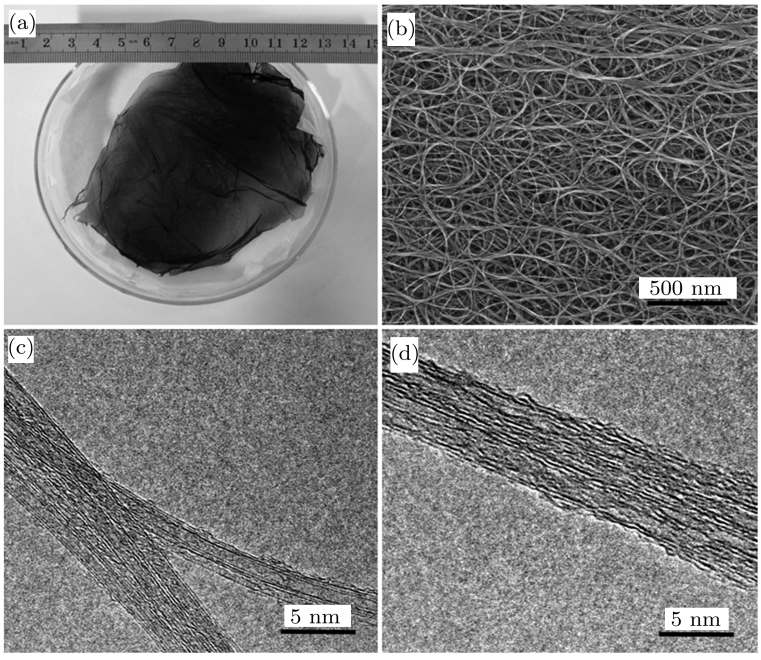


Fig. 1. (a) Optical and (b) SEM images of d-SWCNT film. TEM images of (c) d-SWCNT film and (d) heat-treated SWCNT films.

The clean surface and extremely high surface-to-volume ratio give rise to a strong self-adhesion of the d-SWCNT films, which makes it difficult to spread out the free-standing SWCNT films on substrates uniformly and inhibits practical applications of the d-SWCNT films. To overcome this problem, we applied an easy approach to process the d-SWCNT films. As shown in Fig. 2(a) schematically, the SWCNT film was first spread out onto a holder which has two layers with different diameters. Because of the serious stickiness of the films to the holder, some small wrinkles are usually formed and a uniformly spreading of the films is hard to realize. In order to remove the wrinkles, a "cap" was covered onto the holder with film. With the "cap" covering, the small wrinkles were diminished and finally the d-SWCNT film was perfectly spread out on the top-surface of the holder. Figure 2(b) schematically shows the film before and after the flattening process. When the "cap" was pushed down along the upper layer of the holder, the film was drawn down along with the "cap" on all sides and the small wrinkles were forced to flatten out, thus a flat SWCNT film was achieved on the top-surface of the holder. Benefiting from the excellent mechanical property of the d-SWCNT films, the proposed approach is a physical method that does not affect the surface of the film but eliminates the influence of the contamination of solvents on the electric properties of the SWCNT.

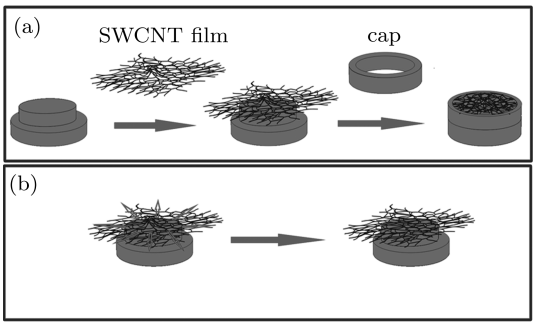


Fig. 2. Schematic diagrams of (a) the process of spreading out SWCNT films and (b) the film before and after flattening process.

Although it has been suggested that electron transfer may occur only at the ends or defect sites of SWCNTs,[6] evidence is emerging that directly synthesized SWCNTs show good characteristics as electrode material.[20,21] As a new type of SWCNT films, the free-standing and highly conducting SWCNT films are suitable for electrodes and are expected to exhibit good electrochemical properties. We have designed the d-SWCNT film electrodes to investigate the inherent electrochemical properties of SWCNT film. It is well known that the CVs of SWCNT film electrodes can be the superposition of two contributions: 1) background current due to the capacitance and 2) the redox current of potassium ferricyanide in phosphate-buffered solution (PBS). SWCNT films with large surface area have a large capacitance,[4] and the background currents typically scale with the area of the electrode.[21] Figure 3(a) shows the CVs of d-SWCNT film electrode in PBS normalized to the geometric surface area in the absence (dotted line) and presence (solid line) of 1 mM $K_4[Fe(CN)_6]$. As shown in Fig. 3(a), the background current corresponding to the capacitive charge/discharge of the electrical double-layer at the electrode/electrolyte interface is almost negligible with respect to the redox signals. A pair of well-defined peaks are observed corresponding to the redox reaction of $K_4[Fe(CN)_6]$. The separation of cathodic (I_{pc}) and anodic (I_{pa}) peaks is about 169 mV, which is larger than 60 mV for the ideal reversible one-electron-transfer reaction, and the intensities of the anodic and cathodic peaks are nearly equal, indicating that the electrochemical process on the d-SWCNT film electrodes is quasi-reversible. The redox current of the d-SWCNT film electrodes normalized to the geometric area of the electrode surface is larger than that of the SWCNT paper electrodes (Fig. 3(c)). It is noteworthy that the current intensity in CV measurement is approximately proportional to both the film thickness and the film area for the SWCNT film electrodes due to their porous property, so the volume instead of the geometric area of the SWCNT film should be considered in the analysis of CV.[22] The CVs of d-SWCNT film and SWCNT paper electrodes in PBS normalized to the geometric volume in the absence and presence of 1 mM $K_4[Fe(CN)_6]$ are shown in Figs. 3(b) and 3(d), respectively. The intensities of I_{pa} and I_{pc} for the d-SWCNT film electrodes are about 70 times larger than those for SWCNT papers, indicating that d-SWCNT films have much higher sensitivity as sensors. For SWCNT papers or SWCNT-modified electrodes, the surfaces of SWCNTs were coated by other molecules or conductive binder, which will reduce the porous size of the electrodes. In contrast, the surface of SWCNTs and bundles in d-SWCNT films is clean. Therefore, in d-SWCNT films, the diffusion of the electrolyte can access almost all available pores of the film electrodes and the penetration of electrolytic ions into the pores will be much deeper, leading to the high redox current peaks. Besides, the molecules or conductive binder coated on the surface of SWCNTs in the SWCNT papers or SWCNT-modified electrodes increase the intertube contact resistances between SWCNTs and reduce the sensing capability of the SWCNTs.

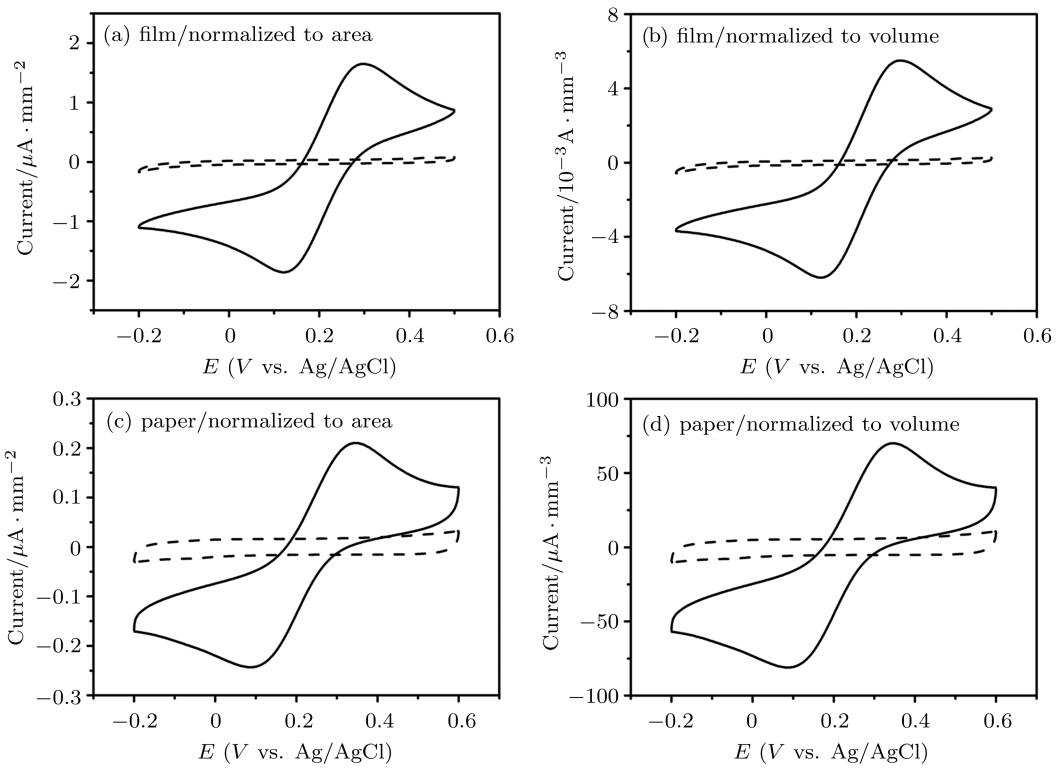


Fig. 3. The CVs of ((a) and (b)) d-SWCNT film and ((c) and (d)) SWCNT paper normalized to the geometric surface area ((a) and (c)) and volume ((b) and (d)) in the absence (dotted lines) and presence (solid lines) of 1.0 mM $K_4[Fe(CN)_6]$ in PBS; scan rate: 20 mV/s.

The voltammetric responses of d-SWCNT film electrodes in PBS with 1 mM $K_4[FeCN)_6]$ were investigated in a scan range of 5 mV/s–200 mV/s, as shown in Fig. 4(a). The peak-to-peak separation is increased with the increase of scan rates. As depicted in Fig. 4(b), the I_{pa} and I_{pc} are linear function of the square root of the scan rates at moderate scan rates (5 mV/s to 50 mV/s), which is similar to a solid macroelectrode rather than nanoelectrode ensembles.[22,23] But when the scan rate is higher more than 50 mV/s, the I_{pa} and I_{pc} deviates from the linear relationship. The deviation increases with the scan rate and the voltammograms begin to exhibit the behaviours of nanoelectrode. The reason for this transition from macroelectrode to nanoelectrode behaviours may be ascribed to the changes of overlapping diffusion layers with the increase of the scan rate.[21,24] As it is known, the extent to which the diffusion fields associated with neighbouring SWCNTs overlap plays an important role in the electrochemical response of the SWCNT film electrodes. Figure 5 shows the schematic diagram of the transition mechanism from macroelectrode to nanoelectrode behaviours of the d-SWCNT film electrodes. The diffusion layers originate from individual SWCNT or SWCNT bundle in SWCNT film electrodes. At low scan rate, the thickness of diffusion layers is much larger than the pore size of SWCNT films, thus the diffusion layers produced by individual SWCNT or bundle are heavily overlapped, resulting in a linear or close to linear diffusion of bulk redox species similar to a solid planar macroelectrode,[25] as shown in Fig. 5(a). With the increase of scan rate, the diffusion layer thickness will be reduced, so that the "overlapping" regions are shrunken,[24] as shown in Fig. 5(b). Finally the diffusion layer of individual SWCNT or bundle does not overlap with each other and the true radial diffusion dominates, as shown in Fig. 5(c). However, since the SWCNT bundles in the films form tangled network instead of a well-aligned network, the true nanoelectrode behaviours would not be observed in the SWCNT film electrodes. In other words, although transition from macroelectrode to nanoelectrode behaviours could be observed with the increase of the scan rate, the complete nanoelectrode behaviour would not be displayed for the SWCNT film electrodes.

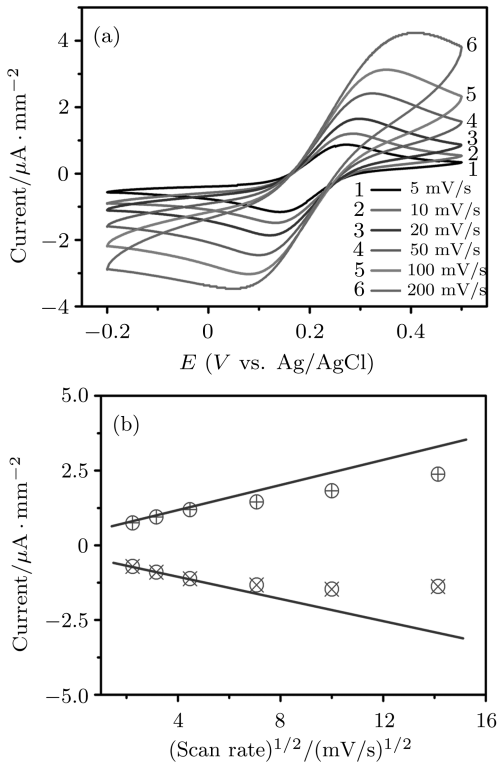


Fig. 4. (a) CVs for 1 mM $K_4Fe(CN)_6$ in PBS on d-SWCNT film electrode at different scan rates: 5, 10, 20, 50, 100, 200 mV/s. (b) The fitted anodic and cathodic current peaks of the CV versus the square root of the scan rate.

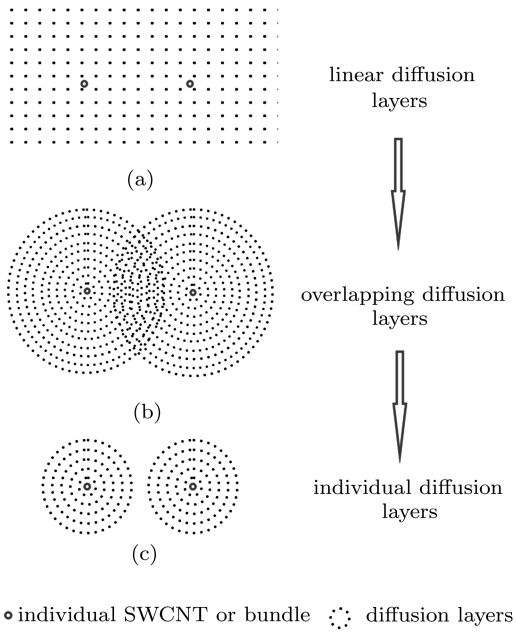


Fig. 5. Schematic diagram of the transition mechanism from macroelectrode to nanoelectrode behaviours in SWCNT film electrodes.

Furthermore, the capacitive background current increases much faster than the Faradaic current with the increase of the scan rate. It is difficult to fit the precise peak height at high scan rate (above 200 mV/s) due to the huge effective capacitance of SWCNT film electrodes. The peak separation also increases from 125 mV to 350 mV with the increase of the scan rate in the range of 5 mV/s to 200 mV/s, suggesting a quasi-reversible process likely as the result of the slow electron transfer in the SWCNT film and the slow diffusion through the narrow pores at high scan rate.

Figures 3(a) and 3(c) represent the CVs of d-SWCNT film and post-deposited SWCNT paper electrodes normalized to the geometric surface area in PBS with 1 mM $K_4Fe(CN)_6$) at 20 mV/s, respectively. The two well-defined redox peaks due to the Fe^{3+}/Fe^{2+} redox couple were observed in forward and reverse scans, respectively. The effective electroactive surface area of d-SWCNT film and post-deposited SWCNT paper can be estimated, respectively, according to the Randles–Sevcik equation:[26]

$$I_{\rm p} = 2.69 \times 10^5 A D^{1/2} n^{3/2} \gamma^{1/2} C,$$

where A is the electroactive surface area of the electrode (cm^2), D is the diffusion coefficient of the molecule in solution (cm^2/s), n is the number of electrons participating in the redox reaction, γ is the scan rate (V/s) and C is the concentration of the probe molecule in the bulk solution (mol/cm^3). The $Fe(CN)_6^{4-/3-}$ redox system used in this study is one of the most extensively studied redox couples in electrochemistry, and it exhibits a heterogeneous one-electron transfer ($n = 1$) and the diffusion coefficient (D) is 6.70×10^{-6} cm^2/s. When the scan rate γ is 20 mV/s and $K_4Fe(CN)_6$) concentration C is equal to 1 mM, according to the above equation, the calculated value of the electroactive surface area for d-SWCNT film and post-deposited SWCNT paper electrodes are 4.75 mm^2 and 0.83 mm^2, respectively. It indicates that the electroactive surface area of d-SWCNT films is larger than that of SWCNT papers and the actual geometrical area of d-SWCNT films. The relative electroactive surface area of d-SWCNT film electrode is also larger than that of the CNT-modified electrode reported before.[26,27]

Since the electrochemical response and sensitivities of SWCNT electrodes could be varied by changing the surface properties of SWCNTs, the electrochemical properties of heat-treated SWCNT films are of great interest. Before preparing SWCNT film electrodes, the d-SWCNT films were heat-treated in air at 420 °C for 3 h. As expected, a pair of well-defined peaks is still observed in the CV of the heat-

treated SWCNT film electrodes, as shown in Fig. 6(a), and the peak-to-peak separation in the CV is about 90 mV, which is close to 60 mV for the ideal reversible one-electron-transfer reaction, indicating that the electrochemical process is close to reversible process. The peak-to-peak separation of the heat-treated SWCNT film electrodes is smaller than that of the d-SWCNT film electrodes, indicating that the electron transfer rate in the heat-treated SWCNT film electrodes is faster than that in the d-SWCNT film electrodes. In addition, the intensities of the redox peaks in the CV of the heat-treated SWCNT film electrodes are larger in comparison with the case of the d-SWCNT film electrodes. Similarly, compared to the d-SWCNT film electrodes, capacitive background current is also increased for the heat-treated SWCNT film electrodes, as shown in Fig. 6(b). When the SWCNTs were oxidized, an amount of oxygen-containing groups were inevitably introduced on the surface of SWCNTs[28] and part of the walls of the SWCNT bundle were etched, as shown in Fig. 1(d). Oxygen-containing groups on the SWCNT surface can improve the electrochemical properties and enhance the electron transfer rate, as previously reported.[22,29,30] Besides, oxygen-containing groups on the SWCNT surface made the surface of SWCNTs more hydrophilic, so the aqueous solution could contact better with the SWCNT surface and penetrate the interior of the film more easily.[22] As a result, more SWCNT surface was accessible by the electrolyte and both of redox current and capacitive background current were increased.

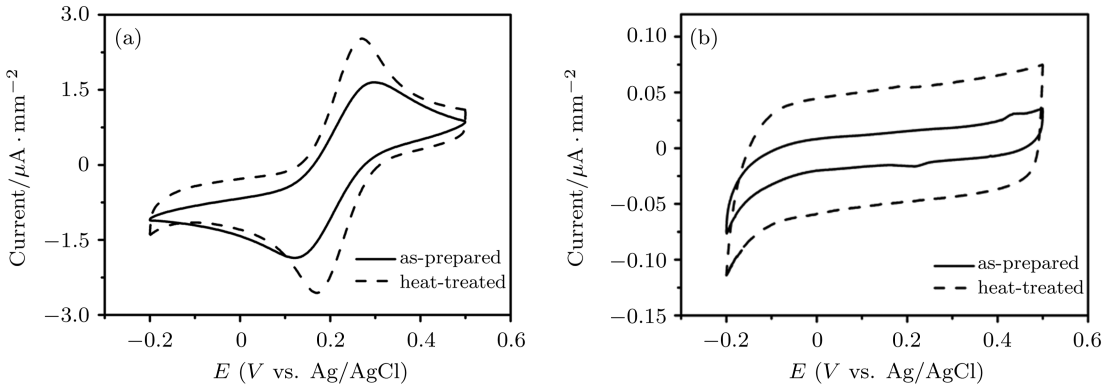


Fig. 6. CVs of the directly grown (solid lines) and heat-treated (dotted lines) SWCNT film electrodes in PBS (pH = 6.8±0.2) in the presence (a) and absence (b) of 1.0 mM $K_4Fe(CN)_6$ normalized to geometric surface area.

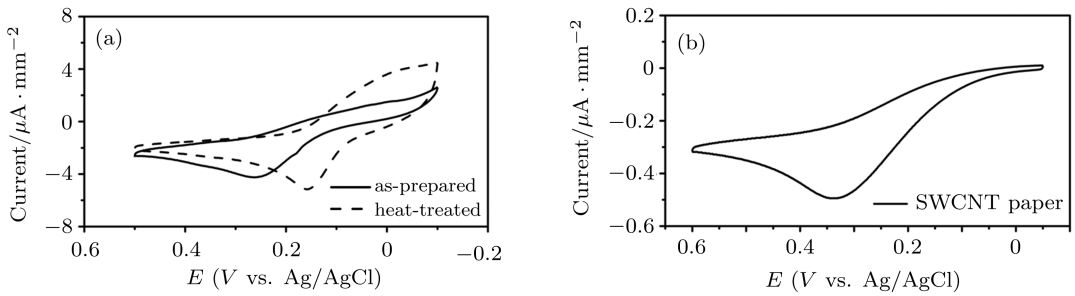


Fig. 7. (a) CVs of AA in PBS at directly grown (solid lines) and heat-treated SWCNT (dotted lines) film electrodes. (b) CV of AA in PBS at SWCNT paper electrode; scan rate: 20 mV/s.

The SWCNT films exhibit excellent electrochemical behaviours, so they could be used as electrodes to explore biological and analytical applications. In this work, the electrochemical processes of the biomolecule ascorbic acid (AA) on the SWCNT paper directly grown and heat-treated SWCNT film electrodes were measured, as shown in Fig. 7. For d-SWCNT film electrodes, the irreversible oxidation peak of AA is located at +263 mV (Fig. 7(a)), which exhibits an obvious negative shift in the potential in comparison with the SWCNT paper (Fig. 7(b)). Furthermore, the intensity of the oxidation peak of AA on

the d-SWCNT films is nearly one order of magnitude lager than that on SWCNT papers. The excellent electrocatalytic activity of the d-SWCNT film electrodes indicates that the films can actively catalyze the oxidation of AA. The CV on heat-treated SWCNT film electrodes for the oxidation of AA is also shown in Fig. 7(a). The irreversible oxidation peak of AA on heat-treated SWCNT film electrodes is located at +159 mV, which shows an obvious negative shift in the potential in comparison with that on the d-SWCNT film electrodes. Therefore, the heat-treated SWCNT film electrodes can effectively improve the electrocatalytic activity of SWCNT films due to oxygen-containing groups on the walls of SWCNTs.[30]

4. Conclusions

An easily manipulative method was presented to spread out the free-standing SWCNT films onto substrates uniformly. The electrodes based on the d-SWCNT films exhibit excellent electrochemical properties. A transition from macroelectrode to nanoelectrode behaviour was observed with the increase of scan rate. Heat-treatment can effectively improve the electrochemical properties of SWCNT films by creating more defects on the walls of SWCNTs and making the surface of SWCNTs more hydrophilic. The excellent electrochemical properties of the directly grown and heat-treated free-standing SWCNT film electrodes show the potentials in biological and electrocatalytic applications.

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