

# Noncovalent nanohybrid of ferrocene with single-walled carbon nanotubes and its enhanced electrochemical property

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## Abstract

The nanoscale hybridization adduct of ferrocene (Fc) and single-walled carbon nanotubes (SWNTs) was prepared and it shows high stability and greatly enhanced sensitivity toward hydrogen peroxide reduction. The electrochemical and hydrolysis results suggest that the strong  $\pi$ – $\pi$  stacking interaction between Fc and SWNTs play a critical role for its enhanced electrochemical catalytic property. The combined advantages from SWNTs and Fc and the cooperative effect due to this  $\pi$ – $\pi$  stacking could make this adduct an excellent choice for ultrasensitive electrochemical detections.

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## 1. Introduction

Since the discovery of single-walled carbon nanotubes (SWNTs) in 1993, their potential applications have attracted considerable attention due to their unique mechanical, chemical and electrical properties. As an intrinsic nanowire and molecular wire with high conductance and exceptional current-carrying capacity [1,2], SWNTs make such a material an ideal candidate for chemical and biochemical sensing. They greatly enhance electron transfer when used as electrode materials in electrochemical reactions. Li et al. studied cyclic voltammetric behavior of SWNT films functionalized with carboxylic acid groups and found that the SWNT-modified electrode showed highly electrocatalytic behavior toward several biomolecules [3]. Using Nafion as a solubilizing agent for carbon nanotubes (CNTs) [4], Wang et al. prepared hydrogen peroxide and NADH biosensors. Also, the high ratio with large surface area of SWNTs has advantage to immobilize probe molecules with high density via either covalently

bonding or van der Waals interaction to offer controllable means tethering molecular species. For example, Davis et al. found that via noncovalent adsorption, proteins and enzymes can be immobilized on SWNTs and show enhanced electrochemical detection capability [5]. Also Wang et al. have shown that SWNTs can amplify electrochemical signals through carrying numerous nanoparticles [6] and enzyme tags [7].

Many systems with aromatic rings and SWNTs via noncovalent bonding have been pursued in the past few years. For example, using pyrene as an anchor by  $\pi$ – $\pi$  stacking interaction, Dai et al. developed a method to immobilize proteins and small biomolecules noncovalently on SWNTs [8]. Kobuke et al. succeeded in synthesizing stable porphyrin/diaminopyrene/SWNT composites by a noncovalent wrapping approach [9]. Nakashima et al. prepared porphyrin functionalized carbon nanotubes in solution via the physical adsorption of porphyrins onto the sidewall of the nanotubes [10]. Ferrocene (Fc) is a well-known substance as a mediator in the electrochemical and biosensor detections, such as in the detection of hydrogen peroxide [16,17], dopamine [18] and ascorbic acid [19], and recently has been widely studied as a label and/or redox active specie for DNA detection [11–15]. Therefore, it would be

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important to study the interactions between Fc and SWNTs and their hybrid electron transfer behaviors for electrochemical detections. Recently, using SWNTs covalently functionalized with a Fc derivative, Guldi et al. have studied the intramolecular electron transfer behavior between SWNTs and Fc species [20]. Here, we report a novel noncovalent nanohybrid formed by Fc with SWNTs and the dramatically enhanced reduction response of hydrogen peroxide at the electrode modified with this adduct.

## 2. Experimental

### 2.1. Preparation of hybridization adducts

The SWNTs were prepared by our direct current arc-discharge method [21], purified using nitric acid and cut using mixture acid as reported in the literature [22]. The functionalization reaction was processed by suspending purified SWNTs (1 mg) and Fc (20 mM) in a mixture (10 mL) of water and DMF (1:4). The reaction mixture was mechanically agitated and immersed in a laboratory sonication bath alternatively at room temperature for 4 days. The hybridization adduct (Fc–SWNTs) was collected with centrifugation and washed thoroughly by several sonication and centrifugation cycles using DMF. Similar adduct Fc–COOH–SWNTs was prepared in the same manner for a comparison and model study (see below).

### 2.2. Characterization of hybridization adducts

The hybridization adduct of Fc and SWNTs was characterized by Transmission electron microscopy (TEM) equipped with energy-dispersive X-ray spectroscopy (EDS) capabilities (FEI, TECNAI-20), Fourier transform infrared spectroscopy (FT-IR) (BRUKER, Tensor 27) and Raman spectroscopy (RENISHAW, inVia).

Electrochemical studies were performed with a micro-computer-based electrochemical analyzer (LANLIKE, LK98BII). The working electrode, the Ag/AgCl reference electrode and the platinum counter electrode were inserted into the 10 mL cell through holes in its Teflon cover. The hybridization adduct of Fc–SWNTs was first suspended to 0.02–0.03 mg/mL in DMF using an ultrasonic bath. Then 6  $\mu$ L of suspension was cast on the surface of glassy carbon (GC,  $\Phi = 4$  mm) electrode. The electrochemical measurements were carried out in 4 mM H<sub>2</sub>O<sub>2</sub>, and a phosphate buffer (0.05 M, pH 7.4) and KCl (0.1 M) were used as the supporting electrolyte media. The electrochemical behaviors of the bare GC and SWNTs modified electrodes were also performed similarly as comparison.

### 2.3. Hydrolysis of hybridization adducts

Fc–SWNTs adduct was sonicated in ultrasonic bath in neutral (pH 7.0) and alkaline aqueous solutions (NaOH, pH 12.0) for 1 h, respectively. The solid products were col-

lected by centrifugation and then washed with centrifugation and ultrasonication using double distilled water for several cycles. Finally, the product was re-suspended to 0.02–0.03 mg/mL in double distilled water and was cast on the surface of GC electrode. The electrochemical measurements were performed similarly as above.

The hybridization adduct of Fc–COOH and SWNTs was characterized similarly.

## 3. Results and discussion

### 3.1. Microscopy confirmation of the hybridization adduct

Fig. 1 shows the typical TEM images, photo and the corresponding EDS data of the purified SWNTs and SWNTs hybridization adduct with Fc. Clear and numerous Fc assembling on the surface of SWNTs bundles were observed from the TEM image of Fc–SWNTs adduct, which was not observed from that of purified SWNTs. The congregated particles of Fc were about 1.2–2.5 nm. Yellowish-black colored transparent solution of Fc–SWNTs strongly suggests that Fc is immobilized on the surface of SWNTs and this immobilization also make SWNTs more soluble in organic solvents such as DMF. Similar observation has been reported for other aromatic systems such as porphyrin [10]. The presence of the expected iron in the adduct structures was also confirmed by EDS spectra with  $\sim 4.9$  wt% Fe in Fc–SWNTs.

Fig. 2 shows the Raman spectra of Fc–SWNTs, purified SWNTs and Fc. An up-shifted and broadened peak at 1130  $\text{cm}^{-1}$ , which did not appear in the spectrum for the purified SWNTs, is observed for the adduct. Compared with the sharp peak at 1095  $\text{cm}^{-1}$  of Fc, we argue that this up-shift and broadening is caused by the strong interaction between Fc and SWNTs.

### 3.2. Electrochemical property of the hybridization adducts

We investigated the electrochemical property of the adduct of Fc and SWNT and found it shows much enhanced electrochemical catalytic property toward hydrogen peroxide redox reaction. As many reports indicated before [4,23], SWNTs modified GC electrode shows enhanced reduction currents around  $-0.48$  V for hydrogen peroxide compared to the bare GC electrodes (Fig. 3) and slightly less response was observed for the GC electrode modified with 6  $\mu$ L 20 mM Fc (not shown). However, Fc–SWNTs adduct modified GC electrode exhibits significantly enhanced current response starting around 0.0 V and peaks at  $-0.26$  V associated with the hydrogen peroxide reduction. This significantly lowering of the hydrogen peroxide overvoltage and enhanced redox reaction current features are important for a sensitive and convenient low-potential amperometric detection.

In order to further understand the interaction and electron transfer mechanism between Fc and SWNTs, we used the similar hybrid of Fc–COOH with SWNTs as a model

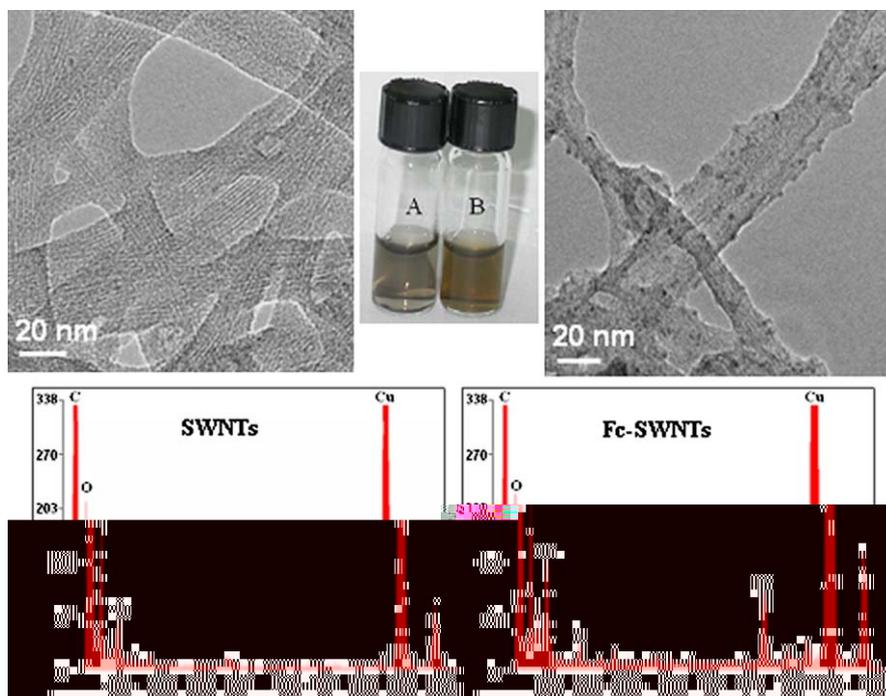


Fig. 1. TEM images with EDS for purified SWNTs (left) and Fc-SWNTs adduct (right). The photo is for (A) purified SWNT solely and (B) Fc-SWNTs in DMF.

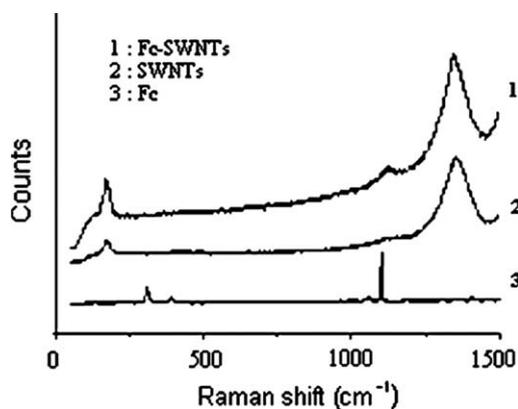


Fig. 2. The Raman spectra of Fc-SWNTs, purified SWNTs and Fc, respectively, excited at 514 nm.

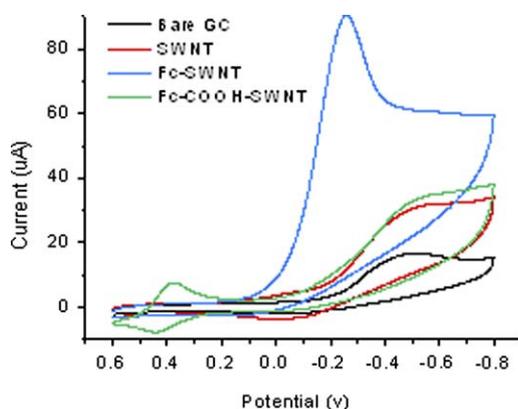


Fig. 3. Cyclic voltammograms of bare GC, SWNTs, Fc-SWNTs, Fc-COOH-SWNTs modified GC electrodes in 4 mM  $\text{H}_2\text{O}_2$ , 0.05 M phosphate buffer (pH 7.4), 0.1 M KCl at a 50 mV/s scan rate.

for a model study. As shown in Fig. 3, the hybrid of Fc-COOH with SWNTs displays a very different electrochemical behavior compared with Fc-SWNTs, though the loading of Fc and Fc-COOH on SWNTs was similar as estimated with the EDS. In fact, the cyclic voltammogram curve of Fc-COOH-SWNTs modified GC electrode is quite similar to that of bare SWNT modified electrode and the only difference is that a new pair of redox peaks from Fc-COOH between 0.36 and 0.45 V was found for this Fc-COOH-SWNTs modified GC electrode. These results indicate that Fc-COOH-SWNTs behaves electrochemically as a simple mixture of Fc-COOH and SWNTs and no cooperation effect for electron transfer or catalytic

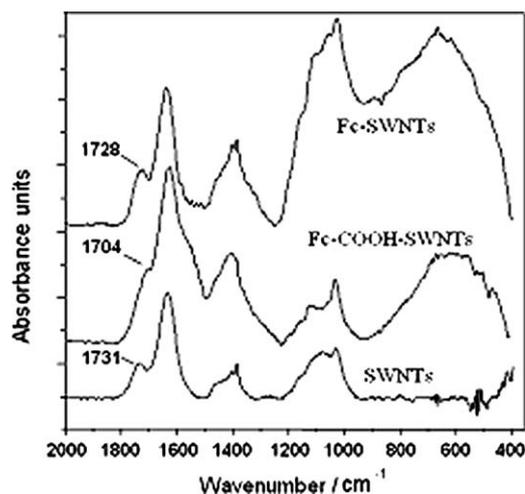


Fig. 4. The FTIR spectra of purified SWNTs before and after hybridization.

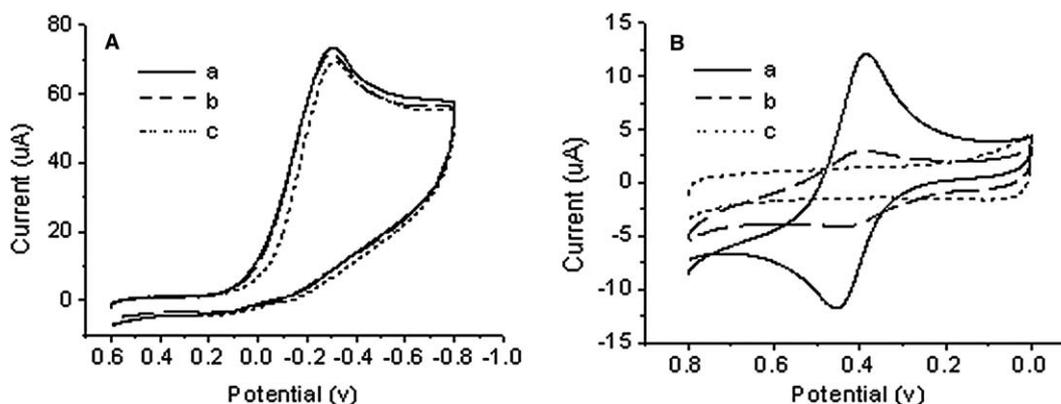


Fig. 5. (A) Cyclic voltammetry curves of Fc-SWNTs modified GC electrode (a) Fc-SWNTs modified electrode after 1 h sonicating in aqueous (pH 7.0) (b) and Fc-SWNTs modified electrode after 1 h sonicating in aqueous (pH 12.0) (c) in 4 mM H<sub>2</sub>O<sub>2</sub>. (B) Cyclic voltammetry curves of Fc-COOH-SWNTs modified GC electrode (a), Fc-COOH-SWNTs modified electrode after 1 h sonicating in aqueous (pH 7.0) (b) and Fc-COOH-SWNTs modified electrode after 1 h sonicating in aqueous (pH 12.0) (c) in 0.05 M phosphate buffer (pH 7.4), 0.1 M KCl at a 50 mV/s scan rate.

capability exist as which was observed for Fc-SWNTs. Therefore, the excellent electrocatalytic property of Fc-SWNTs modified electrode may be attributed to the cooperation effect due to the  $\pi$ - $\pi$  stacking between Fc and SWNTs and this cooperation interaction could dramatically accelerate the heterogeneous redox reaction through the direct electron transfer between the electrode and redox species in solution. The only structural difference due to the -COOH group between Fc and Fc-COOH make us suspect that the possible hydrogen bonding between the -COOH groups on the surface of purified SWNTs and Fc-COOH would make the  $\pi$ - $\pi$  stacking between Fc-COOH with SWNTs more difficulty. This is further supported with the results that the similar electrochemical studies show the behaviors of the annealed SWNTs with Fc-COOH is very similar with that of Fc with purified SWNTs. The hydrogen bonding between Fc-COOH and SWNTs is also supported by the FTIR spectra, shown in Fig. 4. The peak at 1731 cm<sup>-1</sup> corresponding to  $\nu$  (C=O) in the spectrum of purified SWNTs indicates the presence of -COOH group formed during the purification of SWNTs [3]. The C=O peak (1728 cm<sup>-1</sup>) for Fc-SWNTs adduct is at almost the same position as that of purified SWNTs, but it shifts to a lower position at 1704 cm<sup>-1</sup> for Fc-COOH-SWNTs hybridization adduct, indicating the hydrogen bonding between the two groups of -COOH. Similar result has been observed for the nanohybrid materials formed by polystyrene latex nanospheres and SWNTs via hydrogen bonding [24].

### 3.3. The stability of the hybridization adducts

Since most SWNT modified materials for biosensor applications involve further functionalization under sonication, we thus tested the stability of Fc-SWNTs adduct for further manipulation.

As shown in Fig. 5a, the electrochemical behavior of Fc-SWNT adduct is almost the same before and after sonication in alkaline and neutral aqueous solutions for 1 h.

This result shows that sonication in neutral and alkaline aqueous solutions have no influence on the adduct of Fc and SWNTs, suggesting that the interaction between Fc and SWNTs be strong and stable and Fc immobilized on SWNTs did not break off. Surprisingly, the adduct between Fc-COOH and SWNTs behaved dramatically different. Fig. 5b shows cyclic voltammetry curves of Fc-COOH-SWNTs modified GC electrode in phosphate buffer before and after sonicating in neutral and alkaline aqueous solutions for 1 h. The considerable decrease of the redox currents between 0.36 and 0.45 V indicates sonication can make break off most Fc-COOH from SWNTs in neutral aqueous solutions and entirely in alkaline aqueous solutions due to the acid-base reaction. This result clearly shows that the dominating interaction between Fc-COOH and Fc with SWNTs is different and hydrogen bonding should play a critical role for the adduct of Fc-COOH and SWNTs.

## 4. Conclusions

In this Letter, we have prepared Fc functionalized SWNT adduct via noncovalent bonding. The excellent electrochemical catalytic property and stability could make it a useful avenue for preparing CNT-based biosensors. The dramatically enhanced electrocatalytic action toward hydrogen peroxide is believed due to the accelerated electron transfer prompted by the stable and strong  $\pi$ - $\pi$  stacking interaction between Fc and SWNTs. Thus, this noncovalent Fc functionalized SWNT adduct, without impairing SWNT properties otherwise in covalent bonding structures, could provide a convenient yet stable electrode material to allow a marked decrease in the overvoltage and low-potential amperometric detection for electrochemical sensing when hydrogen peroxide is involved, such as in the detection of glucose, oxalate, phenylalanine and so on. Additional experiments are underway for gaining further insights into the  $\pi$ - $\pi$  stacking interaction between Fc and SWNTs.

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