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Copper Nanoparticles with Copper Hexacyanoferrate and Poly(3,4-ethylenedioxythiophene) Hybrid Film Modified Electrode for Hydrogen Peroxide Detection

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An electroactive polynuclear hybrid films of copper nanoparticles with copper hexacyanoferrate (copper NPs-CuHCF) have been deposited on PEDOT electrode surfaces from KNO_3 solution (pH 5.6) containing $CuCl_2$ and $K_3[Fe(CN)_6]$ by multiple scan cyclic voltammetry. The films were characterized using field emission scanning electron microscopy and energy dispersive spectroscopy. The advantages of these films were demonstrated for the detection of hydrogen peroxide (H_2O_2) using cyclic voltammetry and amperometric techniques. The electrocatalytic reduction of H_2O_2 at different electrode surfaces, such as the bare GCE, the CuHCF/PEDOT/GCE, and the copper NPs/PEDOT/GCE modified electrodes, was determined in KNO_3 solution (pH 5.6). The H_2O_2 electrochemical sensor exhibited a linear response range (from $1 \text{ x } 10^{-6}$ to $5.4 \text{ x } 10^{-4}$ M, $R^2 = 0.9975$, lowest detection limit (1×10^{-7} M) and fast response time (3 s) for H_2O_2 determination. In addition, the copper NPs-CuHCF/PEDOT/GCE was advantageous in terms of its simple preparation, specificity, stability and reproducibility.

Keywords: Copper nanoparticles, Copper Hexacyanoferrate, PEDOT, Electrocatalysis, Hydrogen Peroxide, Modified Electrodes

1. INTRODUCTION

The application of the metal hexacyanoferrate chemical film modified electrodes [1–4] has uses in both chemistry and material science, including the areas of electroanalysis, chemical sensing and electrocatalysis, in studies on interfacial charges, in ion exchange and electron transfer studies [5, 6], and in research on surface chemical composition [7]. 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 [2, 8, 9]. 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.

The hybrid metal hexacyanoferrates also showed ability to mediate electrochemical reactions [10–16], however, not yet studied extensively. In our previous studies, we have also prepared hybrid films of mixed-valent zinc oxide/zinchexacyanoferrate and ruthenium oxide hexacyanoferrate [4], ruthenium oxide/ruthenocyanide [2], ruthenium oxide/hexacyanoferrate and ruthenium hexacyanoferrate [17] and zinc oxide/zinc hexacyanoferrate [3] on electrode surface by repetitive cyclic voltammetric scans and tested for their electrocatalytic behavior.

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 [18, 19]. 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 [20-23]. 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 [24-26]. The electrochemical formation of copper NPs-CuHCF films on a glassy carbon electrode was carried out using consecutive cyclic voltammetry in KNO_3 solutions. The copper NPs-CuHCF films showed three redox couples with formal potentials between –0.6 and 1.0 V.

2. MATERIALS AND METHODS

2.1. Chemicals

Anhydrous copper(II) chloride ($CuCl_2$) and potassium ferrocyanide ($K_3Fe(CN)_6$) 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. Different concentration of hydrogen peroxide has been prepared in in 0.1 M KNO_3 solution (pH 5.6) for all the electrochemical studies.

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 (φ = 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 φm), 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)).

2.3. Fabrication of copper NPs-CuHCF/PEODT film, copper NPs /PEODT film, CuHCF/PEODT film

Prior to the electrochemical deposition process, the GCE was well polished with the help of BAS polishing kit with aqueous slurries of alumina powder (0.05 μm), rinsed and ultrasonicated in double distilled deionized water. The PEDOT film was performed by electrochemical polymerization of EDOT monomers with repeatedly scanning potential from +0.2 V to +1.3 V at a scan rate of 0.1 V s^{-1} in 0.1 M sulfuric acid solution (pH 1.5) containing 0.01 M EDOT monomers. After preparing the PEDOT film on the electrode surface, the electrodeposition of CuHCF films at the GCE in 0.1 M KNO_3 solution (pH 5.6) between 0 and +1.0 V, at the scan rate of 0.1 V s^{-1} for 20 cycles [7]. The copper NPs were deposited electrochemically onto PEDOT/GCE between +1.0 and –0.6 V. After scanning in KNO_3 solution, the copper NPs–CuHCF film was formed on the PEDOT/GCE.

3. RESULT AND DISCUSSION

3.1. Electrochemical Properties of Copper NPs-CuHCF/PEDOT Hybrid Film Modified Electrode

The repetitive cyclic voltammograms recorded during electrodeposition of copper oxide/copper hexacyanoferrate (copper NPs-CuHCF) hybrid film at PEDOT/GCE from KNO_3 solution containing 1 mM $CuCl_2$ and 1 mM $K_3[Fe(CN)_6]$. In Fig. 1(A), curve (a) indicates the CV signals of copper NPs-CuHCF/PEDOT/GCE, (b) copper NPs/GCE, and (c) CuHCF/PEDOT/GCE in 0.1 M KNO_3 solution (pH 5.6). The $(E_{pa} + E_{pc})/2$, ($E^{0'}$) of copper NPs-CuHCF/PEDOT/GCE are separated as +687, +287 and –162 mV. In the same buffer solution, there are only two redox peaks at curve (b) copper NPs/PEDOT/GCE and one redox peak (c) CuHCF/PEDOT/GCE. The above results confirm the successful electrodeposition of copper NPs-CuHCF film on PEDOT/GCE.

The copper NPs-CuHCF/PEDOT/GCE was used in several scan rate studies in 0.1 M KNO_3 solution (pH 5.6). Fig. 2B exhibits the different scan rate results of copper NPs-CuHCF/PEDOT/GCE in the range 0.1–1 V/s. Here, the linear increase in the anodic and cathodic peak currents of copper NPs-CuHCF/PEDOT/GCE according to the scan rate revealed that the film exhibited the typical characteristics of surface controlled thin-layer electrochemical behavior. The inset (I), (II) and (III) in Fig. 1A shows the plot of the copper NPs-CuHCF/PEDOT/GCE signal of the anodic and cathodic peak current vs. scan rate. The corresponding linear regression equations are (I) : I_{pa} (μA) = 1.425v (V/s) + 1.006, R^2 = 0.9982, and I_{pc} (μA) = -1.05v (V/s) – 20.05, R^2 = 0.9934; (II) : I_{pa} (μA) = 0.747v (V/s) + 7.74, R^2 = 0.9961, and I_{pc} (μA) = -0.721v (V/s) – 2.932, R^2 = 0.9991; (III) : I_{pa} (μA) = 0.471v (V/s) +

15.81, R^2 = 0.9926, and I_{pc} (μA) = -0.404v (V/s) – 2.267, R^2 = 0.9977. Furthermore, as the electrodeposition film and the follow-up testing process used by the electrochemical buffer solution with different cations [27], which lead to differences in the electrochemical signal. All the above results indicate that copper NPs/PEDOT film modified GCE shows a stable and higher current in 0.1 M KNO_3 solution.

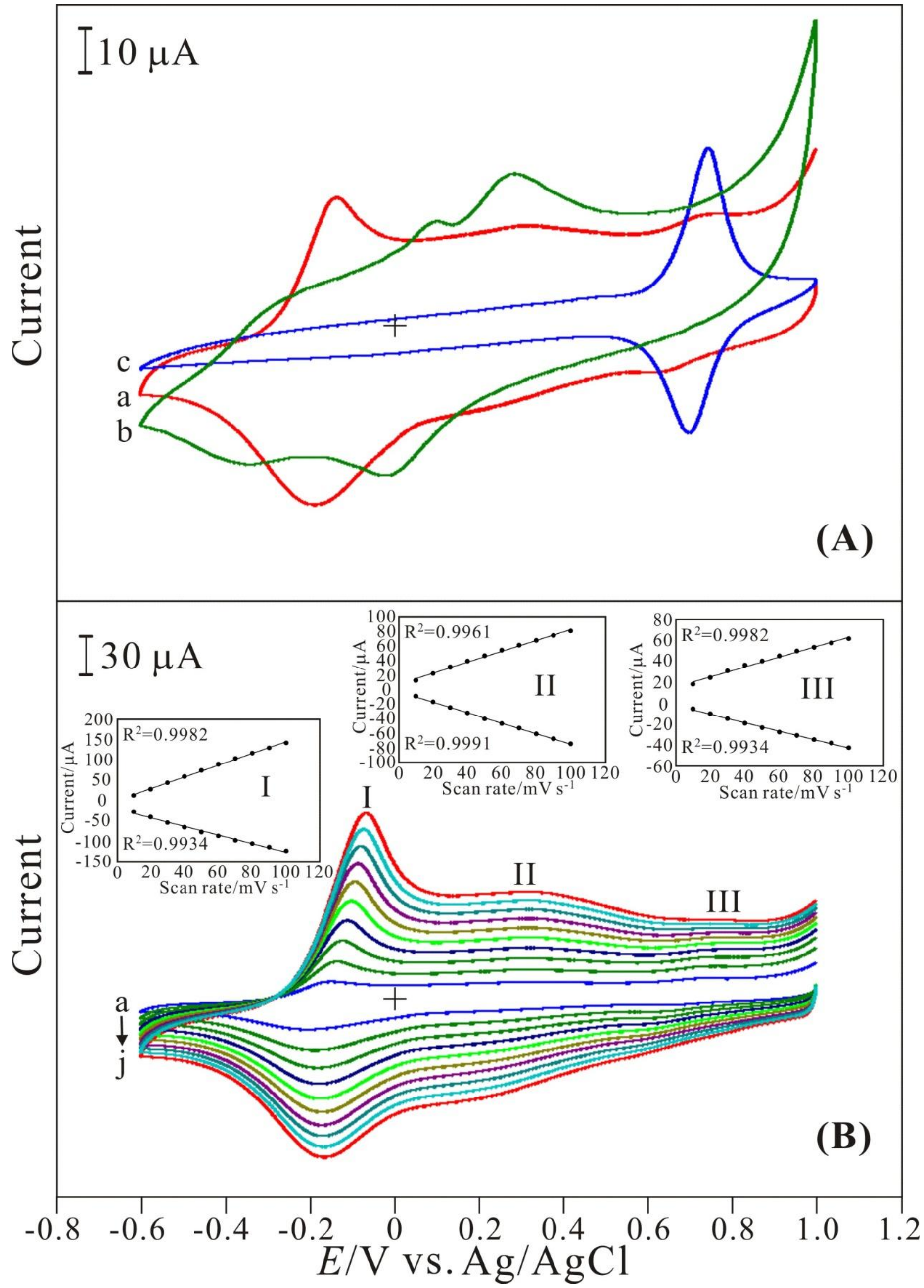

Figure 1. (A) Cyclic voltammograms of (a) nano-Cu-CuHCF/PEDOT/GCE, (b) CuHCF/PEDOT/GCE, and (c) nano-Cu/PEDOT/GCE examined in 0.1 M KNO_3 (pH 5.6) solution, scan rate = 0.1 V s^{-1}. (B) Cyclic voltammograms of copper NPs-CuHCF-PEDOT/GCE examined in 0.1 M KNO_3 (pH 5.6) solution with various scan rate 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}, (g) 350 mV s^{-1}, (h) 400 mV s^{-1}, (i) 450 mV s^{-1}, and (j) 500 mV s^{-1}, respectively.

3.2. SEM and EDS analysis

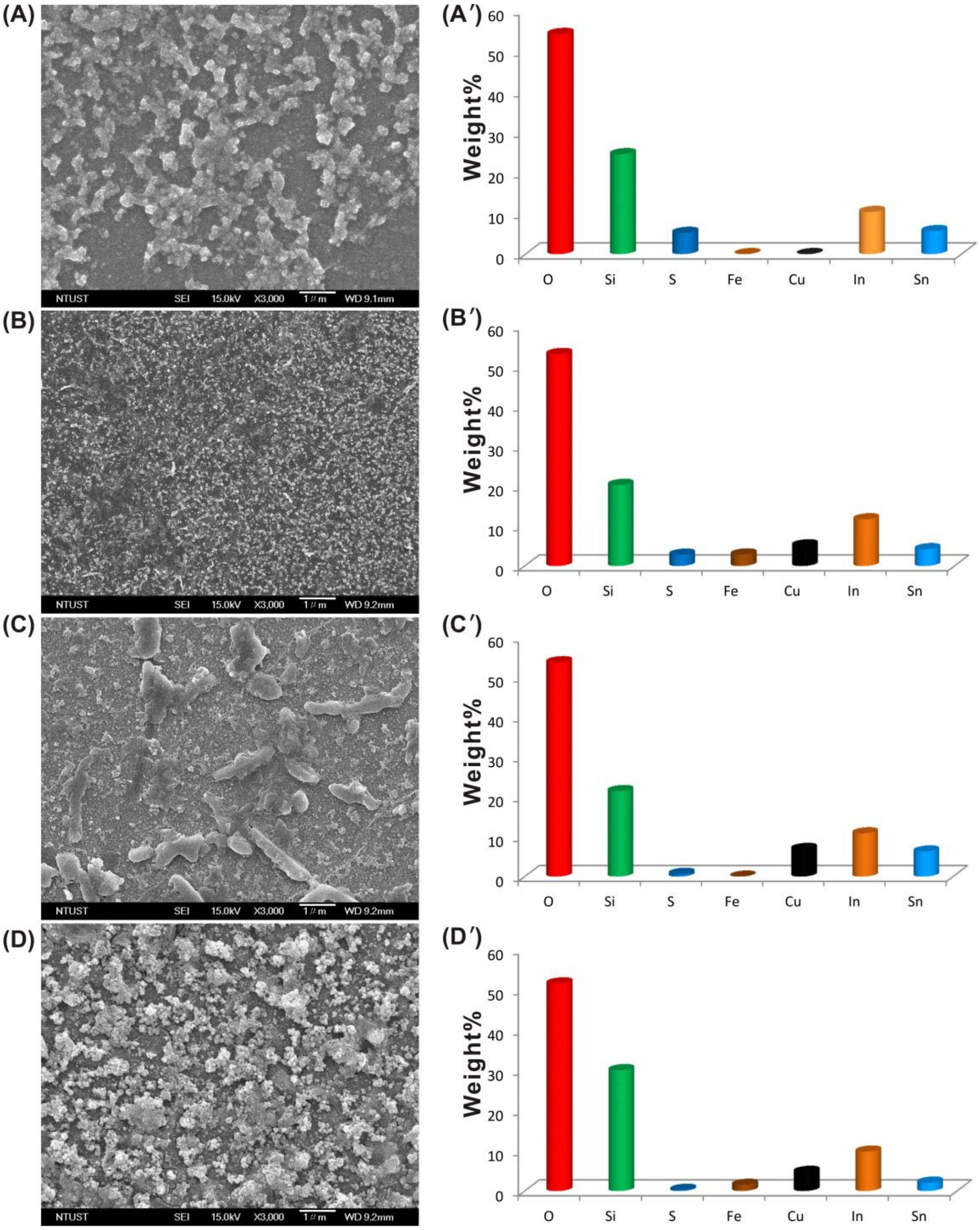

Figure 2. SEM images of different electrode surface including (A) PEDOT/GCE, (B) Copper NPs/PEDOT/GCE, (C) CuHCF/PEDOT/GCE, and (D) Copper NPs-CuHCF/PEDOT/GCE, respectively. EDS element analysis including (A') PEDOT/GCE, (B') Copper NPs/PEDOT/GCE, (C') CuHCF/PEDOT/GCE, and (D') Copper NPs-CuHCF/PEDOT/GCE, respectively.

Based on the different electrode surface, the morphology of these films is studied by SEM and EDS. The PEDOT/GCE image (Fig. 2A) shows a network structure of 100~200 nm. The copper

NPs/PEDOT/GCE and CuHCF/PEDOT/GCE surface as shown in Fig. 2B and C, the electrode surface provide a different particle size of 30~100 nm and 500~2000 nm. By comparison, the morphology of the copper NPs-CuHCF film uniformly distributes on the PEDOT film with a particle size of 50~300 nm. These films are further examined by EDS, Fig. 2A'-D' show EDS analysis results for PEDOT film, copper NPs, CuHCF film and copper NPs-CuHCF/PEDOT film, respectively. It can be seen, these 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.

3.3. EIS analysis

The electrochemical activity of copper NPs-CuHCF/PEDOT, CuHCF/PEDOT, copper NPs/PEDOT and PEDOT modified GCE has been examined using electrochemistry impedance spectroscopy (EIS) technique.

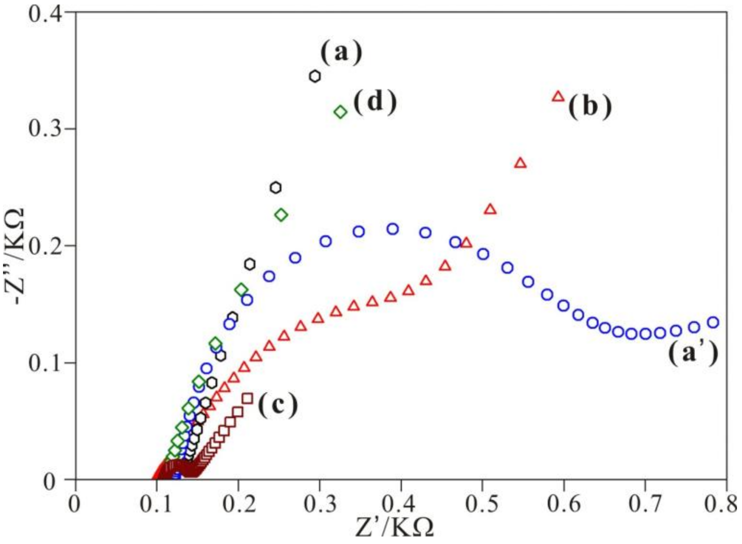

Figure 3. EIS curves of (a) copper NPs-CuHCF/PEDOT, (b) CuHCF/PEDOT, (c) copper NPs/PEDOT, (d) PEDOT film modified GCE and (a') bare GCE in 0.1 M KNO_3 (pH 5.6).

EIS is an effective method to probe the features of surface modified electrodes. This study was employed to analyze detailed electrochemical activities of different modified electrodes with same condition. The complex impedance can be presented as a sum of the real impedance (Z'(Ω)) and imaginary impedance (Z''(Ω)), which are 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 extracted. The respective semicircle parameters correspond to the electron transfer resistance (R_{et}) and the double layer capacity (C_{dl}) nature of the modified electrodes. As shown in Fig. 3, curve (a) indicates the Nyquist plot of copper NPs-CuHCF/PEDOT/GCE (R_{et} = 124.2 (Z'/Ω), (b) CuHCF/PEDOT/GCE (R_{et} = 409.2 (Z'/Ω), (c) copper NPs/PEDOT/GCE (R_{et} = 136.5

(Z’/Ω), (d) PEDOT/GCE (R_{et} = 108.5 (Z’/Ω) and (a’) bare GCE (R_{et} = 651 (Z’/Ω) in 0.1 M KNO_3 (pH 5.6) solution, which were performed at the open circuit potential. This is due to the PEDOT film provides a network structure to disperse the metal particles and accelerate the electron transfer [28, 29]. These results clearly illustrate the electrochemical activities of copper NPs-CuHCF/PEDOT, CuHCF/PEDOT and copper NPs/PEDOT film modified GCEs, respectively.

3.4. Electrocatalytic Properties of copper NPs-CuHCF/PEDOT Film

3.4.1. Hydrogen Peroxide Electrocatalysis Comparison of Copper NPs-CuHCF/PEDOT, Copper NPs/PEDOT, and CuHCF/PEDOT Film Modified Electrodes

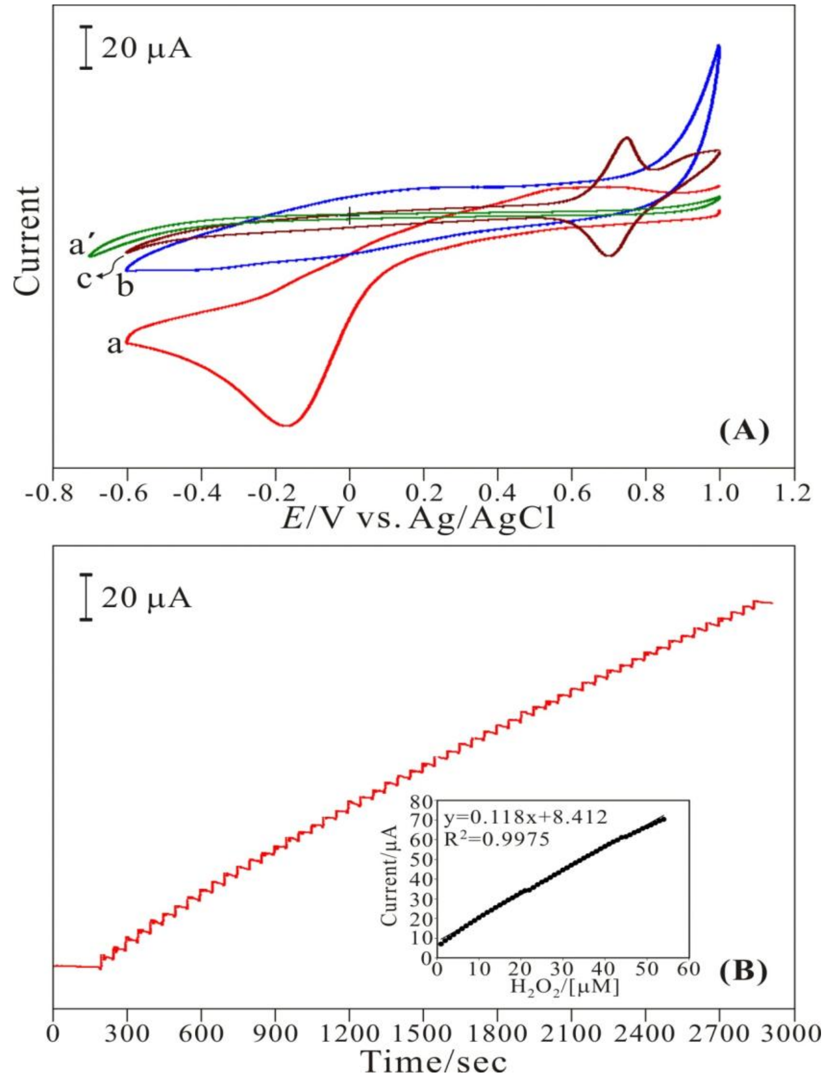

Figure 4. (A) Cyclic voltammograms of (a) copper NPs-CuHCF/PEDOT/GCE, (b) copper NPs/PEDOT/GCE, (c) CuHCF/PEDOT/GCE, and (a’) bare GCE examined in 0.1 M KNO_3 (pH 5.6) solution containing 10^{-4} M H_2O_2, scan rate = 0.1 V s^{-1}. **(B)** Typical amperometric curve obtained for a copper NPs-CuHCF/PEDOT/GCE in 0.1 M KNO_3 (pH 5.6) solution at –0.2 V. Successive additions of H_2O_2 in the range 1 × 10^{-6} to 5.4 × 10^{-4} M (s/n = 3). Inserted figure shows the corresponding calibration plot with the concentration of H_2O_2 between 1 × 10^{-6} to 5.4 × 10^{-4} M. Stirring rate 1000 rpm.

The electrocatalytic reduction of H_2O_2 is studied and compared with different film modified electrodes in the deoxygenating KNO_3 (pH 5.6) solution by voltammetry. Fig. 4A showed the cyclic voltammograms of (a) copper NPs-CuHCF/PEDOT/GCE, (b) copper NPs/PEDOT/GCE, (c) CuHCF/PEDOT/GCE, and (a') bare GCE examined in 0.1 M KNO_3 solution (pH 5.6) containing 10^{-4} M H_2O_2. The proposed composites, (a) copper NPs-CuHCF/PEDOT/GCE, shows high electrocatalytic reduction current for H_2O_2 with a sharp cathodic peak and a lower over-potential of around –0.2 V as comparing to other electrodes. By comparison, the copper NPs-CuHCF/PEDOT/GCE shows uniquely electrocatalytic ability of lower over-potential and higher electrocatalytic current better than that of copper/PEDOT/GCE and CuHCF/PEDOT/GCE. It represents copper NPs-CuHCF/PEDOT film has potential to develop H_2O_2 sensor.

3.4.2. Amperometric Response of Hypochlorite Electrocatalysis by Copper NPs-CuHCF/PEDOT Film

Table 1. Comparison of the efficiency of hydrogen peroxide sensor based on metal hexacyanoferrate composite films. Limit of detection (LOD). Linear concentration range (LCR).

Modified electrode	E_p (mV)	Electrolyte	LCR (M)	LOD (M)	Sensitivity (μA mM^{-1} cm^{-2})	Reference
CrHCF/PIGE[a]	–300 (Ag/AgCl)	PBS (pH 7)	2.5x10^{-6}-1.0x10^{-4}	2.5x10^{-6}	---	[30]
PVA-SbQ[b]/VHCF	+100 (Ag/AgCl)	50 mM Tris (pH 7.0)	1x10^{-5}-3x10^{-3}	4x10^{-6}	---	[31]
Cu-rich-CuHCF/GCE	0 (SCE)	PBS (pH 5.5)	5x10^{-7}-3.5x10^{-5}	5x10^{-7}	31.7	[32]
CuHCF/FTO	0 (Ag/AgCl)	PBS (pH 7)	2.5x10^{-5}-3.25x10^{-4}	---	29.7	[33]
RuCoHCF/GCE	+50 (Ag/AgCl)	0.5 M KCl (pH 3)	1x10^{-5}-5x10^{-4}	2.8x10^{-6}	---	[34]
PEDOT-PB-insoluble/GCE	0 (Ag/AgCl)	PBS (pH 7.2)	1x10^{-5}-5x10^{-5}	---	643	[35]
PB@Pt$_{nano}$/PCNTs/GCE	+100 (Ag/AgCl)	0.1 M KCl (pH 2)	2.5x10^{-7}-1.5x10^{-3}	1.5x10^{-7}	850	[36]
Copper NPs-CuHCF/PEDOT/GCE	–200 (Ag/AgCl)	0.1 M KNO_3 (pH 5.6)	1x10^{-6}-5.4x10^{-4}	1x10^{-7}	1670	This work

[a] Paraffin impregnated graphite electrodes
[b] photocrosslinkable polyvinyl alcohol with styrylpyridinium residues

Fig. 4B showed amperometric responses of sequential additions of H_2O_2 (each 10^{-6} M) tested by copper NPs/PEDOT/GCE in 0.1 M KNO_3 (pH 5.6) solution, respectively, rotating speed = 1000 rpm, $E_{app.}$ = –0.2 V. During 200 — 2800 s, it could be found almost linearly dependence between amperometric current and H_2O_2 concentration. For standard H_2O_2 detection (as shown Fig. 4B), the sensitivity of copper NPs-CuHCF/PEDOT/GCE was 1670 μA mM^{-1} cm^{-2} and the linear range spans the concentration of H_2O_2 from 1×10^{-6} to 5.4×10^{-4} M with a correlation coefficient of 0.9975. The modified electrode was found has a lowest concentration detection limit of 1×10^{-7} M with a 'signal-to-noise ratio' of 3. Hence, copper NPs-CuHCF/PEDOT/GCE for the detection of H_2O_2 also has a higher sensitivity. The linear range and sensitivity observed with copper NPs-CuHCF/PEDOT/GCE is in general comparable with most of the modified electrode reported in the literature [30–36] (Table 1). The higher linear concentration range (LCR) and lower limit of detection (LOD) of copper NPs-CuHCF/PEDOT modified electrode, which compared with Cu rich CuHCF-PEDOT/GCE [32] and

CuHCF/FTO [33], may be the result of the copper NPs with CuHCF film bound to the PEDOT film on electrode surface. Similarly, the copper NPs-CuHCF/PEDOT/GCE modified electrode for the detection of H_2O_2 also has a higher sensitivity (1670 μA mM^{-1} cm^{-2}).

4. CONCLUSION

A stable and electroactive hybrid film of copper NPs and copper hexacyanoferrate was successfully prepared on PEDOT modified GCE surface by cycling repetitively in KNO_3 solution containing $CuCl_2$ and $K_3[Fe(CN)_6]$. The surface analysis by SEM shows that the hybrid film was uniform. EDS results on the composition of hybrid coating confirm the existence copper NPs-CuHCF/PEDOT. These films can be used for the electrocatalytic reduction of H_2O_2 and investigated using the amperometric methods. The copper NPs-CuHCF/PEDOT film facilitated the reduction of H_2O_2 with a low overpotential of –0.2 V and a sensitivity of 1670 μA mM^{-1} cm^{-2}. In addition, the copper NPs-CuHCF/PEDOT modified electrodes exhibited a distinct advantage of simple preparation, specificity, stability and reproducibility.

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