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A Study of Copper(II) Hexacyanoferrate-PEDOT Films and Their Sensitivity for Ascorbic Acid and Acetaminophen

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The conducting polymer (PEDOT) modified electrode was used to investigate the formation of copper(II) hexacyanoferrate by adjusting molar ratio of ferricyanide and copper(II) chloride with 20 scan cycles of 0 — 1 V. Three film types of copper(II) hexacyanoferrate/PEDOT have been successfully prepared and discussed using PEDOT film modified electrodes in $[K_3Fe(CN)_6]:[CuCl_2]$ = 1:1, 1:5, and 1:10, respectively. The copper(II) hexacyanoferrate/PEDOT films exhibit significant voltammograms and can be classified from Type I to Type III due to their different CuHCF content. All of these films exhibit specific fiber-like structure due to the doping of ferricyanide and copper(II) hexacyanoferrate on PEDOT surface. Furthermore, these films could simultaneously determine AA and AP. Particularly, the film with higher CuHCF content could provide much higher sensitivity. The current response can be expressed as $I_{pa1}(\mu A) = 25.93[AA](mM) + 147.2$ ($R^2 = 0.9946$) and $I_{pa2}(\mu A) = 19.79[AP](mM) + 189.6$ ($R^2 = 0.9972$). The linear range is found in $0.18–1.8\times10^{-2}$ M and $0.16–1.6\times10^{-2}$ M for AA and AP, respectively.

Keywords: Copper(II) hexacyanoferrate (CuHCF), poly(3,4-ethylenedioxythiophene) (PEDOT), ascorbic acid (AA), acetaminophen (AP)

1. INTRODUCTION

Metal hexacyanoferrates show interesting redox chemistry that is accompanied by changes in their electrochromic, ion exchange, and electrocatalytic properties. Of particular interest in chemistry and materials science are electropolymerized polynuclear metal hexacyanoferrate films, and in particular, their use in modified electrodes. Use of polynuclear metal hexacyanoferrates has led to the synthesis of conducting polymers [1,2]. 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., were prepared through an electropolymerization procedure and used as modifiers for the construction of chemically modified electrodes [3-5].

Among various conducting polymers, poly(3,4-ethylenedioxythiophene) (PEDOT), which is a relatively new and well-known p-conjugated conducting polymer of the polythiophene class, has received much attention because of its high electrical conductivity, moderate band gap, and excellent environmental stability [6-9]. Moreover, PEDOT thin films can vary from light to dark blue. These unique properties mean that PEDOT can be applied in many fields, such as chemical and biochemical sensors, antistatic coatings, electrically switchable windows, and polymer light-emitting diodes [10-12].

Ascorbic acid (vitamin C, AA), a water-soluble vitamin, is widely present in many biological systems and in multivitamin preparations. AA is commonly used to supplement inadequate dietary intake and as an antioxidant. Its deficiency leads to the development of the well-known syndrome called scurvy. It is administered in the treatment of many disorders, including Alzheimer’s disease, atherosclerosis, cancer, infertility, and in some clinical manifestations of HIV infections. Because of its importance, many modified electrodes have been developed and reported for the electrochemical determination of this compound [13-16]. However, AA is considered to be a major interferent both to an on-line sensor and to an in vivo probe because of a combination of its high concentration and low oxidation potential. The differences in the redox behavior and specific chemical interactions allow one to achieve selectivity for several particular analytes. For example, voltammetric detection of redox-active compounds was used for the detection of ascorbic acid [17-22].

Acetaminophen (*N*-acetyl-*p*-aminophenol or Paracetamol, AP) is a long-established substance, being one of the most extensively employed drugs in the world. It is an antipyretic and analgesic drug commonly used against mild to moderate pain and for reduction of fever. It is also noncarcinogenic and an effective substitute for aspirin for patients who are sensitive to aspirin, and is safe in therapeutic doses. AP is metabolized predominantly in the liver, where it generates toxic metabolites. Overdose ingestions of AP lead to accumulation of toxic metabolites, which may cause severe and sometimes fatal hepatotoxicity and nephrotoxicity, in some cases associated with renal failure. The large-scale therapeutic use of this drug generated the need for the development of fast, simple, and accurate methodologies for the detection of AP, for quality control analysis (in pharmaceutical formulations), and for medical control (in biological fluids such as urine, blood, and plasma) [23-24]. Unfortunately, easy availability has resulted in its increased use in attempted suicides. Hence, the need has arisen for the development of rapid and reliable methods for the determination of AP concentration. Many methods have been used for the determination of AP in pharmaceutical formulations and biological fluids, including titrimetry [25], UV–vis spectrophotometry [26-27], spectrofluorimetry [28], near infrared transmittance spectroscopy [29], and chromatography [30,31]. In addition, electrochemical methods have attracted much attention because of their quick response, high sensitivity, and potential for miniaturization [32-36].

In this report, copper(II) chloride ($CuCl_2$), ferricyanide (FCN), and PEDOT were selected to investigate the film formation of metal hexacyanoferrate/conducting polymer. The electrochemical behaviors and morphology of these films were studied with prepared molar ratio of FCN and copper(II) chloride in $[K_3Fe(CN)_6]$:$[CuCl_2]$ = 1:1, 1:5, and 1:10, respectively. The electropolymerization formation of PEDOT film was first performed on GCE electrodes before studying the electrochemical behavior and morphology of the proposed film. Then, the PEDOT/GCE was transferred to 0.1 M KNO_3 (pH 5.6) solution and the concentration ratio of $CuCl_2$ to FCN was adjusted to form metal hexacyanoferrate/conducting polymer film using repeated cyclic voltammetry. The formed films were classified and recognized by cyclic voltammograms and SEM images. They were compared with bare GCE, PEDOT/GCE, and FCN-PEDOT/GCE at the same time. Furthermore, simultaneous determination of AA and AP by FCN-CuHCF-PEDOT/GCE is also discussed and compared.

2.MATERIALS AND METHODS

2.1. Chemicals

Anhydrous copper(II) chloride ($CuCl_2$) and FCN were purchased from Wako (Japan) and 3,4-ethylenedioxythiophene (EDOT) was purchased from Sigma-Aldrich (USA). Double distilled deionized (DDDI) water was used to prepare all solutions. All chemicals used were of analytical grade. Pure nitrogen was purged through all of the experimental solutions.

2.2. Apparatus

All of the electrochemical experiments were performed using a CHI 1205a electrochemical workstation (CH Instruments, Austin, TX). A conventional three-electrode system, which consists of Ag/AgCl/saturated KCl as the reference electrode, GCE (d = 0.3 cm in diameter) as the working electrode, and platinum wire as the counter electrode, was used for all of the electrochemical experiments. Prior to electrochemical experiments, bare GCE was well polished with aqueous slurries of alumina powder (0.05 μm), using a BAS polishing kit, then rinsed and ultrasonicated in DDDI water. Energy dispersive spectroscopy (EDS) was performed using an Oxford EDS (133 eV (Mn Ka: 5.899 keV)).

3. RESULTS AND DISCUSSION

3.1. Preparation of PEDOT and copper(II) hexacyanoferrate/PEDOT films

The PEDOT film was formed by repeatedly cycling potential at the range of 0–1 V with 20 cycles (scan rate = 0.1 V s^{-1}) in sulfuric solution (pH 1.5). Subsequently, the PEDOT film modified

GCE (PEDOT/GCE) could be further used to prepare copper(II) hexacyanoferrate/PEDOT in different molar ratio of ferricyanide ions and copper(II) ions. To study the film types of copper(II) hexacyanoferrate, the PEDOT/GCE was used and transferred to 0.1 M KNO_3 solution (pH 5.6) containing different molar ratio of ferricyanide ions and copper(II) ions ($[K_3Fe(CN)_6]:[CuCl_2]$ = 1:1, 1:5, and 1:10) to do repeatedly potential cycling of 0–1 V with 20 cycles. Hence, three hybrid films were electrochemically synthesized and discussed with their prepared molar ratio of ferricyanide ions and copper(II) ions.

Based on the repeatedly potential cycling (0–1 V) using PEDOT/GCE in the arranged stoichiometry, the electrochemically synthesized copper(II) hexacyanoferrate/PEDOT films can be classified as Type I, Type II, and Type III corresponding to their prepared molar ratio of ferricyanide ions and copper(II) ions in 1:1, 1:5, and 1:10, respectively. For convenient discussion, these three films would be abbreviated as Type I, Type II, and Type III of copper(II) hexacyanoferrate/PEDOT films for prepared condition of $[K_3Fe(CN)_6]:[CuCl_2]$ = 1:1, 1:5, and 1:10, respectively.

3.2. Characterization of copper(II) hexacyanoferrate/PEDOT films

3.2.1. Cyclic voltammogram of different types of copper(II) hexacyanoferrate/PEDOT films with various scan rate

To study the electrochemical behaviors, the different types of copper(II) hexacyanoferrate/PEDOT films were prepared in different molar ratio of $[K_3Fe(CN)_6]:[CuCl_2]$ = 1:1, 1:5, and 1:10, respectively. They were individually examined in the blank solution by cyclic voltammetry.

Fig. 1A-C individually shows their significant cyclic voltammograms of Type I-III films examined in 0.1 M KNO_3 (pH 5.6). As compared with the voltammetric background of bare electrode and PEDOT modified electrode (a' & b), all these films (presented as symbol "a") have characteristic peaks and thick voltammograms.

They exhibit higher current response than bare GCE or PEDOT/GCE in each case (Fig. 1A-C). For Type I film (Fig. 1A(a)), it has an obvious redox couple 1 ($E^{0'}$ = +0.25 V) relative to that of hexacyanoferrate [37], it means this film has rich ferricyanide doped in PEDOT film so that it shows the sharp redox couple (redox couple 1) similar to ferricyanide in the solution. In addition, it can be seen one small redox couple 2 ($E^{0'}$ = +0.7 V) relative to that of CuHCF [38]. Therefore, the PEDOT film modified electrode (PEDOT/GCE) could be doped by ferricyanide and copper(II) hexacyanoferrate is verified and found the significant redox couples relative to ferricyanide and copper(II) hexacyanoferrate.

As prepared copper(II) hexacyanoferrate/PEDOT film, most of anions ($Fe(CN)_6^{3-}$) and cations (Cu^{2+}) should be spontaneously reacted to generate $CuFe(CN)_6^-$ in the bulk solution (as shown in equation 1). The formed $CuFe(CN)_6^-$ will further dope in PEDOT modified electrode (as shown in equation 2 & 3).

The redox process of copper(II) hexacyanoferrate/PEDOT films can be expressed as equation 4 & 5. Consequently, these films should show similar characteristic peaks even prepared from different molar ratio of ferricyanide ions and copper(II) ions. However, the cyclic voltammograms of these films are not the same.

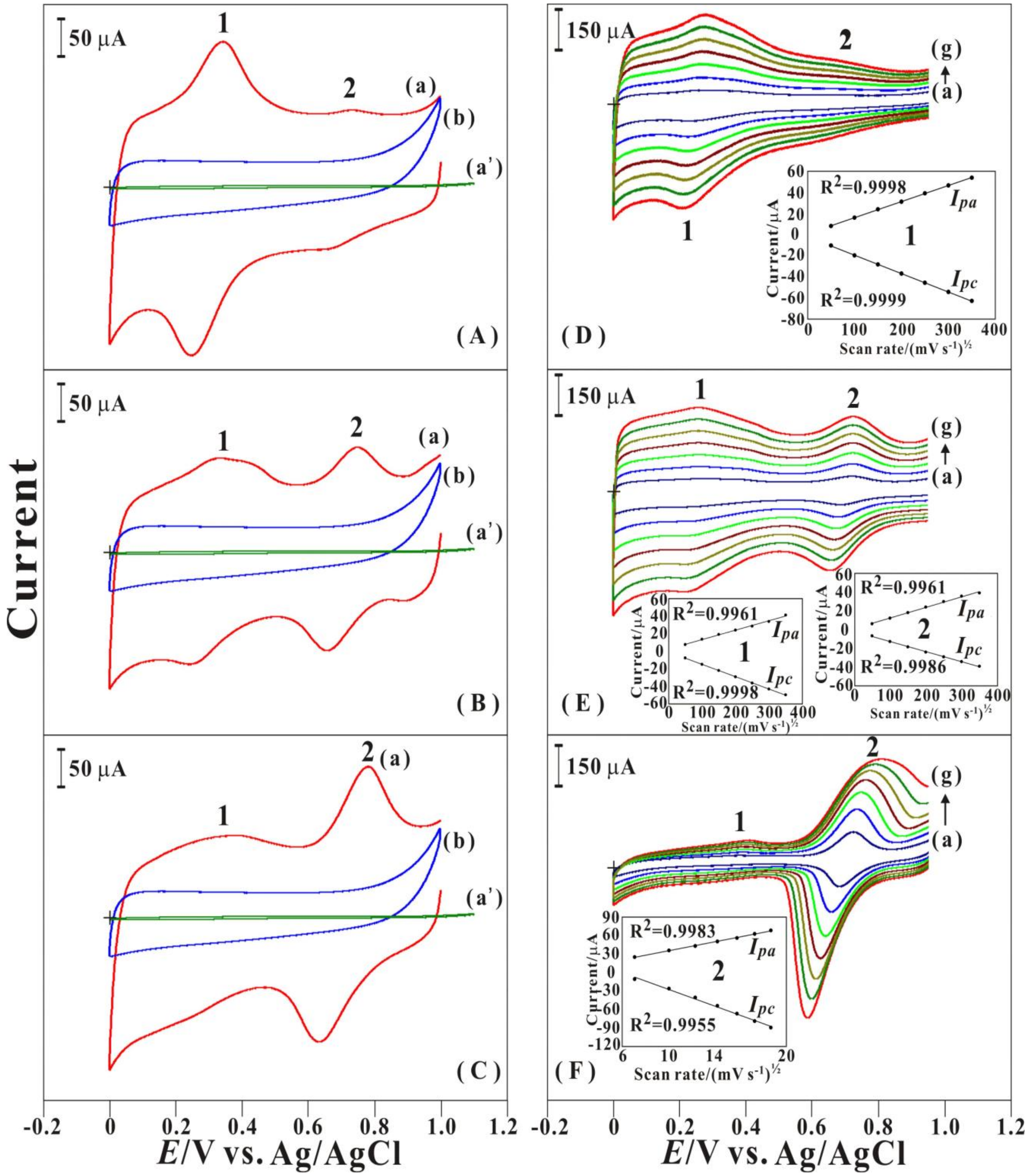


Figure 1. Cyclic voltammograms of three different film types represent in (a) of (A) Type I, (B) Type II, and (C) Type III of FCN-CuHCF-PEDOT/GCE examined in 0.1 M KNO_3 (pH 5.6), all these films are compared with (b) PEDOT/GCE and (a') bare GCE in each case, scan rate = 0.1 V s^{-1}. Cyclic voltammograms of three different film types including (D) type I, (E) type II, and (F) type III of FCN-CuHCF-PEDOT/GCE examined in 0.1 M KNO_3 (pH 5.6) with various scan rate of (a) 50 mV s^{-1}, (b) 100 mV s^{-1}, (c) 150 mV s^{-1}, (d) 200 mV s^{-1}, (e) 250 mV s^{-1}, (f) 300 mV s^{-1}, and (g) 350 mV s^{-1}, respectively.

$$Fe(CN)_6{}^{3-}{}_{(aq)} + Cu^{2+}{}_{(aq)} \rightarrow CuFe(CN)_6{}^{-}{}_{(aq)} \qquad (1)$$

Doping on PEDOT/GCE:

$$Fe(CN)_6{}^{3-}{}_{(aq)} + PEDOT^{+}/GCE \rightarrow (Fe(CN)_6\text{-}PEDOT)_{film}{}^{2-}/GCE \qquad (2)$$

$$CuFe(CN)_6{}^{-}{}_{(aq)} + PEDOT^{+}/GCE \rightarrow (CuFe(CN)_6\text{-}PEDOT)_{film}/GCE \qquad (3)$$

Redox process of copper(II) hexacyanoferrate/PEDOT/GCE:

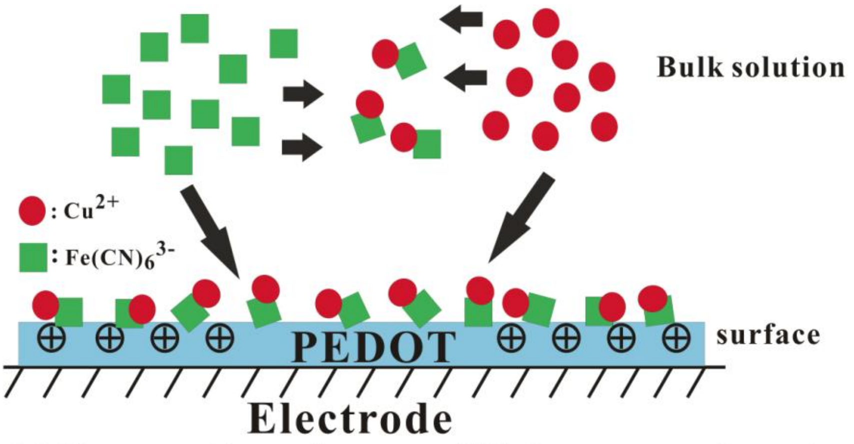
$$(Fe^{III}(CN)_6\text{-}PEDOT)_{film}{}^{2-}/GCE + e^{-} \rightleftharpoons (Fe^{II}(CN)_6\text{-}PEDOT)_{film}{}^{3-}/GCE \qquad (4)$$

$$(CuFe^{III}(CN)_6\text{-}PEDOT)_{film}/GCE + e^{-} \rightleftharpoons (CuFe^{II}(CN)_6\text{-}PEDOT)_{film}{}^{-}/GCE \qquad (5)$$

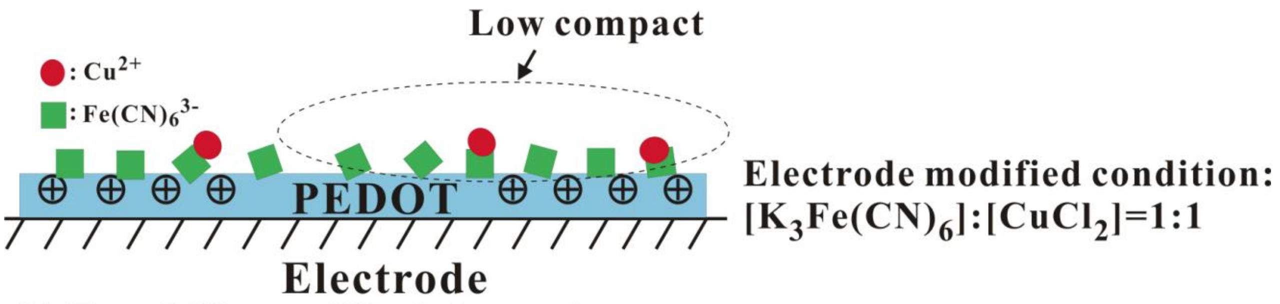
This could be further explained as scheme 1(a), which illustrates how the film formation of copper(II) hexacyanoferrate films on PEDOT/GCE. In bulk solution, most of $Fe(CN)_6{}^{3-}$ and Cu^{2+} are reacted to generate $CuFe(CN)_6{}^{-}$. Then, the formed $CuFe(CN)_6{}^{-}$ would transfer and dope in PEDOT (process 1). In the surface of PEDOT/GCE, some of $Fe(CN)_6{}^{3-}$ ions are attracted by positive charge of PEDOT film and they would transfer and dope in PEDOT particularly in positive scan on the surface of PEDOT/GCE. Furthermore, some of Cu^{2+} ions are attracted by the ferricyanide ions (which have been doped in PEDOT/GCE) to form CuHCF on PEDOT/GCE surface (process 2). In ideal case, both process 1 & 2 would lead to form CuHCF on PEDOT surface. Actually, the process 2 might lead only $Fe(CN)_6{}^{3-}$ to dope in PEDOT particularly in positive scan. In the period of potential cycling (0–1 V), PEDOT surface is initially doped by some $Fe(CN)_6{}^{3-}$. The residual Cu^{2+} (except of Cu^{2+} reacted with $Fe(CN)_6{}^{3-}$ in bulk solution) might not transfer and react with the $Fe(CN)_6{}^{3-}$ which have been doped in PEDOT (here means FCN/PEDOT) due to positive scan. Therefore, the process 2 is not always completed to form CuHCF on PEDOT surface. As the result, this film (as Fig. 1A(a)) shows one obvious redox couple 1 of ferricyanide ($Fe(CN)_6{}^{3-}$ dope in PEDOT) and one small redox couple 2 of copper(II) hexacyanoferrate ($CuFe(CN)_6{}^{-}$ dope in PEDOT) when the film is prepared from $[K_3Fe(CN)_6]:[CuCl_2] = 1:1$.

From Fig. 1A-C, these films show more and more obvious redox peaks of $CuFe(CN)_6{}^{-}$ with increase of copper(II) molar ratio. As increasing copper(II) molar ratio in the prepared condition, the Cu^{2+} ions are getting relatively rich to react with most $Fe(CN)_6{}^{3-}$ to form $CuFe(CN)_6{}^{-}$ which will transfer and dope in PEDOT (process 1). At the same time, it will also get more possibilities for the rich Cu^{2+} ions which were reacted with $Fe(CN)_6{}^{-}$ and doped in PEDOT (process 2) even in the positive scan. The redox couple of $CuFe(CN)_6{}^{-}$ was dependent on Cu(II) molar ratio in the preparation. From Fig. 1B, it is clear that the two redox couples (1 & 2) of $Fe(CN)_6{}^{3-}$ and $CuFe(CN)_6{}^{-}$ (doped in PEDOT) exhibits almost identical anodic peak currents (I_{pa}) when the ratio of $[K_3Fe(CN)_6]:[CuCl_2]$ is 1:5 rather than 1:1.

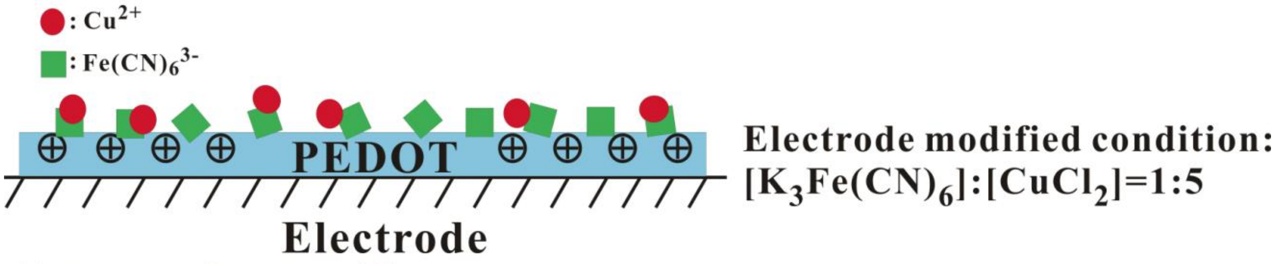
Moreover, the film types of copper(II) hexacyanoferrate formed on PEDOT can be further classified by compact degree of $CuFe(CN)_6{}^{-}$.



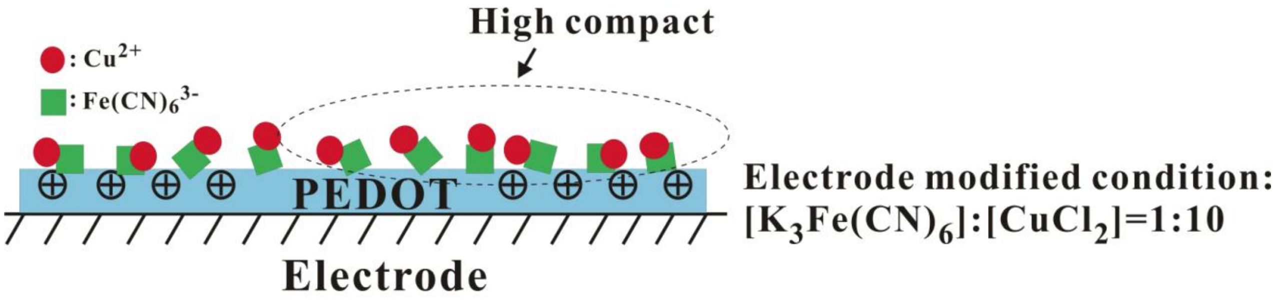
(a) Preparation of copper(II) hexacyanoferrate modified electrode



(b) Type I film modified electrode



(c) Type II film modified electrode



(d) Type III film modified electrode

Scheme 1. Preparation of copper(II) hexacyanoferrate/PEDOT using PEDOT modified electrode in different molar ratio of $K_3Fe(CN)_6$ and $CuCl_2$. (a) Ferricyanide ions reacted with copper ions in bulk solution and doped in PEDOT film on the electrode surface; Different CuHCF compact degree of (b) low compact, (c) middle compact, and (d) high compact in the copper(II) hexacyanoferrate/PEDOT composite.

As shown in Scheme 1 (b)-(d), it illustrates copper(II) hexacyanoferrate/PEDOT films have low, middle, and high compact degree of $CuFe(CN)_6^-$ doped in PEDOT. The redox peaks of this composite are highly dependent on the CuHCF content resulted from different prepared molar ratio of copper and ferricyanide ions.

These three films were further examined in 0.1 M KNO_3 solution (pH 5.6) with various scan rates of 50－350 mV s^{-1}. Fig. 1D–F shows the cyclic voltammograms of these film modified electrodes with various scan rates in the potential range from 0 to 1.0 V. From Fig. 1D & E, the peak currents of redox couples are directly proportional to scan rates up to 350 mV s^{-1} (as insets in Fig. 1D & E) as expected for surface confined process.

As can be seen in insets of Fig. 1D & E (Type I & II of copper(II) hexacyanoferrate/PEDOT), the regressing equation of peak current and scan rate can be expressed as $I_{pa1}(\mu A) = 0.1523v(mV\ s^{-1}) + 0.63423$ ($R^2 = 0.9998$) for Type I; $I_{pa1}(\mu A) = 0.1523v(mV\ s^{-1}) + 0.63423$ ($R^2 = 0.9961$), $I_{pa2}(\mu A) = 0.1123v(mV\ s^{-1}) + 1.2797$ ($R^2 = 0.9961$) for Type II; and $I_{pa2}(\mu A) = 3.6699v(mV^{1/2}\ s^{-1/2}) - 1.8708$ ($R^2 = 0.9983$) for Type III. Particularly, the linear correlation between peak current and square root of scan rate was found in Type III film as shown in the inset of Fig. 1F. This demonstrates that the process is diffusion control. And the slow diffusion rate might be caused by the more CuHCF content in the film involving mass transfer resistance.

3.2.2. SEM images analysis for Type I-III of copper(II) hexacyanoferrate/PEDOT films

Based on the different electrochemical behaviors of copper(II) hexacyanoferrate/PEDOT films, the morphology of these films were studied by SEM. Unlike the clear image of the bare GCE surface (Fig. 2A), the image of CuHCF/GCE (Fig. 2B) exhibits grain-like structure with an average diameter of 1.5 μm. And, the PEDOT/GCE image (Fig. 2C) shows net-like structure with an average diameter of 1.0 μm.

Fig. 2D–F shows the images of copper(II) hexacyanoferrate/PEDOT films prepared by different molar ratio of $[K_3Fe(CN)_6]:[CuCl_2]$ = 1:1, 1:5, and 1:10, respectively.

Fig. 2D–F displays the images of specific fiber-like structure among these films correlated to the unique cyclic voltammograms of Type I-III shown in Fig. 1A–C, respectively. The fiber-like structure of Type I was found with an average length of 18 μm and an average width of 2 μm.

For the images of Type II & III (shown in Fig. 2E & F), both of them show not only fiber-like structure (Fig. 2E: 25×1.5 μm; Fig. 2F: 10×0.5 μm) but also grain-like structure (Fig. 2E: 2 μm; Fig. 2F: 1 μm). As compared to the images of CuHCF/GCE and PEDOT/GCE (Fig. 2B & C), the new formation of fiber-like structure is recognized due to the doping of $Fe(CN)_6^{3-}$ and $CuFe(CN)_6^-$ on PEDOT surface. By comparison of SEM images and cyclic voltammograms of these films, they are concluded that the smaller fiber-like structure is contributed by $CuFe(CN)_6^-$ formation on PEDOT film. It also means the film type is tending to form more $CuFe(CN)_6^-$ on PEDOT as process 2 which is involving mass transfer resistance. Hence, Type III (Fig. 2F) exhibits relatively small size of fiber structure.

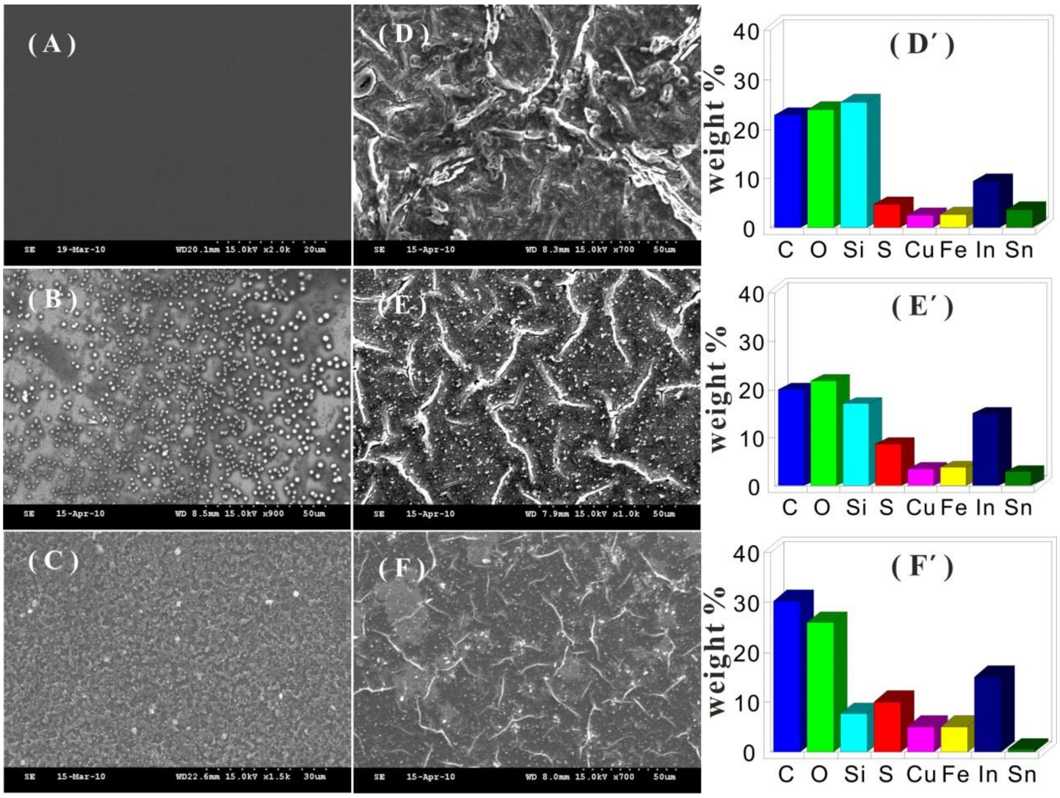


Figure 2. SEM images of different electrode surface including (A) bare GCE, (B) CuHCF/GCE, (C) PEDOT/GCE, and (D) Type I, (E) Type II, and (F) Type III of Copper(II) hexacyanoferrate/PEDOT/GCE, respectively. EDS element analysis including (D’) Type I, (E’) Type II, and (F’) Type III of Copper(II) hexacyanoferrate/PEDOT/ITO, respectively.

3.2.3. EDS element analysis for different types of copper(II) hexacyanoferrate/PEDOT films

These films were further examined by EDS, Fig. 2D’-F’ shows EDS analysis results for Type I, Type II, and Type III of copper(II) hexacyanoferrate/PEDOT/ITO, respectively. It can be seen, these three films have identical Cu/Fe ratio in their composites even they are prepared from different molar ratio of ferricyanide ions and copper(II) ions. The identical Cu/Fe ratio provides the probably evidence of CuHCF composite in these films (as shown in formula 3). Particularly, Type III film has higher content of Cu and Fe is directly related to its prepared condition of higher copper content. It is concluded that the more CuHCF formation in this film (Type III) resulted in obvious redox couple of CuHCF differs from Type I & II. The higher compact of CuHCF in the copper(II) hexacyanoferrate/PEDOT in Type III film is hence verified. From the EDS results, we confirm that CuHCF content in the film increases with increase in ferricyanide and copper(II) molar ratio and thus optimized as 1:10.

3.2.4. EIS analysis for different types of copper(II) hexacyanoferrate/PEDOT films

It is well known that electrochemical alternating current impedance technique is a useful tool for studying the interface properties of surface-modified electrodes [39-42]. Therefore, electrochemistry impedance spectroscopy (EIS) was used to investigate the nature of copper(II) hexacyanoferrate/PEDOT film modified electrodes. EIS data were obtained for the modified electrodes at AC frequency varying between 0.1 Hz and 1 MHz in 0.1 M KNO_3 solution (pH 5.6). Fig. 3 shows Nyquist diagrams (-Z'' vs. Z') of bare GCE (Fig. 3a'), PEDOT/GCE (Fig. 3a), and Type I (Fig. 3b), Type II (Fig. 3c), and Type III (Fig. 3d) of copper(II) hexacyanoferrate/PEDOT/GCE, respectively. PEDOT/GCE exhibits almost a straight line with a much smaller depressed semicircle arc (R_{et} = 0.12 kΩ) than that of bare GCE (R_{et} = 0.67 kΩ). The small depressed semicircle of PEDOT/GCE means that the electron transfer resistance is relative smaller than mass transfer resistance in this electrochemical system. In other words, the electron transfer is fast and mass transfer limits the system. This is because of the electron transfer resistance might be lowered by the conducting polymer of PEDOT. The R_{et} values of copper(II) hexacyanoferrate/PEDOT/GCE are increasing from Type I to Type III and found between bare GCE and PEDOT/GCE except of Type III. By the EDS result, it's tending much higher CuHCF content from Type I to Type III. Therefore, the electron transfer resistance of copper(II) hexacyanoferrate/PEDOT film increases with increase in the CuHCF composition.

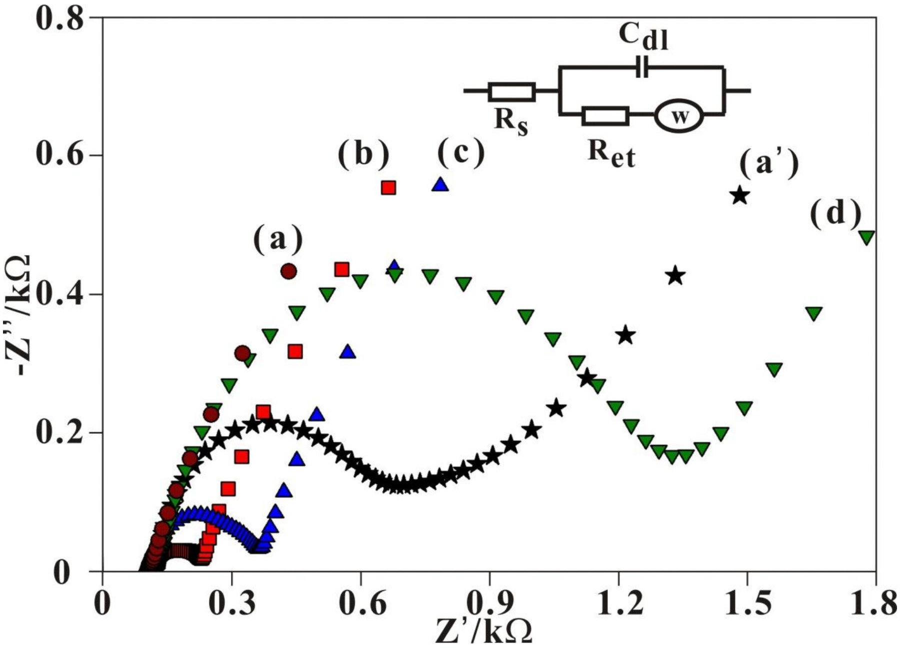


Figure 3. Electrochemical impedance spectra including (a') bare GCE, (a) PEDOT/GCE, and (b) Type I of Copper(II) hexacyanoferrate/PEDOT/GCE, (c) Type II of Copper(II) hexacyanoferrate/PEDOT/GCE, and (d) Type III of Copper(II) hexacyanoferrate/PEDOT in 0.1 M KNO_3 (pH 5.6), respectively.

3.2.5. Simultaneous determination of AA and AP by different types of copper(II) hexacyanoferrate/PEDOT modified electrodes

The eletrocatalytic oxidation of AA and AP was studied and compared using different types of copper(II) hexacyanoferrate/PEDOT modified electrodes.

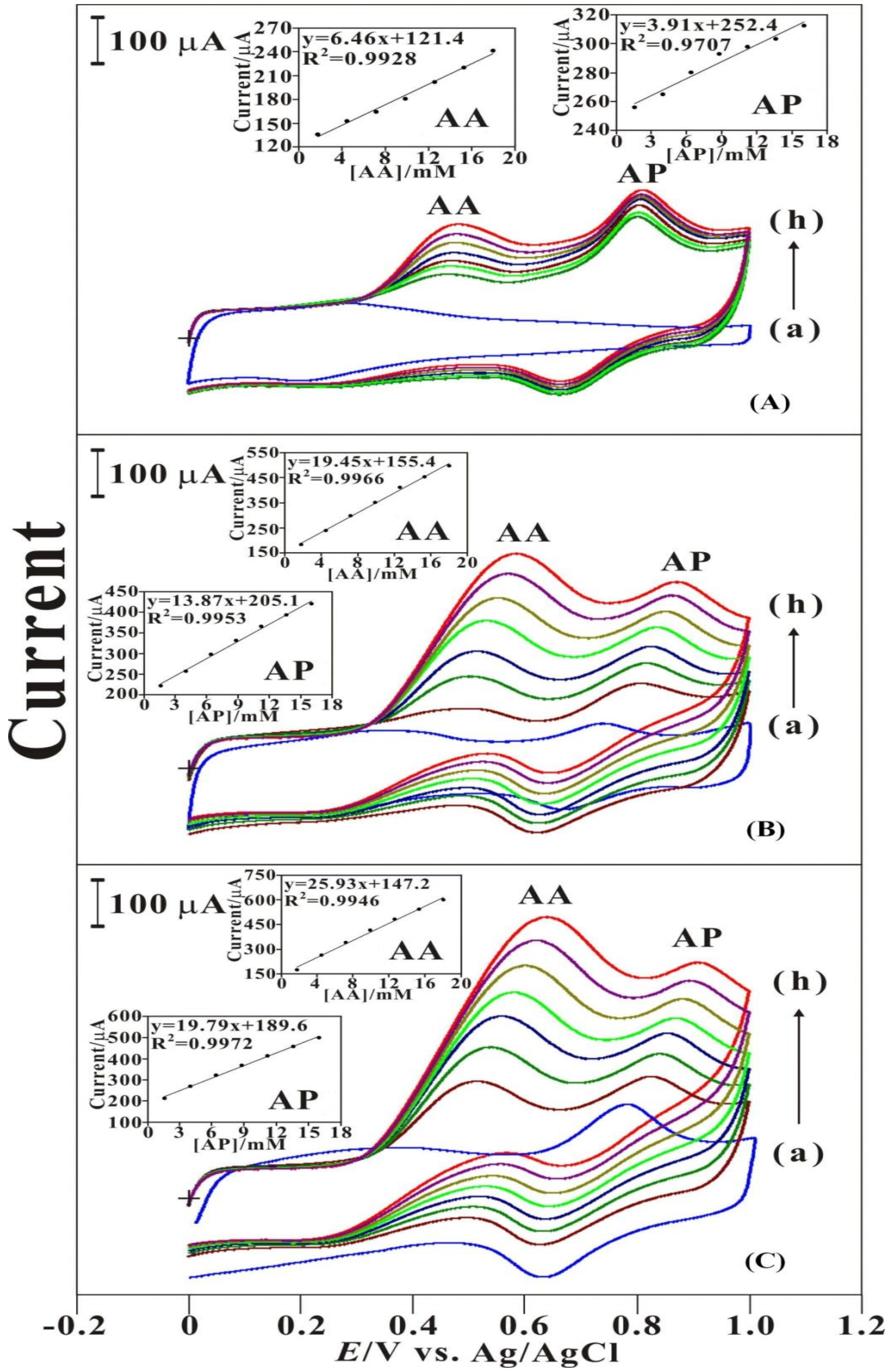


Figure 4. Cyclic voltammograms of simultaneously electrocatalytic oxidation of AA and AP in 0.1 M KNO_3 solution (pH 5.6) containing various concentration of: (a) 0, (b) 2.7×10^{-3} M AA + 2.4×10^{-3} M AP, (c) 5.4×10^{-3} M AA + 4.8×10^{-3} M AP, (d) 8.1×10^{-3} M AA + 7.2×10^{-3} M AP, (e) 1.08×10^{-2} M AA + 9.6×10^{-3} M AP, (f) 1.35×10^{-2} M AA + 1.2×10^{-2} M AP, (g) 1.62×10^{-2} M AA + 1.44×10^{-2} M AP, and (h) 1.89×10^{-2} M AA + 1.68×10^{-2} M AP, respectively. They are examined by (A) Type I, (B) Type II, and (C) Type III of FCN-CuHCF-PEDOT/GCE, respectively. (a′) represents the cyclic voltammogram of bare GCE examined in the presence of 1.89×10^{-2} M AA + 1.68×10^{-2} M AP for each case (A-C), scan rate = 0.1 V s^{-1}. Insets are plots of anodic peak current vs. concentration of (I) AA and (II) AP.

Fig. 4 shows these modified electrodes were individually examined in 0.1 M KNO_3 solution (pH 5.6) in the presence of AA and AP with different concentration. All of them could simultaneously determine AA and AP with two obvious anodic peaks of E_{pa1} = 0.49–0.603 V (for AA) and E_{pa2} = 0.803–0.88 V (for AP) as increasing reagents concentration. As can be seen in the insets of Fig. 4, the linearity of electrocatalytic current can be expressed as $I_{pa1}(\mu A) = 6.46[AA](mM) + 121.4$ ($R^2 = 0.9928$) and $I_{pa2}(\mu A) = 3.91[AP] + 252.4$ ($R^2 = 0.9937$) (I_{pai}: the anodic current of peak i; R^2: coefficient of determination) for Type I of copper(II) hexacyanoferrate/PEDOT film. For Type II, $I_{pa1}(\mu A) = 19.45[AA](mM) + 155.4$ ($R^2 = 0.9966$) and $I_{pa2}(\mu A) = 13.87[AP] + 205.1$ ($R^2 = 0.9953$). For Type III, $I_{pa1}(\mu A) = 25.93[AA](mM) + 147.2$ ($R^2 = 0.9946$) and $I_{pa2} = 19.79[AP] + 189.6$ ($R^2 = 0.9972$). The linear range is found in 0.18–1.8 × 10^{-2} M and 0.16–1.6 × 10^{-2} M for AA and AP, respectively. By sensitivity comparison of these modified electrodes, Type III shows the best sensing result for AA and AP. These films can be concluded that the higher CuHCF content the higher sensitivity for AA and AP.

Table 1. Comparison of sensing abilities for AA and AP with different methods.

Method	Linear range/µM		Sensitivity/ mA M^{-1} cm^{-2}		Detection limit/µM		Reference
	AA	AP	AA	AP	AA	AP	
CV[a]	300-1500	-	64.28	-	-	-	[44]
CV[a]	200-4000	-	354.1	-	50	-	[43]
CV[a]	500-16000	-	24.6	-	-	-	[45]
AMP[b]	10-50	-	72.2	-	-	-	[46]
AMP[b]	10-300	-	201.2	-	-	-	[47]
AMP[b]	50-1200	-	41.7	-	-	-	[48]
RDE[c]	500-15000	-	208.3	-	-	-	[48]
CV[a]	500-15000	-	5.7	-	-	-	[48]
AMP[b]	5-300	-	150	-	1	-	[49]
DPV[d]	-	12-120	-	-	-	2	[50]
DPV[d]	-	3-300	-	-	-	0.6	[51]
DPV[d]	140-1300	7.8-110	-	-	4.1	2.3	[52]
CV[a]	1800-18000	1600-16000	93	55.7	41.1	63.7	Type I (This work)
CV[a]	1800-18000	1600-16000	274.3	195.7	17.7	12.6	Type II (This work)
CV[a]	1800-18000	1600-16000	395.7	308.6	7.1	12.2	Type III (This work)

[a] Cyclic Voltammetry
[b] Amperometry
[c] Rotaing Disk Electrode
[d] Differential Pulse Voltammetry

As compared with other methods, the proposed films have competitive sensing abilities in linear range, sensitivity, and detection limit (as shown in Table 1) for AA and AP. As reported earlier for AA determination, FCN-PEDOT/GCE [43] possesses much higher sensitivity than PEDOT/GCE [44]. By the comparison of EDS element analysis in this work, the higher CuHCF content in Type III means this film type has high CuHCF compact degree. And it shows higher sensitivity for AA than FCN-PEDOT/GCE (Vasantha et al., 2005). It can be confirmed that the sensitivity for AA increases in the increase of CuHCF content in the composites. By the result, copper(II) hexacyanoferrate/PEDOT films would be suitable for the simultaneous determination of AA and AP particularly by Type III.

4. CONCLUSIONS

In this paper, the electrochemical behaviors of copper(II) hexacyanoferrate/PEDOT films regarding to their prepared condition (molar ratio) of ferricyanide and copper(II) chloride, film formation process, and film types were studied. The copper(II) hexacyanoferrate/PEDOT films exhibit significant voltammograms and can be classified from Type I to Type III due to their different CuHCF content. All of these films have fiber-like structure due to the doping of ferricyanide and copper(II) hexacyanoferrate on PEDOT surface. The SEM image of Type III possesses relatively small fiber-like structure since the doping of $CuFe(CN)_6^-$ with PEDOT is a much slower process. This could be due to the slow diffusion of $CuFe(CN)_6^-$ ions from bulk solution to the electrode surface. For Type III film, the higher compact CuHCF in the copper(II) hexacyanoferrate/PEDOT is verified by EDS. From the EDS results, we confirm that CuHCF content in the film increases with increase in ferricyanide and copper(II) molar ratio and thus optimized as 1:10. The EDS results provide a supporting evidence for EIS results that higher CuHCF content in the film could be the possible reason for the increased electron transfer resistance. It is also found the proposed film with higher CuHCF content has much higher current response for AA and AP. It discloses copper(II) hexacyanoferrate/PEDOT films would be suitable for the simultaneous determination of AA and AP as compared with other materials. Particularly, the higher CuHCF content in the composites the higher sensitivity for AA and AP.

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