

# Fabrication of Silver Hexacyanoferrate and Functionalized MWCNT with Poly(3,4-ethylenedioxythiophene) Hybrid Film Modified Electrode for Selectively Determination of Ascorbic Acid And Hydrazine

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The silver hexacyanoferrate functionalized multi-walled carbon nanotubes (AgHCF-*f*-MWCNT) composite has been prepared by a simple chemical method. The poly(3,4-Ethylenedioxythiophene) (PEDOT) was electrodeposited on the AgHCF-*f*-MWCNT modified glassy carbon electrode (GCE). The fabricated composite modified electrode was characterized by electrochemical impedance spectroscopy. The AgHCF-*f*-MWCNT/PEDOT hybrid composite electrode exhibits a good response towards hydrazine. The cyclic voltammetry and amperometric techniques were used for the determination of hydrazine. The fabricated composite electrode showed a high sensitivity (62.169  $\mu\text{A}/\mu\text{Mcm}^2$ ) and fast response time (3 s). In addition, the AgHCF-*f*-MWCNT/PEDOT/GCE exhibited a distinct advantages such as simple preparation, specificity, stability and reproducibility.

**Keywords:** Silver hexacyanoferrate, Poly 3,4-Ethylenedioxythiophene, Electrocatalysis, hydrazine

## 1. INTRODUCTION

Metal hexacyanoferrates (MHCFs) have shown interesting redox chemistry which is accompanied by the changes in their electrochromic, ion exchange, and electrocatalytic properties [1, 2]. In particular, the MHCF have a great interest in the materials science due to use of electropolymerization of polynuclear MHCF films.

Use of polynuclear MHCs has led to the synthesis of conducting polymers [3, 4]. The polymer film-coated electrodes can be differentiated from other modification methods because of their adsorption and covalent bonding, in that they usually involve multilayers as opposed to the monolayers that are frequently encountered for the latter methods. Conductive/electroactive polymers, such as polypyrrole, polyaniline, polythiophene, etc., have prepared through an electropolymerization procedure and used as modifiers for the construction of chemically modified electrodes [5-8].

Among various conducting polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) is a relatively new and well-known p-conjugated conducting polymer of the polythiophene class. Recently, PEDOT has received much attention because of its high electrical conductivity, moderate band gap, and excellent environmental stability [9-13]. These unique properties of PEDOT can be applied in many fields, such as chemical and biochemical sensors, antistatic coatings, electrically switchable windows, and polymer light-emitting diodes [14-16]. In recent reports, MHCs such as NdHCF [17], AgHCF [18], SnHCF [19], CoHCF [20], NiHCF [21], CuHCF [22], etc., have also received much attention in many fields because of their special properties and potential applications [23-25].

PEDOT has been widely investigated as an electronically conducting polymer. It can be easily electrodeposited onto a surface by the electrooxidation of its monomer [26-29]. The PEDOT film in its oxidized form has been found to have high conductivity and stability at physiological pH [30, 31]. MnHCF can be prepared as an electroactive thin film of a Mn substrate in the presence of ferricyanide anions [32, 33]. It is considered to be an attractive material for electrode surface modification owing to its well-defined, reversible, and reproducible responses in supporting electrolytes [34].

Hydrazine and its derivatives are well-known compounds due to their extensive industrial applications such as corrosion inhibitors, rocket propellant, photographic chemicals, plastic blowing agents, explosives, herbicides and catalysts [35-37]. Despite their extensive applications, hydrazine and its derivatives are extremely toxic and carcinogenic [38]. Several analytical methods such as high-performance liquid chromatography [39], spectrophotometric methods [40], flow injection analysis [41], gas chromatography-mass spectrometry and potentiometry [42] have been applied for the determination of hydrazine. However, most of these methods involve time-consuming procedures and require tedious protocols, whereas electrochemical techniques are simple, fast, sensitive and selective. Nevertheless, bare electrodes suffer from serious drawbacks such as high over potential and electrode fouling. Therefore chemically modified electrodes have been explored to overcome the shortcomings of bare electrodes. Even though numerous modified electrodes were reported for the electrochemical determination of hydrazine, only very few offered trace level detection of hydrazine and hence fabrication of highly sensitive modified electrodes for the trace level determination of hydrazine are greatly desirable.

## 2. EXPERIMENTAL

### 2.1. Materials

AgNO<sub>3</sub> were purchased from Wako (Japan). 3,4-ethylenedioxythiophene (EDOT) was purchased from Sigma-Aldrich (USA). Double distilled deionized (DDDI) water was used to prepare

all solutions. The PEDOT film was prepared by electrochemical polymerization, using 0.1 M H<sub>2</sub>SO<sub>4</sub> as supporting electrolyte. The buffer solution of AgHCF-*f*-MWCNT-PEDOT modified electrode tests was prepared using 0.1 M KCl as supporting electrolyte (pH 1.5). Pure nitrogen was passed through all the experimental solutions. All the chemicals used were of analytical grade.

## 2.2. Apparatus

All electrochemical experiments were performed using a CHI 1205a potentiostat (CH Instruments, USA). The Bioanalytical Systems (BAS) glassy carbon electrode (GCE; diameter 0.3 cm, exposed geometric surface area 0.07 cm<sup>2</sup>; Bioanalytical Systems, Inc., USA) was used. A conventional three-electrode system was used; it comprised an Ag/AgCl (saturated KCl) reference electrode, PEDOT/GCE, AgHCF/GCE and AgHCF-*f*-MWCNT/PEDOT/GCE modified electrodes, and a bare GCE electrode, as working electrodes, and a platinum wire as counter electrode. Electrochemical impedance studies (EIS) were performed using a ZAHNER impedance analyzer (Germany).

## 2.3. Preparation of AgHCF-*f*-MWCNT/PEDOT/GCE modified electrode

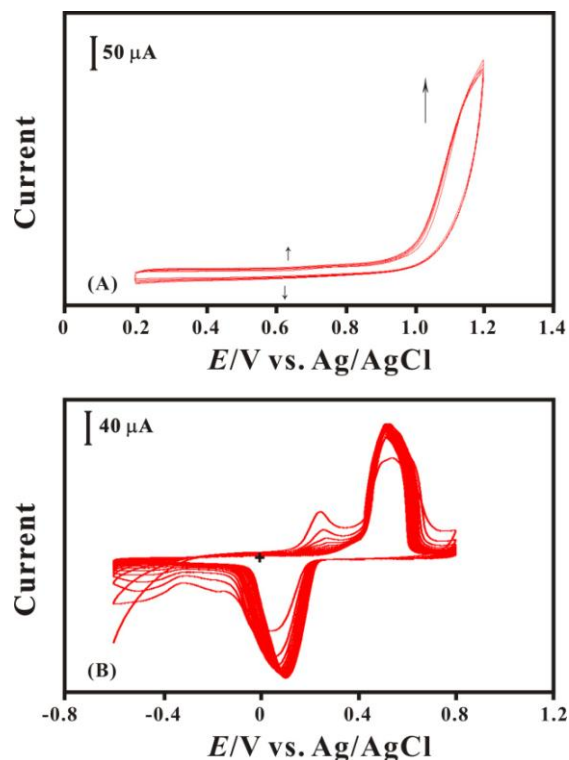
### 2.3.1 Functionalization of MWCNT

As purchased MWCNT was hydrophobic in nature and could not produce a stable and homogeneous dispersion in aqueous media. The MWCNT was pre-treated and functionalized by following the procedures as reported early [43,44]. Briefly, 150 mg of MWCNT was heated at 350°C for 2 h and cooled to room temperature. Then it was ultrasonicated for 4 h in concentrated HCl to remove impurities like amorphous carbon and metal catalysts. It was filtered and washed thoroughly with deionized water until the pH was reached 7. The filtered MWCNT was dried at 100 °C. The carboxylation of MWCNT was done by sonicating the pre-treated MWCNT in a mixture of sulfuric acid and nitric acid in 3:1 ratio for 6 h. It was then washed several times with distilled water until the pH was neutral.

### 2.3.2 Preparation of AgHCF-*f*-MWNCT/PEDOT modified electrode

The AgHCF-*f*-MWNCT modified electrode was fabricated by dissolving of 4 mM AgNO<sub>3</sub> and 1 mM K<sub>3</sub>Fe(CN)<sub>6</sub> in the solution containing hydrochloric acid and nitric acid (v/v % = 3:1) with the help of ultrasonication for 1 h. After the successive sonication, the product was washed until the pH is 7 and dried in an air oven at 50 °C. The fabricated AgHCF-*f*-MWNCT was redispersed in alcohol solution (1mg/ml). To fabricate the AgHCF-*f*-MWCNT/PEDOT modified electrode, 4 μL of AgHCF-*f*-MWCNT solution was drop coated on the pre-cleaned GCE and dried at a room temperature. The fabricated AgHCF-*f*-MWCNT modified GCE was electrodeposited at a cyclic potential sweeping of 0.2 – 1.3 V in the electrolyte solution containing 0.01 M EDOT and 0.1 M H<sub>2</sub>SO<sub>4</sub>, and the results are shown in Fig. 1.

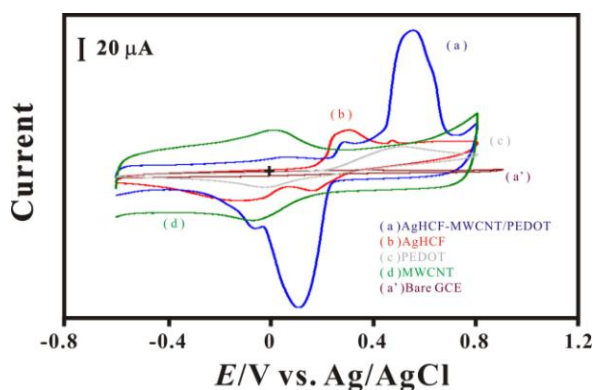
In order to evaluate the stability of the modified electrode, the 20 consecutive CV cycles were performed. As shown in Fig. 1(B), the fabricated AgHCF-*f*-MWCNT/PEDOT/GCE was showed the high stability even after the 20 cycles. The strong interaction between the *f*-MWCNT and Ag makes the fabricated electrode more stable.



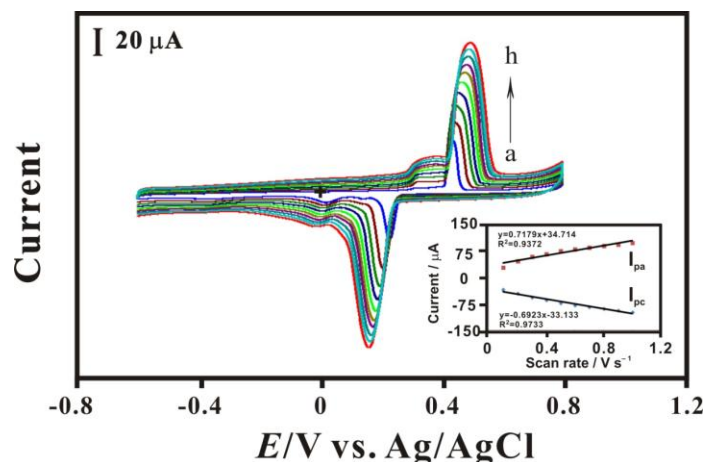
**Figure 1.** (A) CVs obtained by 4 consecutive cycles in 0.1 M H<sub>2</sub>SO<sub>4</sub> solution containing 0.01 M EDOT at a scan rate of 50 mV/s. (B) 20 consecutive cycles of AgHCF-*f*-MWCNT/PEDOT modified electrode in PBS solution at a scan rate of 50 mV/s.

### 3. RESULTS AND DISCUSSION

#### 3.1. Electrochemical characterization of AgHCF-*f*-MWCNT/PEDOT/GCE electrode



**Figure 2.** CVs of (a) AgHCF-*f*-MWCNT/PEDOT, (b) AgHCF, (c) PEDOT film, (d) MWCNT modified, (a') bare GCE in 0.1 M KCl (pH 1.5). Scan rate = 100 mV/s.



**Figure 3.** Results of different scan rate studies of AgHCF-PEDOT modified GCE in 0.1 M PBS (pH 7). Scan rate in the range from 0.01 to 0.1 V/s.

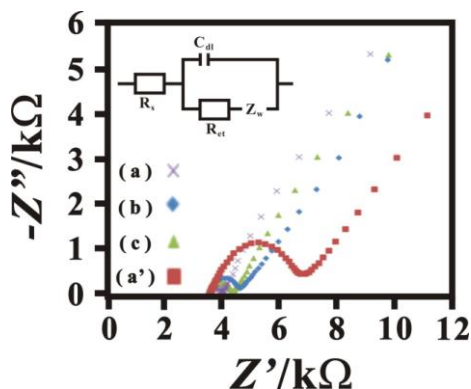
The electrochemical properties of different modified electrode were investigated using CV. In Fig. 2, the CV curves (a), (b), (c), (d), and (a') indicate the AgHCF-*f*-MWCNT-PEDOT/GCE, AgHCF/GCE, PEDOT/GCE, MWCNT, and bare GCE electrode, respectively. Electro-catalytic response of AgHCF-*f*-MWCNT/PEDOT/GCE modified electrode shows the highest current among other modified electrodes.

Fig. 3 exhibits the different scan rate results of AgHCF-*f*-MWCNT/PEDOT/GCE modified electrode in the range 0.01–0.1 V/s. As expected, the CVs of the AgHCF-*f*-MWCNT/PEDOT/GCE modified electrode exhibited a single redox couple, with an anodic peak at +0.49 V and a cathodic peak at +0.16 V versus Ag/AgCl/KCl. The inset in Fig. 3 shows the plot of the AgHCF-*f*-MWCNT/PEDOT/GCE modified electrode signal of the anodic and cathodic peak current vs. scan rate. The linear increase in the anodic and cathodic peak currents of AgHCF-*f*-MWCNT/PEDOT/GCE modified electrode according to the scan rate revealed that the film revealed typical characteristics of surface controlled thin-layer electrochemical behavior. The corresponding linear regression equations were  $I_{pa} (\mu\text{A}) = 0.7179v (\text{V/s}) + 34.714$ , with  $R^2 = 0.9372$ , and  $I_{pc} (\mu\text{A}) = -0.6923v (\text{V/s}) - 33.133$ , with  $R^2 = 0.9733$  for anodic, and cathodic peak currents, respectively.

### 3.2. EIS and Analysis

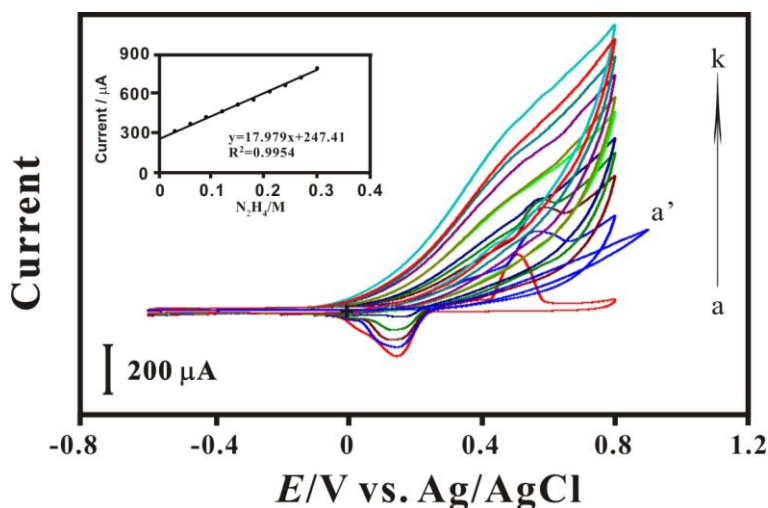
The electrochemical activity of the AgHCF-PEDOT/GCE was examined using the EIS technique. The complex impedance can be presented as a sum of the real  $Z'$  ( $\omega$ ) and imaginary  $Z''$  ( $\omega$ ) components that originate mainly from the resistance and capacitance of the cell. From the shape of an impedance spectrum, the electron transfer kinetics and diffusion characteristics can be determined. The respective semicircle parameters correspond to the electron transfer resistance ( $R_{et}$ ) and the double layer capacity ( $C_{dl}$ ) nature of the modified electrode. As shown in Fig. 4, curve (a) indicates the Nyquist plot of AgHCF-*f*-MWCNT/PEDOT/GCE, (b) AgHCF/GCE, (c) AgHCF/PEDOT/GCE and (a') bare GCE in the presence of 5 mM  $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$  (1:1) in KCl (pH 7) solution. The AgHCF-*f*-MWCNT/PEDOT/GCE shows a very small depressed semicircle arc with an interfacial resistance due to the electrostatic repulsion between the charged surface and probe molecule

$\text{Fe}(\text{CN})_6^{3-/4-}$ . This depressed semicircle arc ( $R_{ct} = 42 \text{ (Z}'/\Omega)$ ) clearly indicates the lower electron transfer resistance behavior compared to that of the AgHCF/GCE ( $R_{ct} = 187 \text{ (Z}'/\Omega)$ ), AgHCF-PEDOT ( $R_{ct} = 71 \text{ (Z}'/\Omega)$ ) and bare GCE ( $R_{ct} = 320 \text{ (Z}'/\Omega)$ ).



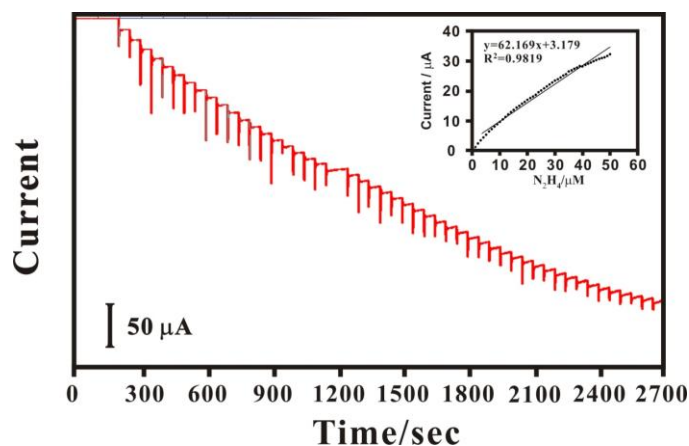
**Figure 4.** Electrochemical impedance spectra curves of (a) AgHCF-*f*-MWCNT/PEDOT/GCE, (b) AgHCF, (c) AgHCF/PEDOT and (a') bare GCE in 0.1 M KCl (pH 7) solution containing  $5 \times 10^{-3}$  M  $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$  (1:1).

### 3.3 Voltammograms of hydrazine oxidation at AgHCF-*f*-MECNT/PEDOT/GCE modified electrode



**Figure 5.** CVs of AgHCF/PEDOT/GCE in 0.1 M PBS (pH 7.0) with different concentration of  $\text{N}_2\text{H}_4$  at (a) 0M, (b) 0.003 M, (c) 0.006 M, (d) 0.009 M, (e) 0.012 M, (f) 0.015 M, (g) 0.018 M, (h) 0.021 M, (i) 0.024 M, (j) 0.027 M and (k) 0.03 M. (a') is bare GCE with 0.3 M  $\text{N}_2\text{H}_4$ . Scan rate is 100 mV/s.

The electrocatalytic reaction of  $\text{N}_2\text{H}_4$  was examined at AgHCF-*f*-MECNT/PEDOT/GCE modified electrode with the potential range of -0.6V – 0.8. V and the scan rate of  $100 \text{ mV s}^{-1}$  in 0.1 M PBS (pH 7.0). Fig. 5 shows the cyclic voltammograms of AgHCF/PEDOT/GCE examined in different concentrations of hydrazine from 0.00 M to 0.03 M. Compared with bare electrode (curve a') examined in the concentration of  $\text{N}_2\text{H}_4$  at 0.03M, the AgHCF-*f*-MWCNT/PEDOT/GCE exhibited a high sensitivity of  $25.684 \mu\text{A}/\mu\text{Mcm}^2$  for  $\text{N}_2\text{H}_4$ .

3.4. Amperometric Response of hydrazine Electrocatalysis by AgHCF-*f*-MECNT/PEDOT/GCE Film

**Figure 6.** Typical amperometric curve obtained for a AgHCF/PEDOT/GCE in 0.1 M PBS buffer solution (pH 7) at 0.3 V with rotation speed of 1000 rpm. Successive additions of hydrazine in the range from 0.1 to 4.4 mM ( $s/n = 3$ ). The inset figure shows the corresponding calibration plot with the concentration range of N<sub>2</sub>H<sub>4</sub> from 10 to 50 M.

Fig. 6 shows the amperometric responses of sequential additions of standard hydrazine (each 10 M) tested by AgHCF-PEDOT/GCE in 0.1 M PBS buffer solution (pH 7) with a rotating speed of 1000 rpm and an  $E_{app}$  of 0.3 V. It was found wide linear dependence on the hydrazine concentration (inset of Fig. 6). For standard hydrazine detection (as shown in Fig. 6), the sensitivity of AgHCF-*f*-MECNT/PEDOT/GCE was  $62.169 \mu\text{A } \mu\text{M}^{-1} \text{ cm}^{-2}$  and the linear range spans the concentration of catechin from 1 to 50 M with a correlation coefficient of 0.9819. The modified electrode was found a lowest concentration detection limit of  $10 \mu\text{M}$  with a signal-to-noise ratio of 3.

#### 4. CONCLUSIONS

AgHCF-*f*-MECNT/PEDOT/GCE hybrid film has been successfully electrodeposited on GCE. The EIS results concluded that PEDOT greatly improved the conductance of the modified electrode. The AgHCF/PEDOT hybrid film modified electrode displays a linear response in the range of 10 to 50 M hydrazine with a correlation coefficient of 0.9819. The detection limit was found to be 10 M and the response time was 3 s. This new method can be applied for the electroanalysis of hydrazine.

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