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ORIGINAL PAPER

# Direct electron transfer of cytochrome C and its electrocatalytic properties on multiwalled carbon nanotubes/ciprofloxacin films

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**Abstract** In this study, stable and homogenous thin films of multiwalled carbon nanotubes (MWCNTs) were obtained on conducting surface using ciprofloxacin (CF, fluoroquinolone antibiotic) as an effective-dispersing agent. Further, MWCNTs/CF film modified electrodes (glassy carbon and indium tin oxide-coated glass electrode) are used successfully to study the direct electrochemistry of proteins. Here, cytochrome C (Cyt-C) was used as a model protein for investigation. A MWCNTs/CF film modified electrode was used as a biocompatible material for immobilization of Cyt-C from a neutral buffer solution (pH 7.2) using cyclic voltammetry (CV). Interestingly, Cyt-C retained its native state on the MWCNTs/CF film. The Cyt-C adsorbed MWCNTs/CF film was characterized by scanning electron microscopy (SEM), UV–visible spectrophotometry (UV-vis) and CV. SEM images showed the evidence for the adsorption of Cyt-C on the MWCNTs/CF film, and UV–vis spectrum confirmed that Cyt-C was in its native state on MWCNTs/CF film. Using CV, it was found that the electrochemical signal of Cyt-C was highly stable in the neutral buffer solution and its redox peak potential was pH dependent. The formal potential (−0.27 V) and electron transfer rate constant ($13\pm1\ s^{-1}$) were calculated for Cyt-C on MWCNTs/CF film modified electrode. A potential application of the Cyt-C/MWCNTs/CF electrode as a biosensor to monitor $H_2O_2$ has been investigated. The steady-state current response increases linearly with $H_2O_2$ concentration from $2\times10^{-6}$ to $7.8\times10^{-5}$ M. The detection limit for determination of $H_2O_2$ has been found to be $1.0\times10^{-6}$ M (S/*N*=3). Thus, Cyt-C/MWCNTs/CF film modified electrode can be used as a biosensing material for sensor applications.

**Keywords** Hydrogen peroxide sensor · Biosensor · Carbon nanotubes · Cytochrome C

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## Introduction

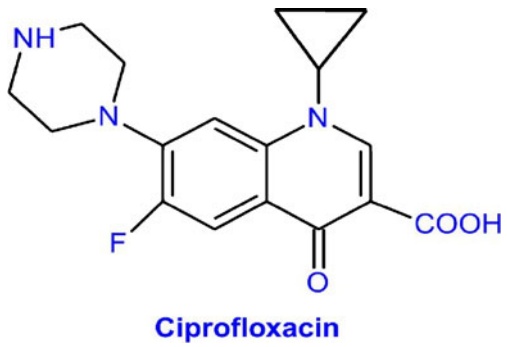
Carbon nanotubes (CNTs) have attracted much attention in recent times as a conducting material suitable for use in biomaterial fabrication. Multiwalled carbon nanotubes (MWCNTs) consist of several concentric cylindrical shells of graphene sheets coaxially arranged around a central hollow core with interlayer separation as in graphite. CNTs are nanoparticles with very high aspect ratio, good mechanical properties, and interesting conducting properties [1, 2]. According to the structural parameters, CNTs can behave as metal or semiconductor [1]. Due to their uniqueness, CNTs have received enormous attention for the preparation of electrochemical sensors [3–8].

However, dispersion of CNTs is a major problem because of their poor solubility and dispersability in both aqueous and organic solvents. They usually tend to form crystalline ropes due to the strong intertube van der Waals

attraction, leading to difficulties in their manipulation and incorporation into different matrixes. For successful utilization of their properties, uniform dispersion of CNTs in various media, especially in aqueous solutions, is required [9]. Recently, CNTs have been dispersed in polyethylenimine [10], fluorinated dendrimer-type copolymers [11], star-like amphiphilic block copolymers [9], and conjugated block copolymers [12].

Ciprofloxacin (CF, Scheme 1), a fluoroquinolone antibiotic, is an antibacterial agent used to treat diverse gram-negative infections. CF can usually act as a bidentate ligand through the pyridone oxygen and one carboxylate oxygen. In the literature, diverse transition metal complexes of CF have been structurally characterized [13, 14]. It was described that CF is a useful stabilizing agent for MWCNTs and this dispersion expected to have potential applications in the preparation of uniform MWCNTs/CF thin films for the development of new electrochemical transducers [15].

Among the various redox proteins, cytochrome C (Cyt-C) is an important heme-containing metalloprotein [16], which is bound to the mitochondrial membrane and functions as an electron carrier in the respiratory chain. In recent decades, a substantial amount of research work has been carried out on the direct electrochemistry and electrocatalysis of Cyt-C [17, 18]. In this paper, for the first time, we report the direct electron transfer of Cyt-C and its electrocatalytic properties using a MWCNTs/CF film modified electrode. A uniform MWCNTs/CF film can be obtained on indium tin oxide-coated glass (ITO) and glassy carbon electrode (GCE). The MWCNTs/CF films have been used as a platform for adsorption of Cyt-C from a neutral buffer solution. Cyt-C is irreversibly attached onto the biocompatible MWCNTs/CF film and retained its native structure. Surface topographies of MWCNTs/CF film and Cyt-C/MWCNTs/CF films were monitored by scanning electron microscopy (SEM). Adsorbed Cyt-C was in its original state on MWCNTs/CF film modified electrode which was confirmed by UV-vis. In addition, electrochemical properties of adsorbed Cyt-C on MWCNTs/CF films were studied by cyclic voltammetry and amperometry.




**Scheme 1** Structural formula of ciprofloxacin

## Experimental

### Chemicals and reagents

CF, MWCNTs (purity >99%; O.D.×length 6–13 nm× 2.5–20 μm), Cyt-C (from horse heart), sodium hydroxide (NaOH), hydrochloric acid (HCl), and disodium hydrogen phosphate ($Na_2HPO_4$) were purchased from Sigma-Aldrich and used without further purification. The 0.1 M phosphate buffer solution (PBS), which was made from $Na_2HPO_4$, was always employed as a supporting electrolyte. The pH value was adjusted with 0.1 M NaOH or 0.1 M HCl. All the solutions were prepared using deionized water (18.1 MΩ).

### Apparatus and measurements

All experiments were performed at room temperature (20± 3 °C). The surface characterization of Cyt-C/MWCNTs/CF and MWCNTs/CF were observed by a SEM (HITACHI S-4700), at an operation voltage of 15 kV. Absorption spectra were recorded using a UV-vis (PerkinElmer Lambda 900). Electrochemical experiments were performed with a CH Instruments (Model: Chi611c, Austin, TX, USA). All electrochemical experiments were carried out with a conventional three-electrode system. The GCE and ITO were used as the working electrodes. ITO glasses were cleaned using detergent solution and distilled water and then sonicated in ethanol for 10 min and finally washed using acetone and dried at room temperature. The GCE (the geometric diameter was 3 mm) was mechanically polished with alumina paste (0.05 μm) up to a mirror finish and ultrasonicated in distilled water and in ethanol for 10 min. Platinum wire and Ag/AgCl (3 M KCl) electrode were used as the counter electrode and the reference electrode, respectively. The electrolyte solution was purged with high-purity argon gas for at least 10 min prior to each electrochemical experiment, and an argon environment was then maintained for the solution in the cell during the electrochemical measurements.

### Preparation of MWCNTs/CF dispersion

A stable dispersion of MWCNTs in CF solution was prepared [15]. Briefly, an accurately weighed CF was dissolved into 0.1 M HCl solution to obtain a 5-mM aqueous solution of CF. A very clear CF solution was obtained by sonication. CF was partially soluble in water, but completely soluble in acidic solution. Here we used 0.1 HCl as a solvent. An accurately weighed 5 mg of MWCNTs were dispersed in 5 mL of CF solution and sonicated for 10 min. Using a small magnetic bar, the MWCNTs dispersion was stirred about 3 h. By this method,

a stable MWCNTs/CF dispersion was obtained and stored at room temperature when not in use.

Cyt-C immobilization

A 10 μL of MWCNTs/CF dispersion was spread evenly onto the surface of GCE which was dried in an air oven at 60 °C for 30 min. The water (solvent) evaporated and left the MWCNTs/CF film on the electrode surface. The MWCNTs/CF film coated electrode was thoroughly rinsed with double-distilled water. Then, the MWCNTs/CF film coated electrode was cycled in pH 7.2 buffer containing 1 mM Cyt-C between 0.0 and −0.6 V for 20 cycles at a scan rate of 50 mV/s. Afterwards, the electrode was thoroughly rinsed with double-distilled water and then dried using argon gas at room temperature about 30 min. When not in use, the electrode was stored in 0.1 M PBS (pH 7.2) at 4 °C. This electrode was noted as Cyt-C/MWCNTs/CF/GCE and then used for further studies. For SEM and UV-vis studies, Cyt-C/MWCNTs/CF and MWCNTs/CF films were prepared onto transparent ITO glasses.

## Results and discussion

CV was used to characterize the modification process of the electrode in 5 mM $[Fe(CN)_6]^{3-/4-}$ and 0.1 M KCl solution. Figure 1 compares the CV responses at GCE (curve a), MWCNTs/GCE (curve b), and MWCNTs/CF/GCE (curve c) electrodes in the above solution, respectively. After modified with MWCNTs, the anodic peak and cathodic peak were increased drastically (curve b), indicating MWCNTs can improve the surface area of the electrode. Interestingly, MWCNTs/CF modified GCE shows higher peak current (curve c) than both of MWCNTs/GCE (curve b) and unmodified GCE (curve a), which is due to the adsorption of CF molecules on MWCNTs. Adsorbed CF molecules on MWCNT surface are stabilizing nanotubes in its solution as well as in solid state on electrode surface. The higher current observed for the redox probe at a MWCNTs/CF/GCE is clearly demonstrating that its high conducting ability than GCE and MWCNTs/GCE which might due to high loading of MWCNTs/CF films on the electrode surface.

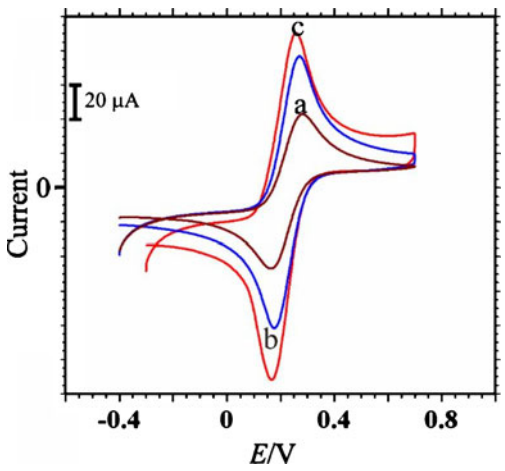



**Fig. 1** CVs of *a* bare GCE, *b* MWCNTs/GCE, and *c* MWCNTs/CF/GCE in 5 mM $[Fe(CN)_6]^{3-/4-}$+0.1 M KCl solution. Scan rate=20 mV/s

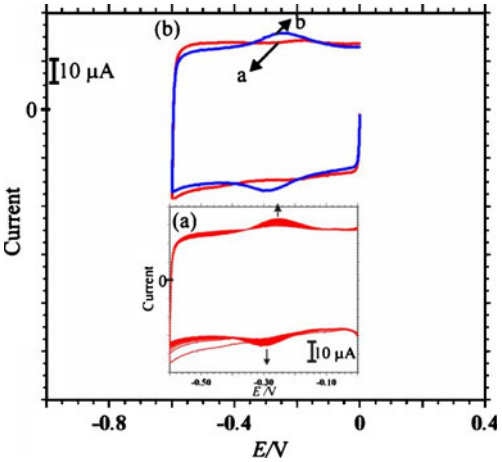



**Fig. 2** *a* CVs recorded in pH 7.2 buffer containing 1 mM Cyt-C using a MWCNTs/CF modified GCE. *b* CVs of a MWCNTs/CF/GCE (*curve a*) and Cyt-C/MWCNTs/CF/GCE (*curve b*) recorded in pH 7.2 buffer. Scan rate=50 mV/s

Figure 2a shows CVs recorded in pH 7.2 buffer containing 1 mM Cyt-C using a MWCNTs/CF film modified GCE. As we observed during consecutive potential cycling, a redox peak at near −0.27 V was observed and the peak currents increase, which should be corresponding to the redox of Cyt-C. The redox peak currents were increased with the number of cycles in the Cyt-C solution which is demonstrating that Cyt-C could adsorb onto a MWCNTs/CF film. When the cycle was above 20, no obvious changes of peak currents could be observed from the CVs, indicating that the adsorption of Cyt-C on MWCNTs/CF reached saturation. The Cyt-C modified MWCNTs/CF film was thoroughly washed with double-distilled water and dried using argon gas.

Figure 2b shows CVs of MWCNTs/CF (curve a) and Cyt-C/MWCNTs/CF (curve b) film modified electrodes recorded in 0.1 M buffer (pH 7.2) at a scan rate of 50 mV/s. It was very clear that after the adsorption of Cyt-C on MWCNTs/CF film, it shows a reversible redox peak of heme protein. The cathodic and anodic peak potentials were located at −0.295 and −0.244 V, respectively. The formal potential $\left(E^{o'} = E_{pa} + E_{pc}/2\right)$ was −0.27 V at pH 7.2. The redox peak separation was 51 mV, indicating a fast electron transfer process. The ratio of the oxidative and reductive

peaks were nearly equal to one and the shapes of the redox peaks were symmetric indicating that all electroactive Cyt-C Fe(III) on the surface of MWCNTs/CF is converted to Cyt-C Fe(II) on the forward cathodic scan and the reduced protein in their Cyt-C Fe(II) forms are fully oxidized back to the Cyt-C Fe(III) forms on the reversed anodic scan.

Effect of scan rate on the redox peak current was studied as shown in Fig. 3a. The redox peak current increases linearly with increasing scan rate and the peak-to-peak separation remained constant up to 200 mV/s (Fig. 3a), indicating a typical surface-controlled electrode process. According to the model of Laviron theory [19], the electron transfer rate constant ($k_s$) and charge transfer coefficient ($\alpha$) can be determined by measuring the variation of peak potential with scan rate. The values of peak potentials were proportional to the logarithm of the scan rate for Cyt-C/MWCNTs/CF/GCE (Fig. 4). The slopes of the $E_{pa}$ and $E_{pc}$ versus log ($\nu$) was about 0.23 and −0.23 V, respectively, so

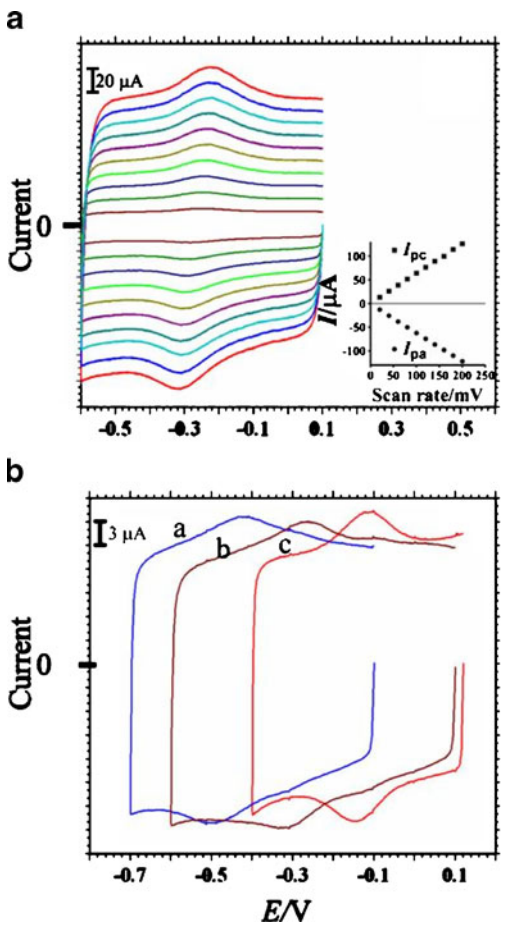



**Fig. 3** **a** CVs recorded in pH 7.2 buffer using a Cyt-C/MWCNTs/CF/GCE at different scan rates from 20 to 200 mV/s. Inset figure shows a plot of Ip versus scan rate. **b** CVs recorded in different pH solutions using a Cyt-C/MWCNTs/CF/GCE (*a*) pH 11.0, (*b*) pH 7.2, and (*c*) pH 2.3

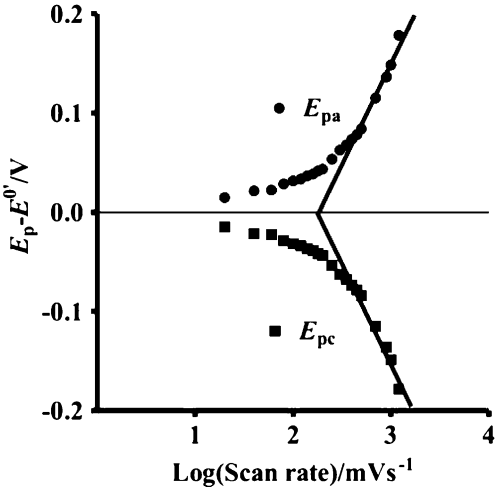



**Fig. 4** A plot of ΔEp versus log (scan rate, 20 mV to 1,200 mV/s)

that $\alpha$ can be calculated as 0.46 from the slope of the straight line using the following Eq. 1 [20, 21].

$$\log \frac{v_a}{v_c} = \log\left[\frac{\alpha}{1-\alpha}\right] \tag{1}$$

According to the Eq. 2 [19], the $k_s$ value was estimated to be 13±1 $s^{-1}$, which is larger than those obtained for Cyt-C immobilized on other CNTs modified electrode (4± 0.2 $s^{-1}$) [22] and gold nanoparticles–chitosan–CNTs-modified electrode (0.97 $s^{-1}$) [23], indicating a faster electron transfer process and a favorable microenvironment for the Cyt-C proteins provided by the biocompatible MWCNTs/CF film.

$$\log\ k_s = \alpha\log(1-\alpha) + (1-\alpha)\log\alpha - \log\left(\frac{RT}{nFv}\right) - \frac{\alpha(1-\alpha)nF\,\Delta E_p}{2.3RT} \tag{2}$$

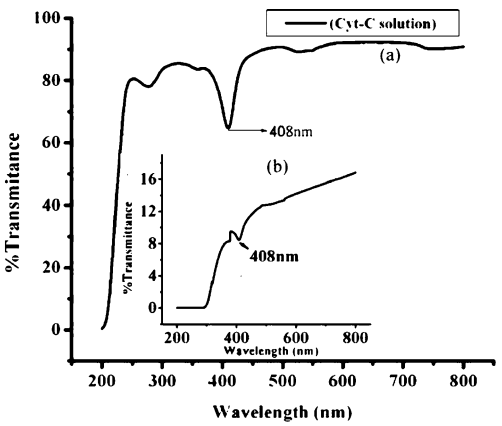



**Fig. 5** UV–vis spectrum of *a* Cyt-C solution and *b* Cyt-C/MWCNTs/CF film

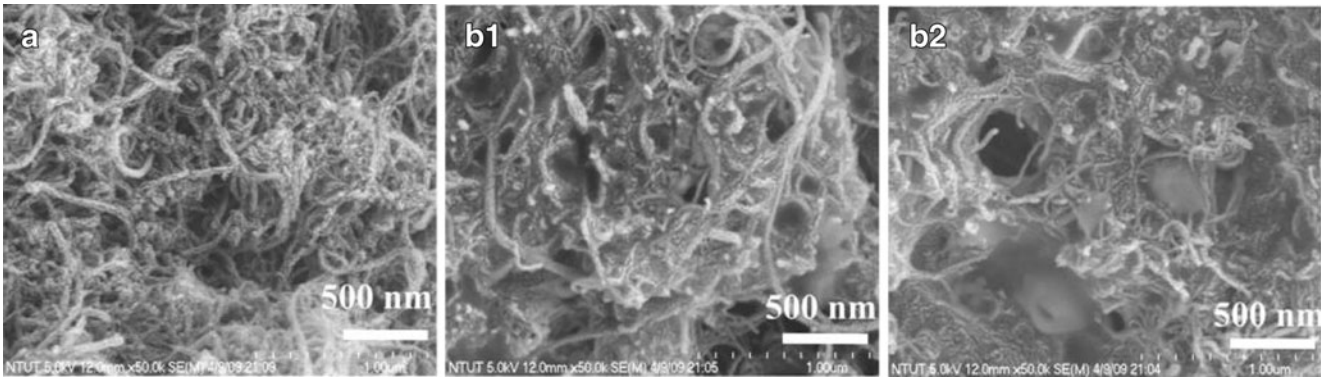



**Fig. 6** SEM images of **a** MWCNTs/CF film and **b1**, **b2** Cyt-C/MWCNTs/CF film

The average surface coverage ($\Gamma$) of Cyt-C was calculated to be $5.35\times10^{-10}$ mol/cm$^2$, which is showing that of approximate monolayer coverage. As can be seen in Fig. 3b, the $E^{\circ'}$ of heme redox couple [Cyt-C Fe(III)-Fe(II)], was pH dependent in the range from 2 to 11. This observation indicates that proton is involving in the electron transfer process of Cyt-C (Equation 3) [23–25].

$$\text{Cyt}-\text{C heme Fe(III)} + \text{H}^+ + \text{e}^- \rightleftarrows \text{Cyt}-\text{C heme Fe(II)} \quad (3)$$

The Soret band of heme protein is usually an indicator of the microenvironment where heme center locates. The peak will be diminished if the protein is denatured [26]. The band for Cyt-C in its solution is located at 408 nm (Fig. 5a). The dry film of Cyt-C/MWCNTs/CF was prepared on ITO glass electrode which showed a Soret band at 408 nm (Fig. 5b). It is suggesting that Cyt-C has a secondary structure nearly the same as its original state in the solution. From these data, it was confirmed that MWCNTs/CF film is an excellent biocompatible material for protein immobilization.

Figure 6a shows the SEM image of MWCNTs/CF film. Surface topography image of MWCNTs/CF clearly shows different morphology from pure MWCNTs [15] and the CF particles can be easily seen on MWCNTs which confirms adsorption of CF (Fig. 6a). Figure 6(b1, b2) depicts the SEM image of Cyt-C/MWCNTs/CF film, which shows several nanoscale particles on MWCNTs/CF film after the adsorption of Cyt-C. The difference in surface topographies between MWCNTs/CF and Cyt-C/MWCNTs/CF clearly revealed that adsorption of Cyt-C particles on the MWCNTs/CF film. Based on these investigations, the MWCNTs/CF is a good biocompatible material and can be used as a platform for immobilization of enzymes or proteins. Also, this new biomaterial can be used as a sensing material for biosensor applications.

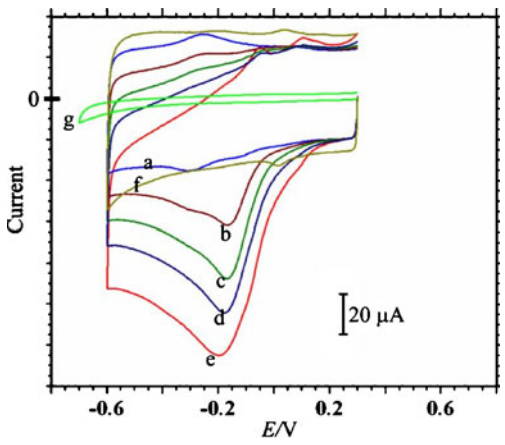



**Fig. 7** CVs of a Cyt-C/MWCNTs/CF/GCE in the absence (*curve a*) and presence of $H_2O_2$; (*b*) 60, (*c*) 150, (*d*) 200, and (*e*) 250 μM. CVs of MWCNTs/CF/GCE (*curve f*) and bare GCE (*curve g*) in the same condition with 250 μM $H_2O_2$ were recorded. Scan rate=50 mV/s

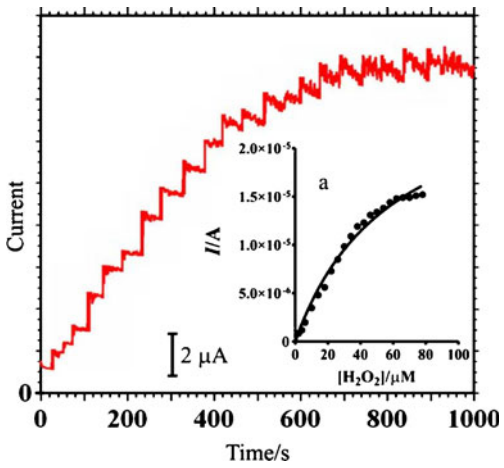



**Fig. 8** Amperometric responses of Cyt-C/MWCNTs/CF/GCE at −0.40 V upon successive additions of $H_2O_2$ from $2\times10^{-6}$ to $7.8\times10^{-5}$ M to 50 mL buffer solution (0.1 M, pH 7.2) with stirring rate of 500 rpm/s. *Inset*: $I_p$ versus [$H_2O_2$]

According to the results, Cyt-C can tightly adsorb on the surface of MWCNTs/CF film to form a stable Cyt-C/MWCNTs/CF biofilm modified electrode. To test the stability of Cyt-C on MWCNTs/CF film, 500 continuous cyclic scans were recorded in the potential range of 0.0 to −0.6 V at a scan rate of 50 mV/s using Cyt-C/MWCNTs/CF/GCE. We have no observed obvious changes in the redox peak currents of Cyt-C. When the Cyt-C/MWCNTs/CF electrode was stored at 4 °C in a pH 7.2 buffer for 4 weeks, nearly 95% of Cyt-C electroactivity can be retained, which suggested that the electrode has an excellent stability. Good stability of Cyt-C on MWCNTs/CF film may be due to the following reasons. First, MWCNTs acts as a bridge of electron transfer between protein and the electrode. Naturally, the MWCNTs could act as "electron antennae" [22, 23], efficiently tunneling electrons between the electrode and Cyt-C. As observed earlier, MWCNTs/CF film might be in neural form and, the carboxylic group ($pK_{a1}$ of 6.10±0.5) of CF might be in deprotonated form and bears negative charge in neutral pH [27]. This intrinsic negative charge on MWCNTs/CF may facilitate adsorption of Cyt-C to the electrode surface (Cyt-C has a positive dipole moment around the heme cleft) [28].

It is well known that heme proteins can catalyze the reduction of $H_2O_2$. The electrocatalytic behavior of Cyt-C/MWCNTs/CF modified GCE was tested by cyclic voltammetric measurements. Upon addition of $H_2O_2$ to 0.1 M pH 7.2 buffer, the cyclic voltammogram of Cyt-C/MWCNTs/CF/GCE for the direct electron transfer of Cyt-C changed dramatically with an increase of reduction peak current and a decrease of oxidation peak current (Fig. 7b–e), while the changes of cyclic voltammograms of MWCNTs/CF modified GCE and bare GCE were negligible (curves f and g), displaying an obvious electrocatalytic behavior of the Cyt-C to the reduction of $H_2O_2$. The electrocatalytic reduction peak of $H_2O_2$ by Cyt-C/MWCNTs/CF/GCE could be used to quantitatively determine the concentration of $H_2O_2$.

Figure 8 illustrates a typical current–time plot for the Cyt-C/MWCNTs/CF/GCE on successive step additions of $H_2O_2$ at a working potential of −0.40 V. When an aliquot of $H_2O_2$ is added into the buffer solution, the reduction current rises steeply to reach a stable value. In addition, from Fig. 8, it can be seen that the time required to reach 95% of the steady-state current was less than 8 s after the addition of $H_2O_2$. This result shows that the current response of the biosensor was rapid. The reduction currents at the biosensor were proportional to the concentration of $H_2O_2$ in the range from $2\times10^{-6}$ to $7.8\times10^{-5}$ M with a correlation coefficient of 0.9872 ($n$=21) and the detection limit was $1.0\times10^{-6}$ M at a signal-to-noise ratio of 3 (inset of Fig. 8). At higher concentration of $H_2O_2$, the cathodic peak current reached saturation, showing the characteristics of Michaelis–Menten kinetics. The apparent Michaelis–Menten constant (Km) can be obtained by an amperometric method as suggested by the Lineweaver–Burk equation (Equation 4) [29].

$$\frac{1}{I_{ss}} = \frac{1}{I_{(max)}} + \frac{\mathrm{K}m}{I_{(max)}C} \tag{4}$$

Where $I_{ss}$ is the steady-state current after the addition of substrate, $I_{max}$ is the maximum current measured under saturated substrate conditions, and $C$ is the bulk concentration of the substrate. Based on the experimental data from Fig. 8 inset, the Km value for this biosensor was estimated to be 0.1±0.04 mM. This value is comparably smaller than 0.45±0.02 mM [20], 0.791 mM [23], 2.1 mM [30], and 0.857 mM [31], which is due to high affinity of the biosensor towards $H_2O_2$.

## Conclusions

In this study, we reported an application of MWCNTs dispersion prepared in CF solution. The as-prepared MWCNTs dispersion can form a thin-film through a simple dropping technique. Cyt-C can strongly adsorb onto MWCNTs/CF film to form a stable biofilm. Due to the promoting effect of MWCNTs, the direct electron transfer between Cyt-C and electrode was reached. Based on this study, new biosensing platform or biosensor can be constructed using this new biofilm modified electrode. Direct electrochemical properties of Cyt-C were evaluated and it was found that MWCNTs/CF film can be used as a biocompatible matrix for enzyme or protein immobilization studies. In addition, we employed Cyt-C/MWCNTs/CF film modified electrode as a biosensor for determination of $H_2O_2$ using amperometry technique. Although, previously MWCNTs were used for immobilization of proteins, here, for the first time, we used thin film made of MWCNTs/CF for immobilization of Cyt-C. According to the obtained results, MWCNTs/CF film is a good biocompatible material and it may be useful for study enzyme and protein electron transfer reactions.

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