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Macroscopic Carbon Nanotube Fiber Film Based Glucose Biosensor

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A macroscopic carbon nanotube (CNT) fiber film based electrode has been designed for electrochemical biosensor applications and its efficacy as an enzymatic glucose biosensor demonstrated. This CNT thin film was spun directly from a chemical-vapor-deposition (CVD) gas flow reaction using a mixture of ethanol and acetone as the carbon source and an iron nano-catalyst. The function of CNT film is not only the immobilized media of glucose oxidase (GOx) enzyme but also the electric conduction for electrochemical electrode. The biosensor performances are improved by the concentrated acid treating for this CNT fiber film electrode. The glucose sensitivity of the acid treated CNT fiber film electrode is 32 fold higher than untreated one. The improvement of the CNT fiber film based biosensor is due to the loose and porous surface by acid treating which is in favor of the adhesion and immoblization of GOx enzyme. Moreover, the specialty of this CNT fiber film is that it is a macroscopic film, so it can directly connected to an electrochemistry workstation without other media or any binding materials.

Keywords: Carbon Nanotube (CNT) fiber film; Glucose biosensor; Glucose oxidase (GOx); Electrochemical performance

1. INTRODUCTION

As biosensor electrodes, carbon nanotube (CNT) based materials have immense potential in clinical diagnostics and environmental monitoring due to their faster response time and higher sensitivity than traditional electrode such as Pt, Au and glassy carbon electrodes [1, 2]. The better performance is attributed to their one dimensional hollow efficient capture and promotion of electron transfer reactions from analysts [3, 4]. However, their integration into biosensor electrodes has been

challenging because concerns often rise regarding the toxicity of nano-sized CNTs leaching from an implanted biosensor [5-8].

To avoid cytotoxicity of nano-sized CNTs, the ways that immobilizing CNTs on surfaces or within composites have been attempted [9-14]. Hence, the development of CNTs in non-particulate forms, such as CNT paste [15, 16], composite [17, 18], films and thin coating [19, 20], is considered a safe way to fabricate electrodes. The alignment of nanotubes in the fiber is an effective way to exploit the exceptional anisotropic properties of individual CNTs and transform them for micro or macroscale applications. These CNT fibers are macroscopic aligned carbon nanotube bundles with a length of over several kilometers and a quality close to conventional textile yarns. They are lightweight, flexible, high specific surface area, superior electrical conductivity and have good mechanical properties [21, 22]. They can be used as electrodes in a biosensor device, while avoiding the potential toxicity caused by individual CNTs in the form of particles during implantation.

Here, we make a CNT fiber thin film based electrode for enzymatic glucose biosensor. The CNT fibers were fabricated by direct spinning of pure CNT fibers from an aerogel formed during a chemical vapor deposition (CVD) process using ethanol and acetone as the carbon source. During the CVD process, the CNTs form and self-assemble in the gas flow by van der Waals interactions at about 1000 ^{o}C, and then spun into nano-yarns along the fiber axis. The CNT fiber thin film is a macroscopic of these self-assembled CNT yarns. The intention of our studies is to exploit the exceptional properties of this CNT fiber thin film as an electrode and an enzyme media for biosensor. The CNT fiber thin film has good electric performance and a large scale of surface area which we think they are benefit for electron transferring and enzyme capture. The objective for this study is to test our thought by immobilizing glucose oxidase on CNT fiber film and utilizing as an amperometric glucose biosensor. Amperometric glucose biosensor [23] has been extensively studies and plays a leading role in monitoring blood glucose levels for diabetes diagnosis; hence, it would serve as an excellent reference to establish the efficacy of CNT fiber film based biosensor.

The nano-topography of CNT fiber film was demonstrated by scanning electron microscopy (SEM) measurements. Cyclic voltammetry measurements were used to compare the electrocatalytic activity of the CNT fiber with that of the traditional Pt electrode. The CNT fiber was directly connect to a work terminal of an electrochemistry workstation without any electric conductor among them. Glucose oxidase (GOx) was immobilized on the CNT fiber film base electrode. The resulting CNT fiber film based glucose biosensor was tested for glucose sensing functional efficacy in buffers. This study demonstrated that the CNT fiber film based sensor, directly connecting to a work terminal of an electrochemistry workstation, performed better than a Pt based sensor. By concentrated hydrochloric acid, sulfuric acid and nitric acid treatment for CNT fiber film, the efficacy and sensitivity of biosensor are even better than untreated one.

2. EXPERIMENTAL

2.1. Materials

Polyvinyl alcohol (PVA) (average molecule weight 70,000-100,000) and glucose oxidase (GOx) (G7141-10ku, type X-S, from Aspergillus, 200 U mg^{-1}) were both purchased from Sigma-

Aldrich Trading Co. Ltd., Shanghai, China. Glucose, concentrated hydrochloric acid, sulfuric acid, nitric acid, NaCl, Na_2HPO_4 and KH_2PO_4 are purchased from Keiwei Co., Tianjin, China. Pt electrode, Ag/AgCl reference electrode are purchased from Chenhua Co., Shanghai, China. All of the reagents were used without further purification.

2.2. Synthesis of CNT Thin Film

The CNT thin film was spun directly from a chemical-vapor-deposition (CVD) gas flow reaction using a mixture of ethanol and acetone as the carbon source and an iron nano-catalyst. Briefly, the synthesis was conducted by the injection of the carbon source dispersed with ferrocene and thiophene into a heated gas flow reactor in flowing hydrogen. The CNTs were generated in the heated chamber and, with the assistance of gas flow, organized into continuous, concentric and discrete layers referred to as a multilayered CNT 'sock'. Initiated from the upper gas flow, the CNT sock traveled downstream into a water tank connected at the end of the CVD reactor. Upon arriving at the water surface, the CNT sock shrank into a fiber, which was collected around a rotator in water. At this process, some of the fibers gathered together to form thin films. After this, the fibers and thin films were further washed and shrunk in acetone. At last, the fibers and thin films were dried by an infrared heater at about 100 ^oC, wound onto a spool and stored at room temperature until further use.

2.3. Fabrication and Characterization of CNT Thin Film Electrode

About a 2 cm diameter irregular circular form CNT thin film was used for the fabrication of electrodes, which can be seen in Fig.1a. Some of the fiber films were immerse into a concentrated hydrochloride acid, sulfuric acid and nitrate acid solution for 3 h at room temperature, respectively, then washed with deionized water for many times. The acid treated CNT fiber films were dried in a vacuum oven at 70 ^oC for 2 h. Both acids treated and untreated fiber films were used to fabricate electrodes for CNT film based glucose biosensors, to test the effect of acid treatment on the function of the biosensor. As Fig.1b shown, a bundle of CNT fiber which is flexible like human hairs, are glued to a side of CNT film by polyvinyl alcohol solution. After GOx coating (the detail was described in 2.4), the CNT film was rolled to a circular column form which was easy to test in electrochemical test instrument. The tail-like part of this CNT film which is actually the CNT fiber bundles, is directly connected to an alligator clip for electrochemistry workstation without any other media, as shown in Fig.3a.

2.4. Fabrication of Glucose Sensor Based on CNT Fiber Film Electrode

Glucose oxidase (GOx) was immobilized directly on the irregular circular form CNT thin film electrode by solution immersing. The acid treated and untreated CNT fiber film electrodes were immersed twice in a fresh enzyme loading solution which contained 2 mg mL^{-1} GOx and 2.5 wt.% PVA for 1 h at room temperature. Then the enzyme CNT film electrodes were dried in the air after the

first and second immersing in the enzyme solution. In the end, the enzyme CNT film electrodes were washed with 0.1 M phosphate buffer solution (PBS, PH 7.0) and stored at 4 ^{o}C before use.

2.5. Morphology of the CNT Fiber Film Electrode

The morphology of the CNT fiber film was evaluated using scanning electron microscopy (SEM, JEOL JSM-6700F, Japan; HRSEM, FEI Nova Nano SEM 230) with an accelerating voltage of 15 kV. The Fourier transform infra-red (FT-IR) spectra of CNT fiber were obtained with Nicolet IR200 automatic infrared microscope (Thermo Corporation, USA). The structures of acid treated and untreated CNT fibers were characterized by Raman spectrometry (Renishaw Invia Raman microscope with a 633 nm excitation laser) and X-ray photoelectron spectroscopy (XPS, PHI5000 Versa Probe).

2.6. Sensor Function Test

Cyclic voltammetry experiments (CVs) were carried out with a computer-controlled electrochemical analyzer (CHI 660C, Chenhua, Shanghai, China). The typical cyclic voltammograms from the as-spun and acid treated CNT fibers and Pt electrode were obtained in 4 mM $K_3Fe(CN)_6$ in 0.1 mM KCl phosphate buffer (PH 7.0) solution at a 50 mV s^{-1} scanning rate.

The function of the sensors was tested by amperometric measurements of glucose in buffers using potentiostats (CHI 660C, Chenhua, Shanghai, China) at 0.3 V versus an Ag/AgCl electrode as the counter-electrode and a platinum electrode as the counter-electrode. All potentials were measured and reported versus the Ag/AgCl. The response time, sensitivity and linear range of the sensors, as a function of time, was determined. The response time represents the time required to reach 90% of maximum response when the glucose concentration increases from 5 to 15 mM glucose solutions) by calculating the sensor's response current (μA) per mM glucoseconcentration. Calibration plots for each sensor were obtained by stepwise addition of 0.5 M glucose solution 0.5-1.9 mL to 20 mL phosphate buffer saline (PBS, 4 mM $K_3Fe(CN)_6$ in 0.1 mM KCl solution, PH 7.0) covering 2.5-30 mM. All experiments were carried out at room temperature (25 ^{o}C).

3. RESULTS AND DISCUSSION

The CNT film used in this biosensor electrode is a black irregular CNT thin film made of several bundles of nano-diameter CNT fibers. The photographs of the CNT film and CNT fibers are seen in Fig.1 and Fig.2. The CNT film consists of multiple micro-layers as seen from SEM photographs in Fig.2a. There are some wrinkles on the surfaces of each CNT layer (Fig.2b). From the partial enlarged view in Fig.2c and Fig.2d, we can see this layered CNT film is a macroscopic thin film which is an assembling of multiple fiber bundles with average diameters of 50 nm. These CNT bundles twisted along the longitudinal axis of the fibers form a loose surface of CNT film that is expected to provide active catalytic coupling of the enzyme redox reaction.

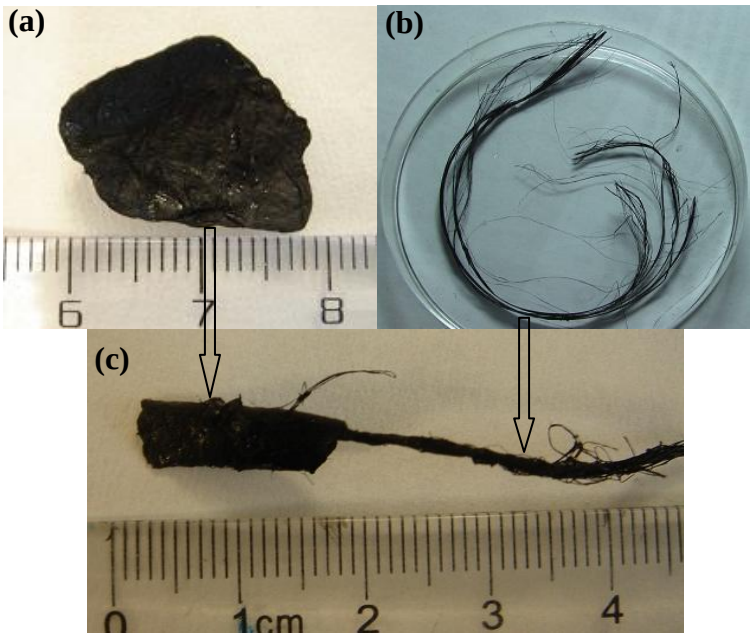

Figure 1. Photographs of a CNT film and CNT fibers: **(a)** a CNT film; **(b)** several bundles CNT fibers; **(c)** a CNT film rolled to a circular column form with its CNT fiber 'tail' as an enzyme electrode.

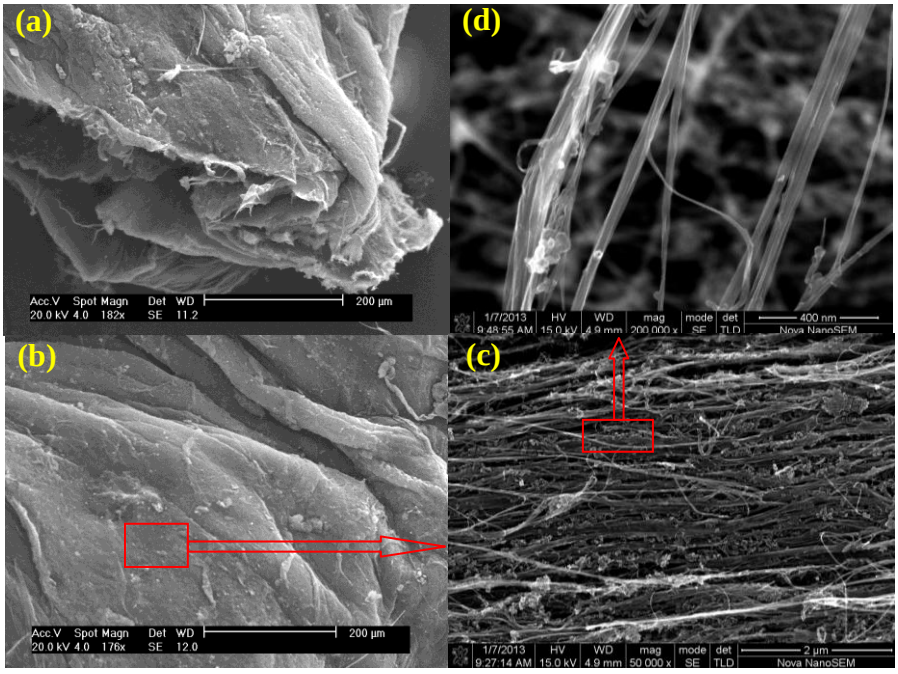

Figure 2. SEM and HRSEM photomicrographs of CNT fiber film **(a-d)**.

As a biosensor electrode, the GOx enzyme was loaded on the CNT fiber film, and a long 'tail' which made of a strand of CNT fiber bundles is connected to a side of this CNT film (Fig.1c). When the enzyme CNT film was dried, it was rolled to a cylinder form as the schematic diagram shown (Fig.3b). The CNT film cylinder was hollow and the top and bottom of the CNT cylinder were opened.

The GOx enzyme was on the inside wall of the CNT film cylinder. The cylinder tail, the CNT fiber bundles were connect to a terminal (the green alligator clip) of an electrochemistry workstation for electrochemistry test as photograph (Fig.3a) shown.

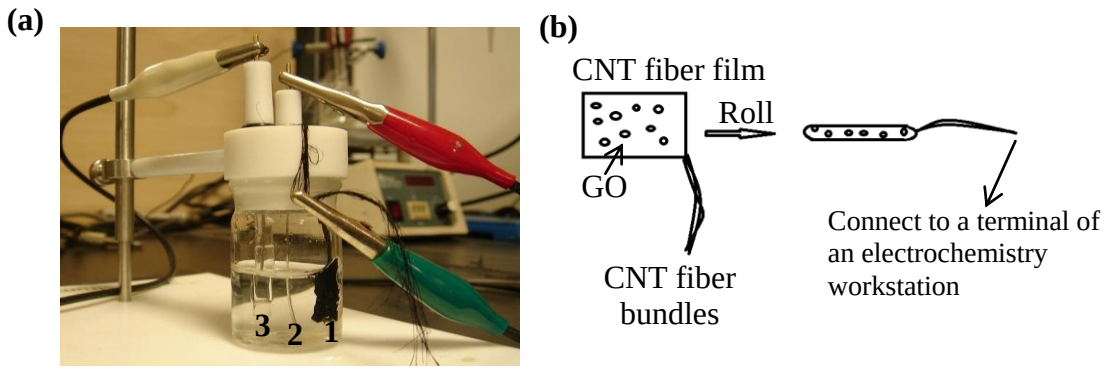

Figure 3. (a) Photograph of three electrodes system of CNT fiber film based biosensor for electrochemical test (1. CNT fiber film based enzyme electrode as working electrode; 2. Pure Pt wire as counter electrode; 3. Ag/AgCl as reference electrode); **(b)** Schematic diagram of CNT fiber film based enzyme electrode.

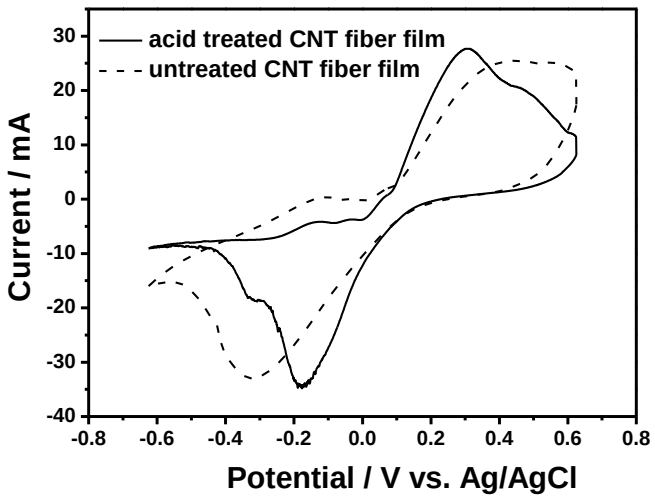

Figure 4. Cyclic voltammograms of acid treated and untreated CNT fiber film based electrode. The curves were obtained in a solution of 4 mM $K_3Fe(CN)_6$ in 0.1 mM KCl at 50 mV s^{-1} scan rate.

The electrochemical properties of the enzyme CNT film electrode were test by using three electrodes system. The enzyme CNT film electrode worked as a working electrode, the pure Pt electrode as a counter electrode and Ag/AgCl as a reference electrode. Cyclic voltammograms of acid treated and untreated CNT fiber film electrode were shown in Fig.4. The curves were obtained in a solution of 4 mM $K_3Fe(CN)_6$ in 0.1 mM KCl at 50 mV s^{-1} scan rate. The well-defined oxidation and reduction peaks due to Fe^{3+}/Fe^{2+} redox couple for the acid treated CNT fiber film are higher than the untreated CNT fiber electrode. The anodic peak current (I_p) of the acid treated CNT fiber film (27.88

mA) is higher than untreated CNT fiber film (25.61 mA). The potential difference ΔE_p between the anodic and cathodic peak is 0.4800 V and 0.7822 V. ΔE_p is reported to be directly related to the electron transfer rate. The lower ΔE_p of the acid treated CNT fiber film indicates that the electron transfer rate for the acid treated CNT fiber is faster than that for the untreated CNT fiber film. These results indicate that the acid treated CNT fiber film electrode has good electrocatalytic activity, and in combination with its excellent affinity with enzymes, it is an attractive electrode material for electrochemical biosensor applications.

The typical amperometric response of the acid treated and untreated CNT fiber film based glucose biosensor is shown in Fig.5a. Numbers in the chart represent the corresponding glucose concentration of the solution. The near instantaneous rise in the sensor response current is following the addition of aliquots of 500 mM glucose stock solution corresponding to 2.5, 5, 10, 15, 20, 25 and 30 mM. Final test concentrations are evident from the stepwise increase in the sensor response curve. The fast response of the biosensor toward glucose can be seen, in that the sensor response current of acid treated CNT film electrode reaches a dynamic equilibrium within tens of seconds (response time) of each addition of glucose, generating a near steady-state current signal. This indicates a fast electron transfer between the redox center of the enzyme and the CNT fiber film.

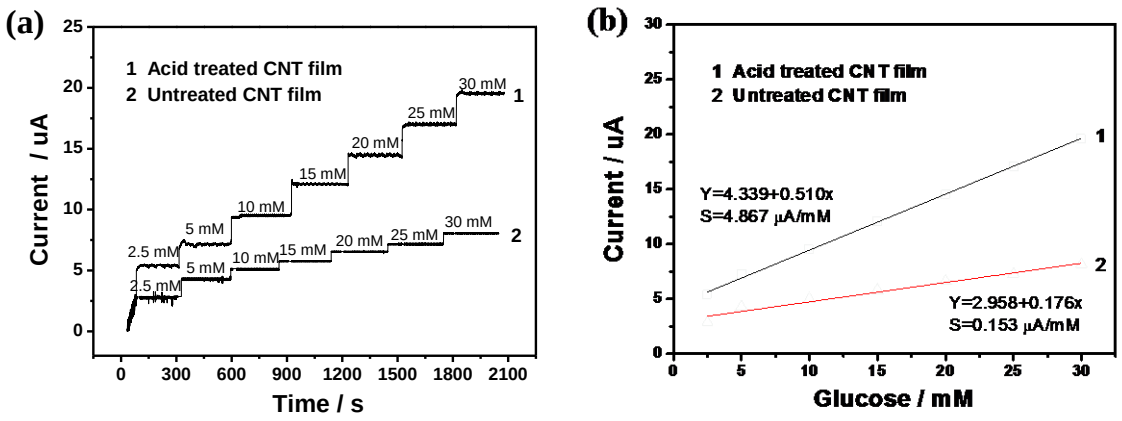

Figure 5. (a) Typical amperometric response curves for acid treated CNT fiber film and untreated CNT fiber film based glucose biosensor; **(b)** Calibration curves of the acid treated and untreated CNT fiber film based glucose biosensor showing linearity for the 2-30 mM glucose solution concentration range.

The linear calibration curves for the acid treated and untreated CNT fiber film based biosensors are presented in Fig.5b. Both the sensors showed a linear increase in sensor response current covering 2-30 mM of glucose concentration range desired for sensing covering the whole range of physiological blood glucose levels. The sensitivity, S, of the sensor was determined by using a two-point method described in equation (1) as follow [24]

$$S=(I_2-I_1)/10 \qquad (1)$$

where I_1 and I_2 represent the sensor response currents obtained in 5 mM and 15 mM glucose solution respectively. The sensitivity for the acid treated CNT fiber film sensor (4.867 μA mM^{-1}) was

significantly higher than that for the untreated CNT fiber film sensor, indicating that the conductivity of the CNT fiber film increased significantly following acid treatment. The acid treatment can get rid of the impurities within the CNT fiber. The impurities are such as the catalyst in the CNT fiber film preparation process and the dust on the surface of CNT fiber film during storage etc. From the sensor test in Fig.5, the acid treatment for CNT fiber film exactly improves the performance of the CNT fiber film based biosensor.

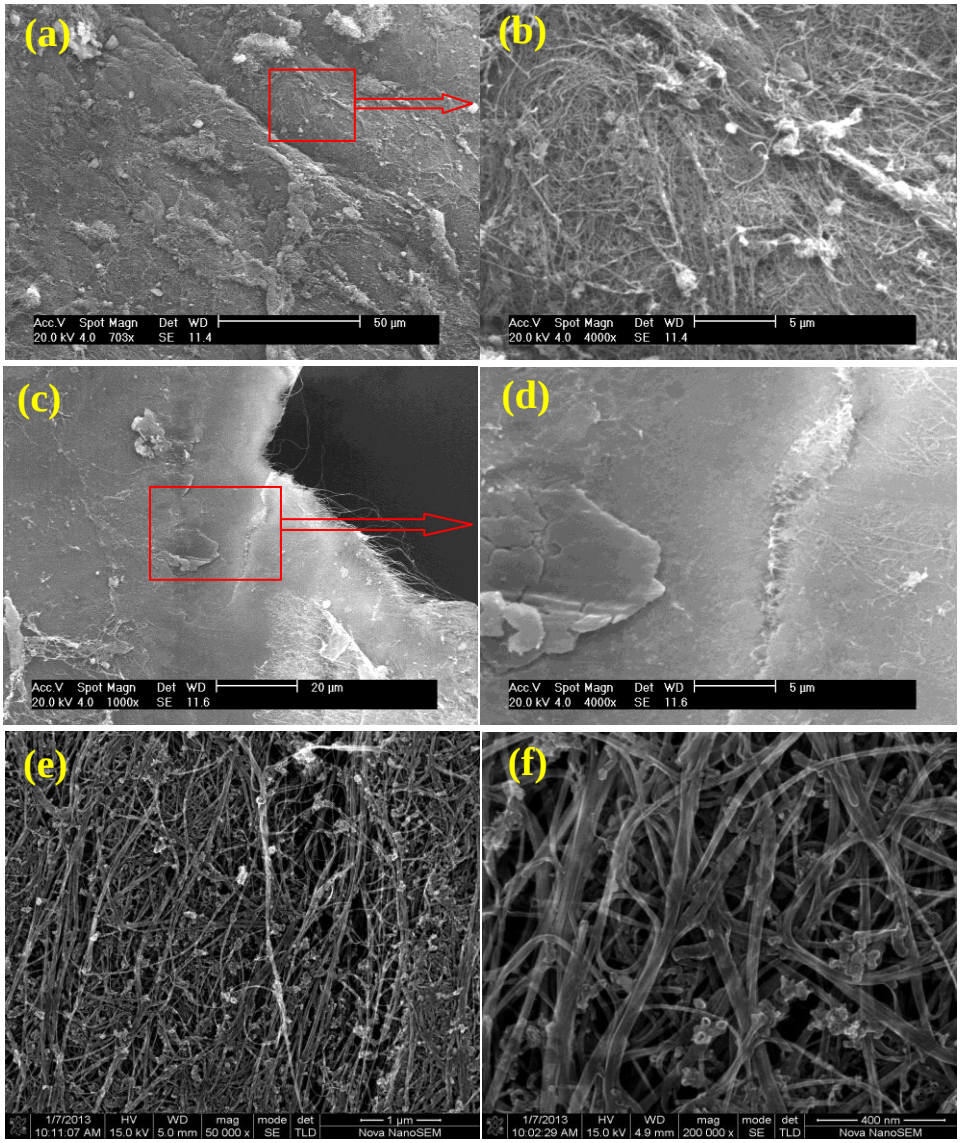

Figure 6. SEM images of acid treated CNT fiber film **(a, b)**; untreated CNT fiber film **(c, d)** and HRSEM images of acid treated CNT fiber film **(e, f)**.

To reveal the reason of the improved biosensor performance by acid treatment, the SEM, FT-IR, Raman spectra and XPS are conducted to the acid treated and untreated CNT fiber film. The SEM images of acid treated and untreated CNT fiber film are shown in Fig.6. We can see there are some wrinkles on the surface of CNT film and the surface of the acid treated CNT film is coarse and loose (Fig.6a). The higher magnification image of the acid treated CNT fiber (Fig.6b) clearly shows that the

acid treated CNT fiber film is well organized and composed of a 3D network of CNT bundles. There are some nano-holes in this 3D network of CNT bundles which is benefit for enzyme immobilization. The nano particles adherent on the surface of CNT bundles are amorphous carbon which are deposited on the surface of the CNT bundles during the condensation process. The HRSEM images of acid treated CNT fiber film in Fig.S4 of Supplementary are clearly shown the microstructure of the acid treated CNT fiber film. Compared to the acid treat CNT fiber film, the untreated one (Fig.6c) is smoother and has less CNT bundles on the surface at the same enlargement ratio. From higher magnification image (Fig.6d), the CNT bundles on the surface of untreated CNT film does not form a 3D network like acid treated CNT fiber film which indicating less location for enzyme immobilization.

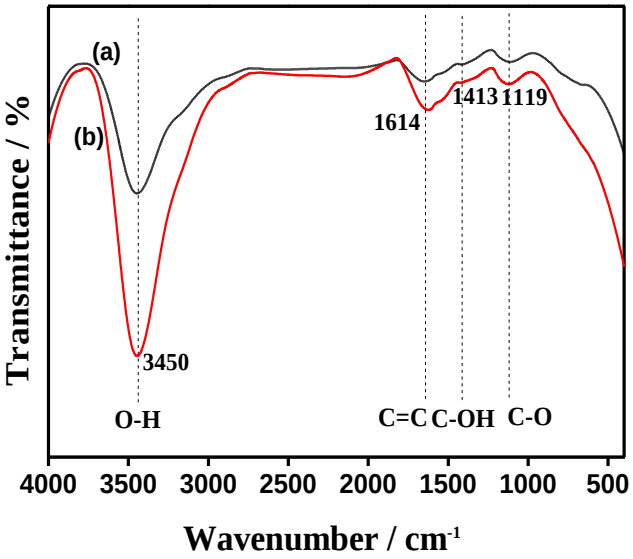

Figure 7. FT-IR spectra of untreated **(a)** and acid treated CNT fiber film **(b)**.

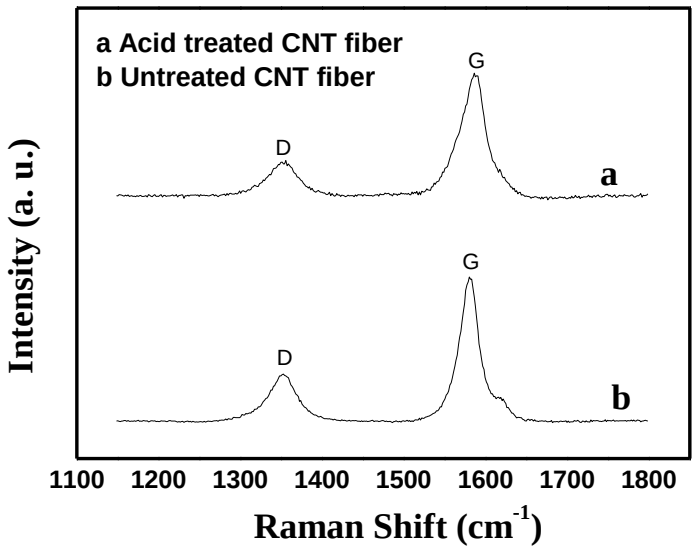

Figure 8. Raman spectra of untreated **(a)** and acid treated CNT fibers **(b)**.

FTIR spectra of acid treated and untreated CNT fibers are shown in Fig.7. There are significant vibration bands for hydroxyl (-OH) at 3450 cm^{-1} and 1413 cm^{-1}, carbonyl (C=O) at 1614 cm^{-1}, and epoxy (C-O) at 1119 cm^{-1}. After acid treated, the IR transmittance of –OH and C=O become stronger, indicating the oxygen functional groups of CNT fiber was reinforced via the treating of concentrate acids. The reinforcement may be attributed to the synergy of oxygen functional groups between CNT fiber and the strong concentrate acids. These oxygen-containing groups in the CNT fiber surface can link with enzyme, which benefit the enzyme immobilization.

Fig.8 is Raman spectra of untreated and acid treated CNT fiber film. The D band peak position is constant for both samples at 1352 cm^{-1}, which is typical of multi-walled CNTs (1330-1360 cm^{-1}), and originates from amorphous carbon and structural defects [24]. After acid treated, the G band peak position shifted from 1580 cm^{-1} to 1586 cm^{-1} which is related to graphite structures, and stems from tangential shearing mode in the graphite plane. The intensity ratio of the D band over the G band, I_D/I_G ratio, is widely used to estimate the density of defects in CNT structure; the bigger the value of the I_D/I_G ratio, the higher the defect density [25]. After acid treatment, the value of the I_D/I_G ratio decrease from 0.31 to 0.27. Combining the results of the SEM images in Fig.5, there are a great amount of impurities, such as amorphous carbon in the structure of untreated CNT fiber, block the porous surface of CNT fiber film. After acid treatment, some impurities were washed by acid and nano-porous morphology on the surface and a 3D CNT fiber network were formed which increase the structural defects in the CNT fiber. They all lead to the decrease of value of I_D/I_G ratio. As previous mentioned, the 3D CNT fiber network with nano-porous structure are benefit for enzyme immobilization and lead to improve the performance of biosensor.

The XPS spectra of untreated and acid treated CNT fiber are shown in Fig.9. The C1s spectra of CNT fiber has no obvious change after acid treated. The binding energy of 284.7 eV and 284.8 eV ascribe to sp^2 carbon, and 285.6 eV ascribes to sp^3 carbon. This is indicated that the acid treatment in our work condition does not damage the sp^2 graphite-like structure of CNT fiber film.

Therefore, according to above SEM images in Fig.6, FT-IR spectra in Fig.7 and Raman spectra in Fig.8, the acid treatments remove part of the amorphous carbon in the CNT structure, make nano-porous structure in the 3D CNT network and reinforce some oxygen containing groups on the surface without damaging the sp^2 graphite-like structure of CNT fiber film.

This CNT fiber film based electrode has two specialties. The first specialty is that the CNT film is a macroscopic film, so it can directly connected to an electrochemistry workstation without other media. Hence, the intensity of electronic signal cannot be decrease by transmission between the enzyme loading on this CNT film and the biosensor electrode. However, the CNTs used as biosensor electrode in most relevant references [1-18] are ‘powder’ like substance, it can neither directly used as electrode nor connect to the terminal of an electrochemistry workstation without binding media. Moreover, the manipulation of our macroscopic CNT fiber film as biosensor electrode is more easily than above ‘powder’ like CNTs. The second specialty of our CNT fiber film is that it has the loose and porous surface which is formed by acid treatment. In the microscopic scale, these pores can adhesion and immoblization of more GOx enzyme for biosensor. From the two above, our CNT fiber film is not only used as an enzyme loading media, but aslo a good electrode for biosensor both in the macroscopic and microscopic scale.

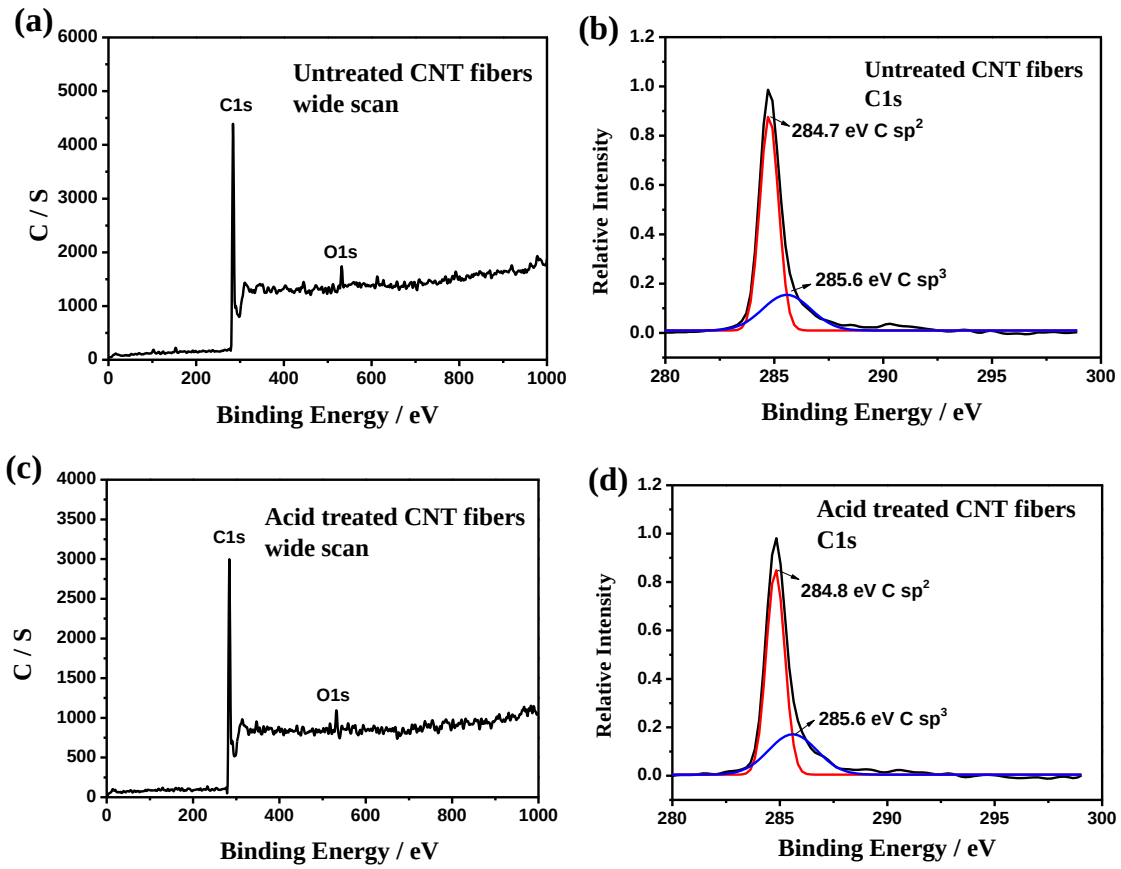

Figure 9. XPS spectra of untreated **(a, b)** and acid treated CNT fibers **(c, d)**.

Compared with traditional CNT films in previous references [15-20], this kind of CNT fiber films has many distinct differences, such as morphology, structure and properties. Furthermore, their biosensor characteristic is better than other traditional CNT film based biosensor electrodes in previous reports [5-20]. Therefore, according to all above, this macroscopic CNT fiber film has a very promising potential for electrochemical biosensor applications.

4. CONCLUSIONS

A macroscopic CNT fiber film based electrode has been designed for an enzymatic glucose biosensor. By acid treatments of the CNT fiber film, the performance of this glucose biosensor was improve significantly. The improvement of the biosensor performances is due to the loose and porous surface by acid treatments which is in favor of the adhesion and immoblization of GOx enzyme. Additionally, this macroscopic CNT fiber film can directly connected to an electrochemistry workstation without other media. Hence, the intensity of electronic signal cannot be decrease by transmission between anlysis substrate and the biosensor electrode. Further studies should involve

addressing the long-term stability of the CNT film based glucose biosensor and stabling the enzyme immorbilization on the CNT film electrode as maximal volume unit.

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