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Electrocatalytic Behavior and H_2O_2 Detection of Carbon Nanotube/Chitosan Nanocomposites Prepared via Different Acidic Aqueous Solutions

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The factors that affect the electrocatalytic activities of carbon nanotube/chitosan (CNT/CS) nanocomposite films that were cast on a glassy carbon electrode from CH_3COOH, HCOOH, HCl, and citric acid aqueous solutions were investigated by cyclic voltammetry (CV). These factors include the extent of functionalization of acid-treated CNT (fCNT), the fCNT content, and the acid type used to prepare the films. The CV results revealed that the fCNT in the fCNT/CS-cast film exhibited electrocatalytic activity to redox reactions of $Fe(CN)_6^{3-/4-}$ used as a probe. The fCNT (having a COOH content 2.51 mmol/100 g sample) exhibited a higher electrocatalytic activity than the untreated CNT and the fCNT1 (having a COOH content 158.50 mmol/100 g sample). Among the four acids, citric acid exhibited the most uniform fCNT dispersion in the CS film, which resulted in the highest electrocatalytic activity. On the other hand, HCl resulted in a brittle fCNT/CS film and a negligible electrocatalytic activity. The fCNT/CS 2/10 film exhibited a higher electrocatalytic activity than the fCNT/CS 1/10 and 3/10 films. The amperometric analysis results revealed that when a nanocomposite film has a high electrocatalytic activity, the sensitivity for H_2O_2 detection in the film is also high.

Keywords: Chitosan, carbon nanotube, electrocatalytic activity, cyclic voltammetry, amperometric sensor

1. INTRODUCTION

Carbon nanotubes (CNT) have gained increasing attention because of its good electrocatalytic activity [1–9]. Pristine CNTs, which consist of cylindrical graphene layers, are hydrophobic but cannot readily disperse in most hydrophobic polymers. This is attributed to a great deal of van der Waals forces present in CNTs and in polymers without specific interactions between CNT/polymer pairs. CNTs can be functionalized with the carboxylic groups on its surface via acid treatment. In this type of treatment, CNTs can be grafted with a desired type of molecules of low or high chain length to tailor its dispersion in water [10] or in a particular polymer. A previous study [11] has demonstrated that without acid treatment, CNTs are hydrophobic and could dissolve or easily disperse in nonpolar or low-polarity solvents such as acetone and alcohols (methanol and ethanol). However, CNTs precipitate in deionized water, which is a highly polar solvent. By contrast, the acid-treated CNT (denoted as fCNT) dissolves or is well-dispersed in deionized water, but not in acetone or alcohols.

Chitosan (CS), a biocompatible polymer, is derived from the deacetylation of chitin, which is a natural polysaccharide found in a wide range of natural sources such as crustaceans, fungi, and insects. CS has various uses in areas such as agriculture, medicine, food, and sewage treatment. Without modification, CS is usually insoluble in water, but is soluble in water with low pH values (pH < approximately 4). However, in water with pH values this low, CNT and fCNT exhibit poor dispersion [10, 11]. To utilize the electrocatalytic property of CNT or fCNT and the bioactive nature of CS in exploring the applications for the pair, such as its application in modifying the working electrode in a biosensor device [12–21], CNT or fCNT has to be well-dispersed in CS because this property is crucial to biosensor performance. Thus, this dispersion has to be examined prior to the preparation of an excellent CNT/CS- or fCNT/CS-modified electrode for a sensor. CS exhibits film-forming abilities, and its film properties depend on the acidic aqueous solutions that are used to cast the films. For the ultimate goal of using CNT/CS or fCNT/CS to modify the working electrode in a sensor device, we began by examining the dispersions of CNT and fCNT in CNT/CS and fCNT/CS films that were cast from four different acidic aqueous solutions. Cyclic voltammetry (CV) was then performed to explore the electrocatalytic activities of the films as a function of CNT treatment conditions, fCNT contents, and acid types that were used to cast the nanocomposite films. Amperometric H_2O_2 detections using these film-modified electrodes were also examined, and the detection sensitivities were correlated with the electrocatalytic activities of these films.

2. EXPERIMENTAL

2.1 Materials

The CNT was synthesized by thermal chemical vapor deposition at 750 °C for 1 h. Acetylene was used as a carbon source, and ferrocene was used as a catalyst in a quartz tube furnace in our laboratories [11]. The deposited product was examined by transmission electron microscopy (TEM, JEOL JEM-100CXII at 300 kV), and consisted of multi-walled CNT. The synthesized CNT was approximately 20 nm to 30 nm in diameter and about 1 μm in length. CS, which was supplied by the Charming & Beauty Corporation (Taiwan), had a viscosity average molecular weight of 350,000 and a degree of deacetylation of approximately 80%.

2.2 CNT Functionalization

The acid treatments were performed to functionalize the CNT. In a typical experiment, 40 mg of pulverized CNT was added to 300 mL of a sulfuric and nitric acid mixture at a volume ratio of 3:2. The sulfuric and nitric acid mixture was sonicated in a water bath for 2 h at room temperature, and was then heated at 60 °C and 80 °C for 3 and 2 h, respectively. This process was performed to obtain the functionalized CNT, fCNT and fCNT1, respectively. At the end of the acid treatment, each mixture was diluted with deionized water and filtered through a 0.2 μm pore-sized membrane. The product on the membrane was washed with deionized water several times, and vacuum-dried at 70 °C for 1 d. The formation of a COOH group on the fCNT was verified by Fourier transform infrared spectrophotometer (FTIR, Perkin Elmer, Spectrum One). The contents of the COOH group were quantitatively determined by titration as previously described [11], and the values were 2.51 and 158.50 mmol/100 g for the acid-treated CNT at 60 °C for 3 h (i.e., fCNT) and 80 °C for 2 h (i.e., fCNT1), respectively [22].

2.3. Preparations of the CNT/CS-, fCNT/CS-, and fCNT1/CS-modified electrodes

The CS aqueous solutions were prepared by adding 2 % wt acetic acid, formic acid, hydrochloric acid, or citric acid. A desired amount of the nanotube fine powders, pristine (CNT) or functionalized (fCNT and fCNT1), was dispersed in 10 mL of the CS aqueous solutions by sonicating the solution for 3 min to obtain dispersions of CNT/CS, fCNT/CS, and fCNT1/CS, each at 1/10, 2/10, and 3/10 in weight ratio. An amount of 20 μL each of CNT/CS, fCNT/CS, and fCNT1/CS dispersion was cast on a prepolished glassy carbon electrode (GCE) and dried at room temperature for 1 d for cyclic voltammetric analysis. The dispersions were also cast on an indium tin oxide (ITO) glass for morphologic analysis. The morphologic analysis was conducted using a field emission scanning electron microscopy (FESEM, HITACHI S-4800) at an operating voltage of 3 keV. The GCE has a circled active area with 3 mm in diameter.

2.4 Electrochemical measurements

A potentiostat (CH611D, CH Instruments) was used to perform CV analyses at 25 °C in a conventional three-electrode system with GCE as the working electrode, a platinum wire as an auxiliary electrode, and Ag/AgCl/3M KCl as a reference electrode. The phosphate buffer solution (PBS, 0.1 M) with a pH of 7.4 was used as the background electrolyte in all experiments. The CNT/CS, fCNT/CS, and fCNT1/CS nanocomposite films on the GCE were prepared by casting the CNT/CS, fCNT/CS, and fCNT1/CS solutions of four acids (citric acid, HCOOH, CH_3COOH, and HCl). The films were allowed to dry in ambient air for 24 h. The modified GCE was immersed in 5 mM potassium ferricyanide [$K_3Fe(CN)_6$] (reagent grade, Nihon Shiyaku Industries) used as a probe to investigate the electrocatalytic behavior of the CNT/CS, fCNT/CS, and fCNT1/CS films. CV was conducted between -0.7 and 0.7 V at a scan rate of 50 mV/s.

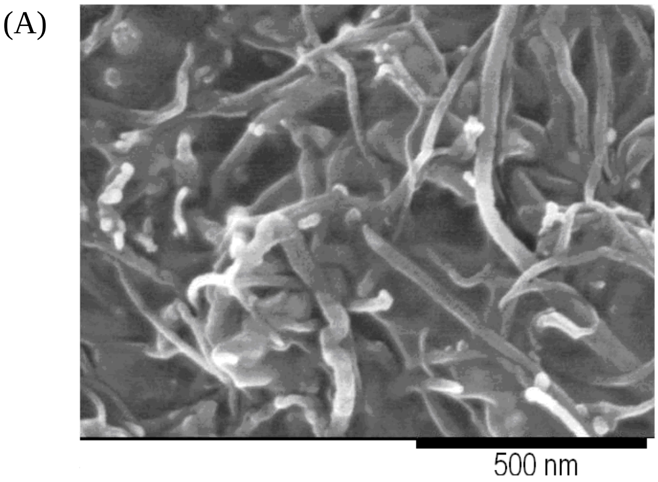
2.5 Amperometric analyses

The CNT/CS film- and fCNT/CS film-modified GCE was investigated for its biosensing sensitivity and linear range by determining the H_2O_2 concentrations. Amperometric analyses were conducted by successive additions of 2 mM H_2O_2 at every 50 s in 10 mL of 0.1 M phosphate-buffer (pH 7.4) aqueous solution at an operating potential of 0.4 V.

3. RESULTS AND DISCUSSION

3.1 Cyclic voltammetric analyses of CS-, CNT/CS-, fCNT/CS-, and fCNT1/CS-modified GCE prepared from CH_3COOH aqueous solutions

CS cannot be dissolved in neutral water, but can be dissolved in water with pH < approximately 4. This pH value can be obtained by adding acid to water. The dissolution in water with low pH was due to NH_2 protonation in CS to form NH_3^+, which weakens H-bondings in molecules, especially among CS molecules. The CNT is made up of graphene, which is non-polar in nature, and exhibits poor dispersion in water over a wide pH range ($1 \leq pH \leq 13$) [11]. The acid-treated CNT (i.e., the COOH-functionalized CNT, denoted by fCNT for acid-treated CNT at 60 °C for 3 h, and fCNT1 for acid-treated CNT at 80 °C for 2 h) exhibits an improved dispersion in water, but does not have long-term stability in aqueous solutions with pH 1 and 3 [22]. The fCNT and fCNT1 aggregations in water with a very low pH can be attributed to the fully protonated carboxylic acid groups on fCNT and fCNT1, which leads to the formation of intermolecular hydrogen bonding. CS can improve the dispersions of CNT, fCNT, and fCNT1 in acidic aqueous solutions [22], although CNT, fCNT, and fCNT1 are poorly dispersed in aqueous solutions with a very low pH [11]. In a previous study [23], the CS macromolecules containing NH_3^+ in acidic aqueous solutions can be adsorbed on the surfaces of CNT, fCNT, and fCNT1 surfaces. Therefore, CS can function as a cationic surfactant to stabilize CNT, fCNT, and fCNT1 by forming stable aqueous dispersions [12].



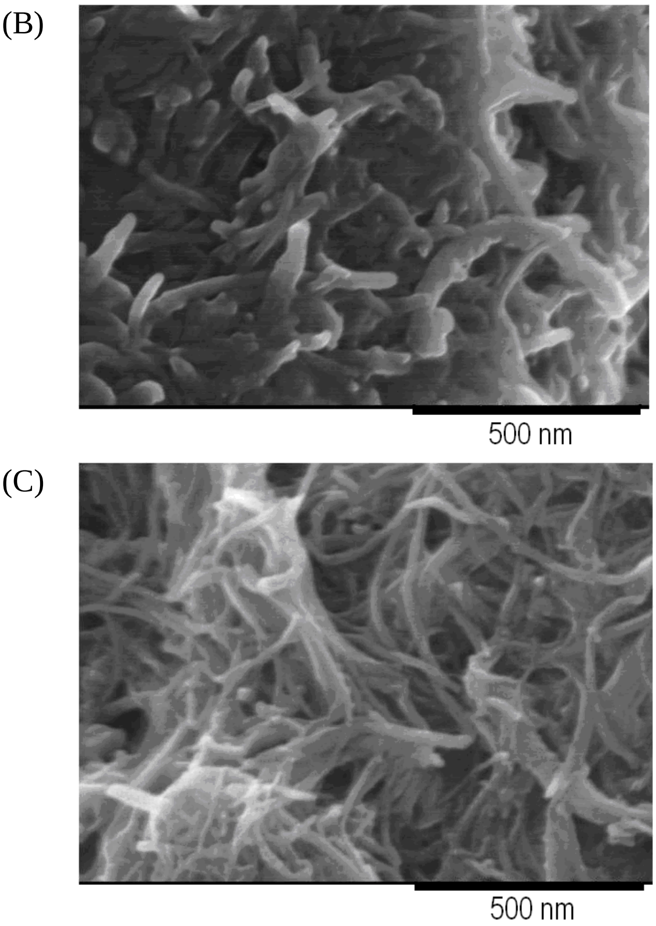


Figure 1. FESEM images of (A) CNT/CS 1/10, (B) fCNT/CS 1/10, and (C) fCNT1/CS 1/10 films cast from the CH_3COOH aqueous solution.

In cast films, CS was found to coat the nanotubes, and the coating on fCNT was more pronounced than on CNT, as shown in Figures 1B and 1A, respectively. Compared with fCNT (Figure 1B), CS does not fully coat fCNT1 (Figure 1C) because fCNT1 have smaller diameters than fCNT. fCNT1 has a smaller diameter than fCNT because the former undergoes a relatively severe acid treatment than the latter.

Figure 2 shows the CV readings recorded from $Fe(CN)_6^{3-/4-}$ aqueous solutions with a pH of 7.4 at bare GCE, CS-, CNT/CS-, fCNT/CS-, and fCNT1/CS-modified GCEs, which were prepared from CH_3COOH aqueous solutions. As shown in Figure 2, the pure CS film-modified GCE exhibited a decreased anodic peak current for the oxidation of $Fe(CN)_6^{3-/4-}$ as a probe compared with the bare GCE because CS functions as an insulator, which hinders electron transfers. Compared with bare GCE and CS-modified GCEs, the fCNT/CS-modified GCE exhibited a relatively high anodic peak current, which indicates that fCNT electrocatalyzed the oxidation of $Fe(CN)_6^{3-/4-}$. This electrocatalysis can be associated with the conductivity of fCNT and its nanoparticle size, which increase the surface area of the electrode. Figure 2 also shows that the nanotube electrocatalytic activity on $Fe(CN)_6^{3-/4-}$ oxidation depended on the acid-treatment conditions for the nanotubes. The untreated CNT exhibited the lowest anodic peak current, which can be increased when fCNT1 is used and can be further increased when fCNT is used. fCNT (having a COOH content 2.51 mmol/100 g sample) had a higher current than fCNT1 (having a COOH content 158.50 mmol/100 g sample). The acid treatment caused fCNT to be well-dispersed in CS, which allows CS to coat fCNT and leads to an increase in the anodic peak current for probe oxidation. However, over-treated fCNT1 can have damaged structure, which lowers its electrocatalytic activity.

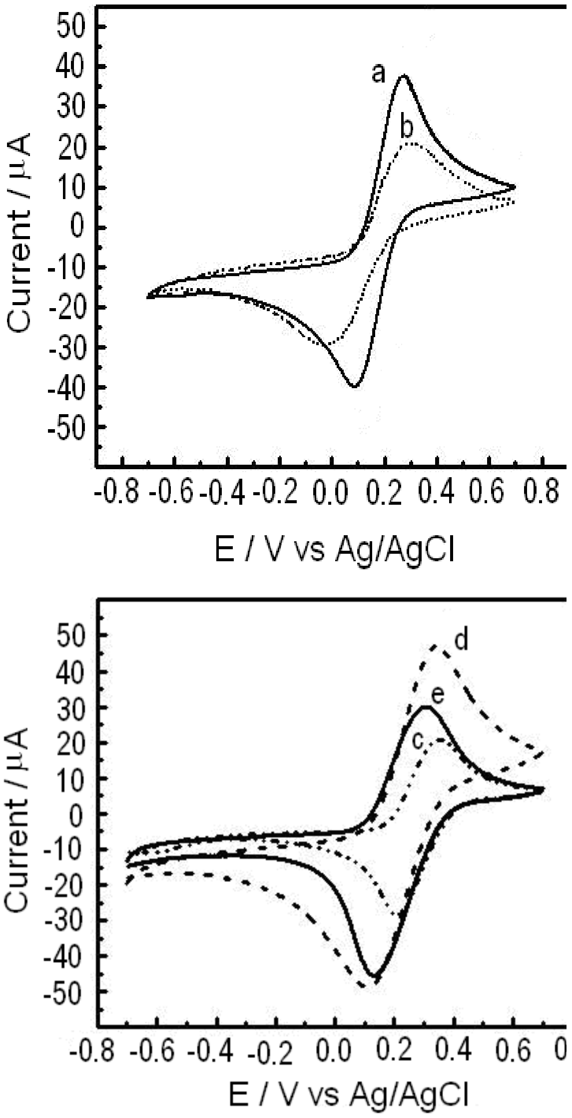


Figure 2. CV data recorded from the 5 mM [$K_3Fe(CN)_6$] and 0.1 M phosphate buffer solutions (PBS, pH 7.4) at (a) bare, (b) CS-modified, (c) CNT/CS 1/10-modified, (d) fCNT/CS 1/10-modified, and (e) fCNT1/CS 1/10-modified GCEs. CS and its nanocomposites were all cast from the CH_3COOH aqueous solution. The CNT, fCNT, and fCNT1 were untreated, acid-treated at 60 °C for 3 h and 80 °C for 2 h, respectively. The scan rate was 50 mV/s.

Figure 3 shows the CV readings recorded at the fCNT/CS-modified GCE in the $Fe(CN)_6^{3-/4-}$ aqueous solution with a pH of 7.4. As shown in Figure 3, the anodic peak current increased by increasing the fCNT content from 1/10 to 2/10 in the fCNT/CS films. However, a further increase in the fCNT content decreased the anodic peak current, which indicates that the optimal ratio of fCNT/CS was 2/10 to obtain a high electrocatalytic activity.

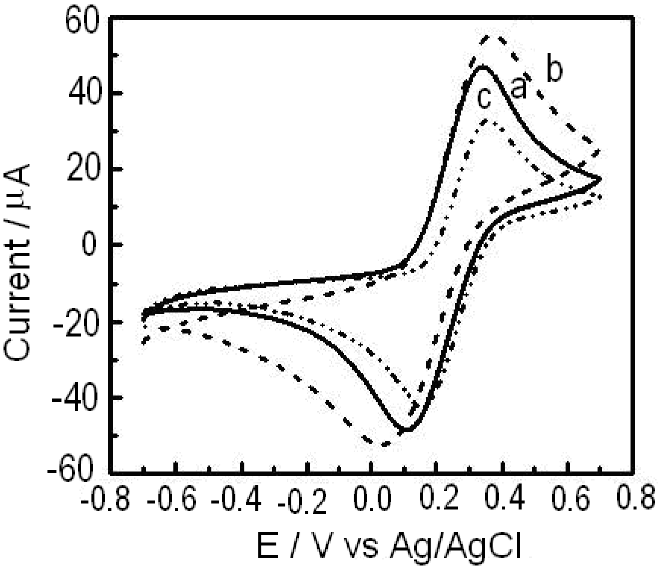
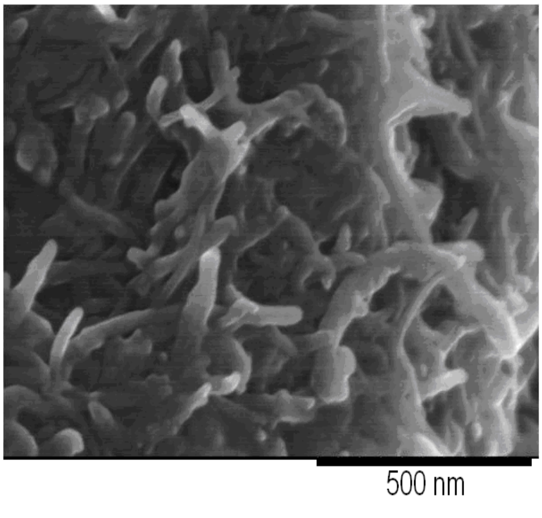


Figure 3. CV data recorded at (a) fCNT/CS 1/10-, (b) fCNT/CS 2/10-, and (c) fCNT/CS 3/10-modified GCEs in 5 mM [$K_3Fe(CN)_6$] and 0.1 M PBS (pH 7.4). These nanocomposites were cast from the CH_3COOH aqueous solution. The scan rate was 50 mV/s.

The electrocatalytic activity that did not monotonically increase with increasing CNT content over a specific content range was also previously observed [1]. This electrocatalytic activity is associated with the amount of CS on the fCNT surface that did not monotonically increase with increasing fCNT/CS ratio. As shown in Figure 4, the coating of CS on fCNT in the fCNT/CS 2/10 cast film was more pronounced, whereas the coating of CS on fCNT in the fCNT/CS 3/10 cast film was less pronounced than that on the fCNT in the fCNT/CS 1/10 cast film.

(A)



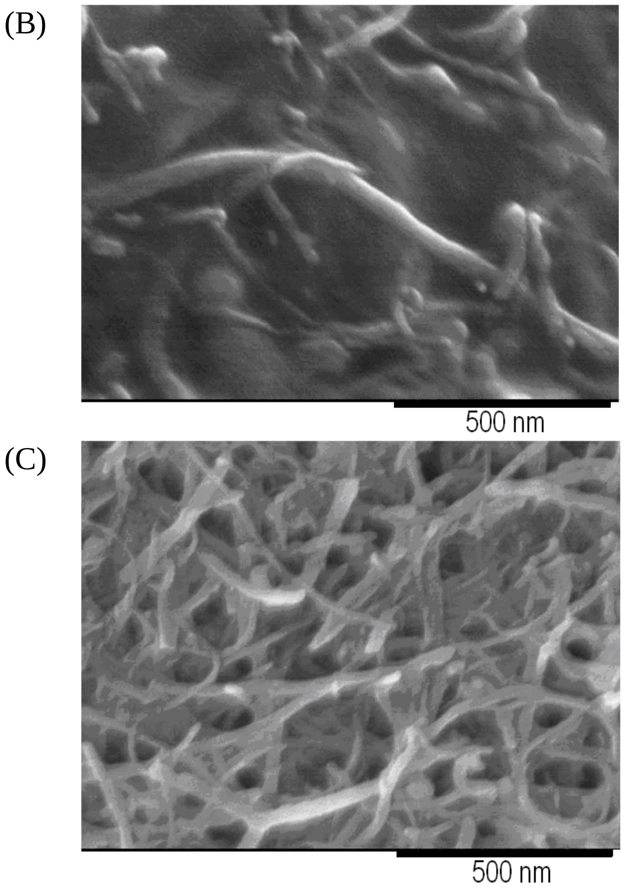


Figure 4. FESEM images of (A) fCNT/CS 1/10-, (B) fCNT/CS 2/10-, and (C) fCNT/CS 3/10 films cast from the CH_3COOH aqueous solution.

The CS coating could interact with the probe (that is, the analyte), which exhibits the fCNT electrocatalytic capacity in the fCNT/CS film. The less pronounced coating of CS on fCNT in the fCNT/CS 3/10 cast film (Figure 4C) can be attributed to a high fCNT concentration present in the cast film, such that the concentration of CS was not enough to coat the entire fCNT.

3.2 Amperometric analyses of fCNT/CS films cast from CH_3COOH aqueous solutions

Figure 5A shows the amperometric response of fCNT/CS 1/10-, fCNT/CS 2/10-, and fCNT/CS 3/10-modified GCEs, which were cast from CH_3COOH aqueous solutions, upon successive additions of 2 mM H_2O_2 every 50 s at an operating potential of +0.4 V. Figure 5B shows the responding anodic currents at 0.4 V as a function of H_2O_2 concentrations. As shown in Figure 5B, the increasing current rates with H_2O_2 concentrations, namely, the sensing sensitivities, were 184, 304, and 99 nA/(mM cm^2) for fCNT/CS 1/10-, fCNT/CS 2/10-, and fCNT/CS 3/10-modified GCEs, respectively. These values were obtained by taking into account the circled active area with a diameter of 3 mm on the GCE. The sensitivity trend was fCNT/CS 2/10 > 1/10 > 3/10, which is consistent with the high-to-low order of the electrocatalytic activity for these three nanocomposites (Figure 3). Although the H_2O_2 detection limit was not determined in this study, the anodic current at 0.4 V for H_2O_2 detection linearly increased with increasing H_2O_2 concentration in the range of 2 mM to 12 mM for all three nanocomposites.

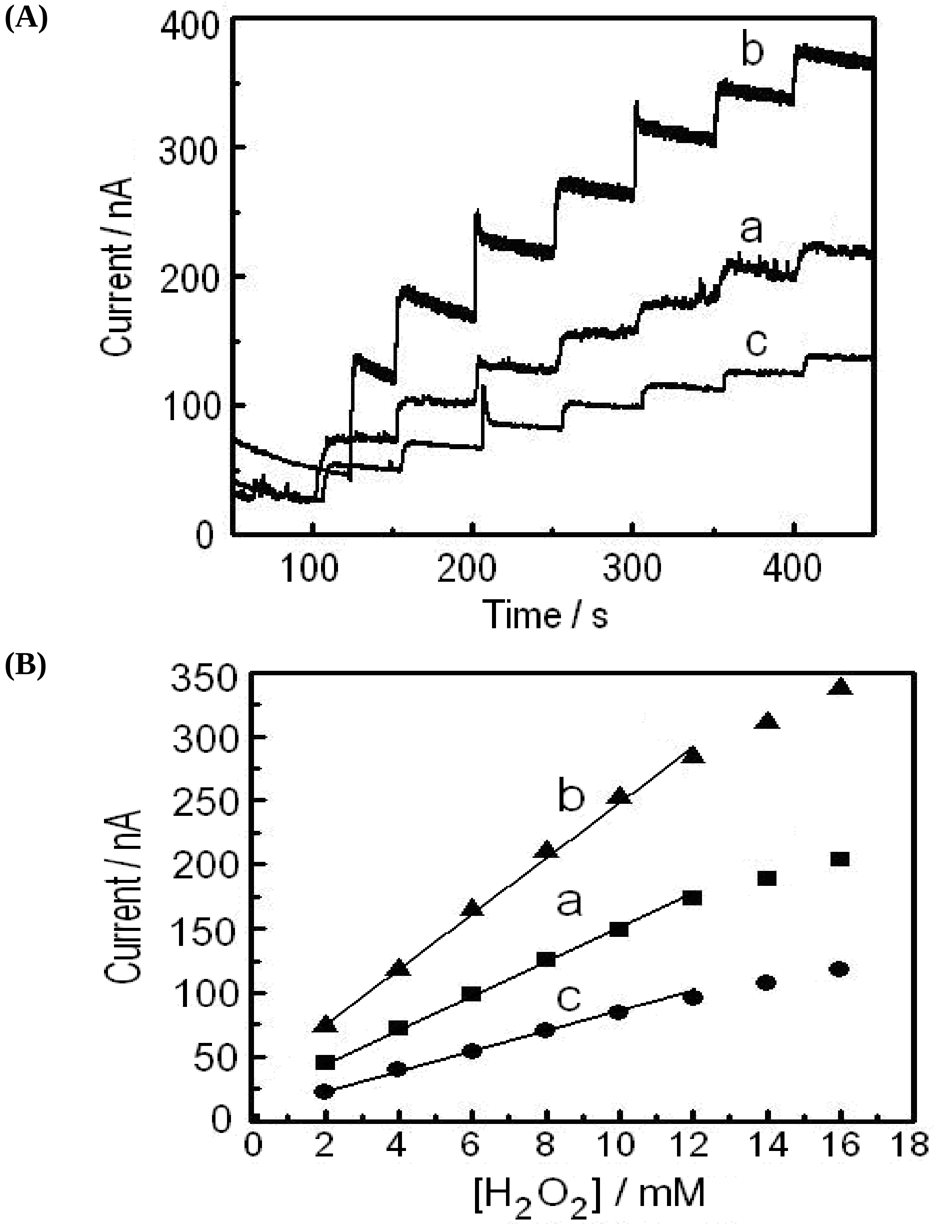


Figure 5. (A) Amperometric responses of (a) fCNT/CS 1/10-, (b) fCNT/CS 2/10-, and (c) fCNT/CS 3/10-modified GCEs, which were cast from the CH_3COOH aqueous solution, upon successive additions of 2 mM H_2O_2 every 50 s in 0.1 M PBS (pH 7.4) at an operating potential of +0.4 V, and (B) the linear regression analysis of the H_2O_2 concentration-current curves.

3.3 Cyclic voltammetric analyses of the fCNT/CS-modified GCE prepared from different acidic aqueous solutions

Aside from CH_3COOH aqueous solutions, CS can also be dissolved in HCOOH, HCl, and citric acid aqueous solutions [22]. All four acidic aqueous solutions, each containing 2 % weight of each acid, have pH values < pH 3.0. CS also improved the dispersions of CNT, fCNT, and fCNT1 in HCOOH, HCl, and citric acid aqueous solutions, although CNT, fCNT, and fCNT1 were poorly dispersed in aqueous solutions with a very low pH. As shown in Figure 2, the fCNT/CS 1/10 nanocomposite exhibited the highest electrocatalytic activity among the three nanocomposites studied. Therefore, the fCNT/CS 1/10 nanocomposite was used to investigate the effects of the acidic solution types used to prepare the nanocomposite on the electrocatalytic behavior and the H_2O_2 detection.

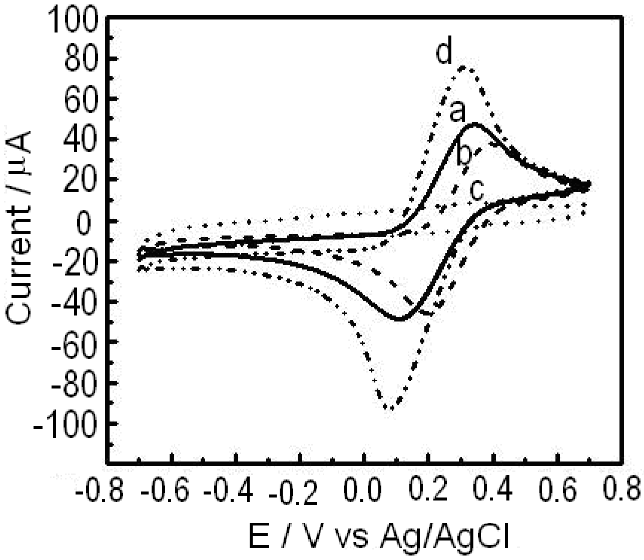
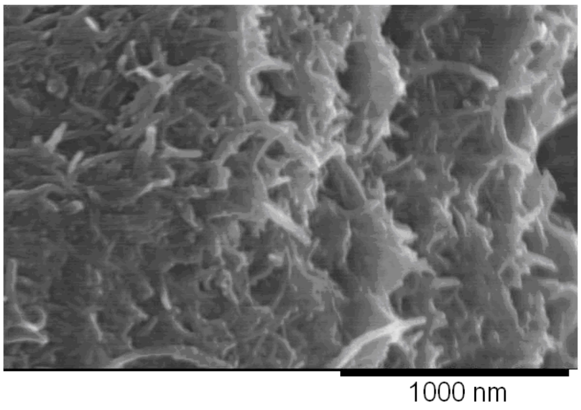


Figure 6. CV data recorded at the fCNT/CS 1/10-modified GCE in 5 mM [$K_3Fe(CN)_6$] and 0.1 M PBS (pH 7.4). The fCNT/CS 1/10 nanocomposites were cast from (a) CH_3COOH, (b) HCOOH, (c) HCl, and (d) citric acid. The scan rate was 50 mV/s.

Figure 6 shows the CV readings recorded at the fCNT/CS 1/10-modified GCE, which was cast from the four acidic aqueous solutions, in 5 mM $Fe(CN)_6^{3-/4-}$ aqueous solutions with a pH of 7.4. As shown in Figure 6, the fCNT/CS 1/10 film cast from the HCl aqueous solution did not exhibit an anodic current peak for $Fe(CN)_6^{3-/4-}$ oxidation. The fCNT/CS films cast from the CH_3COOH and HCOOH aqueous solutions exhibited roughly similar anodic peak currents.

(A)



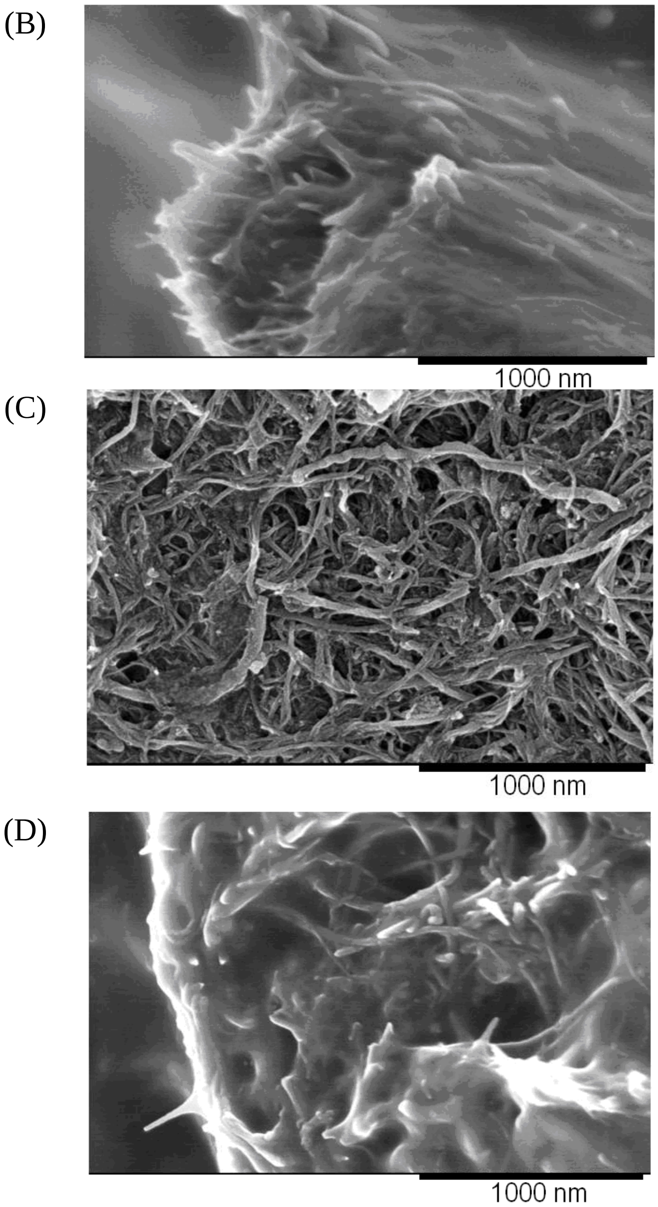


Figure 7. FESEM images of the fCNT/CS 1/10 films cast from (A) CH_3COOH, (B) HCOOH, (C) HCl, and (D) citric acid aqueous solutions.

The fCNT/CS film cast from the citric acid solution exhibited the highest anodic peak current among the four acidic solutions studied. The anodic peak current is associated with the uniformity of fCNT dispersion in the fCNT/CS cast films, with the best from the citric acid, the worst from the HCl, and the moderate from the CH_3COOH and HCOOH. From the FESEM images in Figure 7, the fCNT in fCNT/CS 1/10 film cast from the HCl aqueous solution was very exposed and very little CS can be found. Thus, the film formation was very poor and obtaining a free standing film was difficult. Figure 8 shows a broken film that was cast from the HCl aqueous solution. The fCNT/CS 1/10 film cast from the citric aqueous solution had more CS on fCNT (Figure 7D). Thus, the film formation was good and more interactions occurred between the film and the analyte, which result in a high anodic peak current in the curve in Figure 6.

The schematic diagram in Figure 9 explains the formation of free-standing films in the fCNT/CS dispersion in citric acid and acetic acid aqueous solutions, whereas the same result was not observed in the HCl aqueous solution.

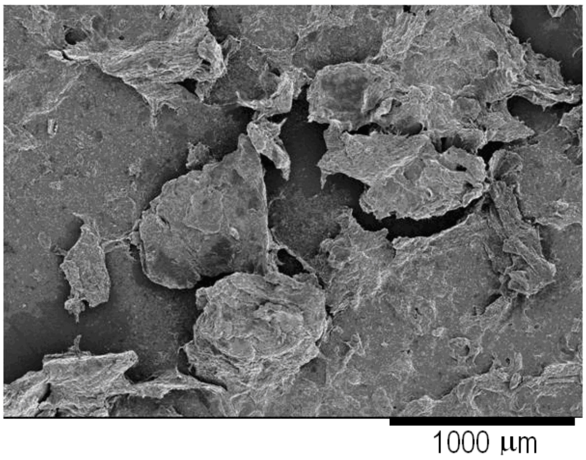


Figure 8. FESEM image of the fCNT/CS 1/10 film cast from the HCl aqueous solution.

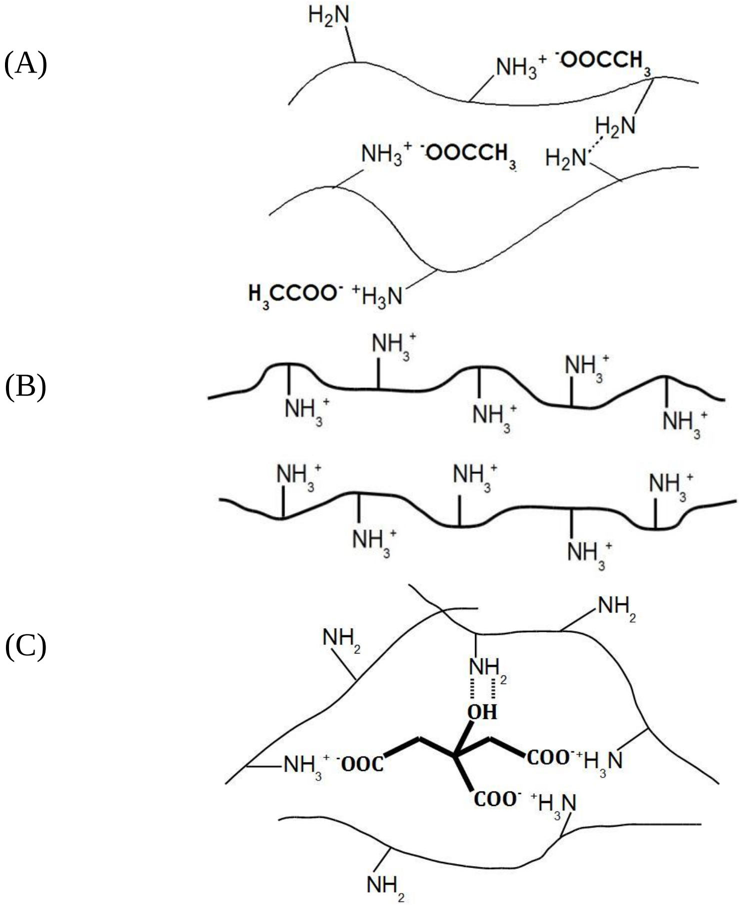


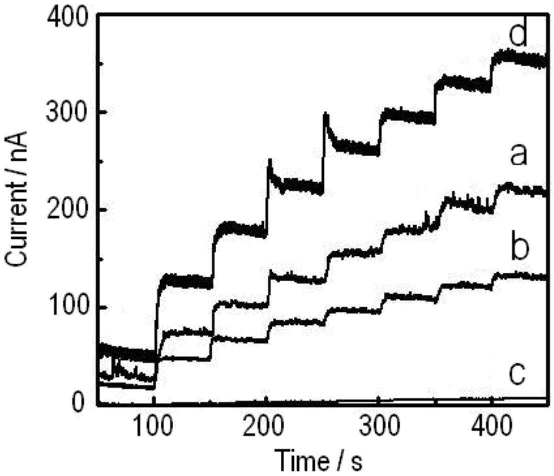
Figure 9. Schematic diagrams of CS molecules in (A) CH_3COOH, (B) HCl, and (C) citric acid aqueous solutions.

As shown in Figure 9, citric acid has three COOH groups and one OH group, and these four groups can all form H-bonds with the NH_2 group of CS. Thus, strong intermolecular interactions and entanglements are produced, which lead to a very uniform fCNT/CS cast film. The COOH group can be ionized in water to release protons for the protonation of the NH_2 groups on CS to form NH_3^+, which expulsively separates from the other NH_3^+ groups to facilitate the dissolution of CS in water. The formed ion pairs can give rise to ionic interactions in CS to produce strong intermolecular interactions and entanglements in CS. In addition, the OH group of citric acid can form H-bonds with NH_2 and OH of CS to produce intermolecular interactions and entanglements into CS, which lead to the formation of a film with moderate mechanical strength. In the HCl solution, the NH_2 group of CS can be protonated at a high level because of a high proton content from the strong acid. Thus, the leftover NH_2 content (i.e., the intact NH_2) on CS is very low for H-bonding. The cast film, as shown in Figure 8, with a low mechanical strength was therefore obtained although the fCNT/CS is well-dispersed in the HCl aqueous solution. In CH_3COOH and HCOOH solutions, which are weak acids, the content of the protonated NH_3^+ groups on CS was fewer than that in the HCl solution. More intermolecular interactions and entanglements in CS were observed in CH_3COOH and HCOOH solutions than in the HCl solution, which led to an improvement in the film formation in the two carboxylic acids. In conclusion, an acidic aqueous solution that can produce an fCNT/CS film with an improved uniformity in the fCNT dispersion can exhibit an improved electrocatalytic activity.

3.4 Amperometric analyses of the fCNT/CS films cast from the different acid aqueous solutions

Figure 10A shows the amperometric response of the fCNT/CS 1/10-modified GCE, which were cast from the four different acidic aqueous solutions, upon successive additions of 2 mM H_2O_2 every 50 s at an operating potential of +0.4 V. Figure 10B shows the responding anodic currents at 0.4 V as a function of H_2O_2 concentrations, which were obtained from Figure 10A. As shown in Figure 10B, the increasing current rates with H_2O_2 concentrations, namely, the sensing sensitivities, were 184, 106, 7, and 290 nA/(mM cm^2) for the fCNT/CS 1/10-modified GCE prepared from CH_3COOH, HCOOH, HCl, and citric acid, respectively.

(A)



(B)

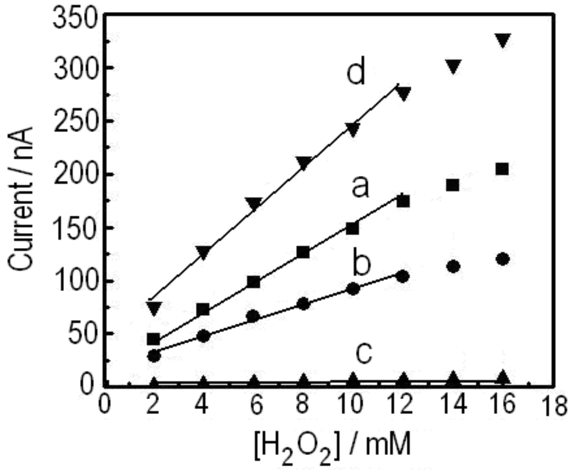


Figure 10. (A) Amperometric response of fCNT/CS 1/10-modified GCE, which were cast from (a) CH_3COOH, (b) HCOOH, (c) HCl, and (d) citric acid, upon successive additions of 2 mM H_2O_2 every 50 s in 0.1 M PBS (pH 7.4) at an operating potential of +0.4 V, and (B) the linear regression analysis of the H_2O_2 concentration-current curves.

These values were obtained by taking into account the circled active area with a diameter of 3 mm on the GCE. The fCNT/CS 1/10-modified GCE prepared from the citric acid solution exhibited the highest H_2O_2 detection sensitivity at 290 nA/(mM cm^2), whereas the one prepared from the HCl solution exhibited negligible H_2O_2 detection sensitivity at 7 nA/(mM cm^2). The H_2O_2 detection sensitivity (Figure 10B) increased with increasing electrocatalytic activity of the fCNT/CS 1/10 film cast from acidic solutions (Figure 6). Although the H_2O_2 detection limit was not determined in this study, the anodic current at 0.4 V for H_2O_2 detection linearly increased with increasing H_2O_2 concentration in the range of 2 mM to 12 mM for all four acidic aqueous solutions from which the fCNT/CS 1/10 film was prepared.

4. CONCLUSIONS

The CV data revealed that the fCNT in the fCNT/CS cast films exhibited electrocatalytic activity to the redox reactions of $Fe(CN)_6^{3-/4-}$ as a probe. The electrocatalytic capability depend on whether the nanotube was acid-treated (fCNT) or untreated (CNT), on the fCNT content, and on the acid type used to prepare the fCNT/CS films. The condition of the acid treatment should be appropriate to achieve optimal electrocatalytic capacity for the fCNT/CS nanocomposite film. The acid treatment resulted in an improved nanotube dispersion in the CS cast film, which leads to an increased electrocatalytic capacity for the nanocomposite film. The optimal fCNT content in the CS cast film resulted in an excellent electrocatalytic capacity for the film. Among the four acids used to cast the fCNT/CS nanocomposites, citric acid exhibited the best fCNT dispersion in the CS film, which resulted in the highest electrocatalytic activity. On the other hand, HCl resulted in brittle fCNT/CS films and negligible electrocatalytic activity. Amperometric analysis results revealed that a higher electrocatalytic activity could lead to a higher sensitivity for the detection of H_2O_2.

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