

Synthesis of Multi Walled Carbon Nanotubes Covered Copper Oxide Nanoberries for the Sensitive and Selective Electrochemical Determination of Hydrogen Peroxide

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Multi walled carbon nanotubes covered Copper oxide nanoberries (CuONBs/*f*-MWCNTs) was prepared via simple chemical method. Field emission scanning electron microscopy (FESEM) and energy-dispersive X-ray spectroscopy (EDX) were used to study the surface morphology and elemental composition of our prepared composite. The crystal structure of the composite was analyzed by X-ray diffraction spectroscopy (XRD). The prepared composite was coated at glassy carbon electrode (GCE) and applied for the electro-reduction of H₂O₂. CuONBs/*f*-MWCNTs/GCE works in a wide linear range from 5 μM to 10.5 mM. The limits of detection (LOD) and sensitivity values are evaluated to be 0.78 μM and 1100 μA mM⁻¹cm⁻². 98.3% of steady state current response was attained within 3 s by our sensor. The high selectivity of CuONBs/*f*-MWCNTs/GCE was evident from the interference studies in presence of various biomolecules. Clinical cleaning lens solutions and urine samples were used for the practical feasibility sensor. Our modified electrode can find its significance in near future applications of biosensing research and energy storage devices due to simple fabrication procedure, excellent electrocatalytic activity with good repeatability and reproducibility as well as better practical feasibility.

Keywords: Copper oxide nanoberries, FESEM, XRD, Cyclic voltammetry, Rotating disc electrode, Amperometry, Hydrogen peroxide

1. INTRODUCTION

Hydrogen peroxide (H₂O₂) is effectively used as disinfectant (strong reducing ability against harmful microorganisms), bleaching agent, oxidizing agent in various industries (food and chemical) and environment diagnosis [1-3]. It is a by-product of several oxidase catalyzed reactions in the

biological system. On the other hand, when the concentration of H_2O_2 exceeds the tolerance limit, it may lead to damage of DNA strand or proteins. Thus, the monitoring of H_2O_2 concentration is very significant. Recently, a number of analytical methods have been developed including spectrophotometry, chemiluminescence, colorimetry and chromatography for H_2O_2 determination [4-7]. These methods are difficult to execute, highly expensive and time consuming with low sensitivity and selectivity. Therefore, current researchers focus on the electrochemical methods owing to its simple operating procedure, low cost, less time consumption as well as good repeatability and reproducibility with high sensitivity [8]. Electrochemical method offers enzymatic and non-enzymatic detection of analytes. Many enzymatic sensors immobilized with active catalysts are available for the detection of H_2O_2 . But, they suffer difficult immobilization procedure, high cost of enzymes, low stability, poor repeatability and reproducibility [9-10]. Thus, the recent researches target on the enzyme less electrochemical method of detection.

In order to overcome the drawbacks of unmodified electrodes (poor electron transfer kinetics and high over potential) utilized in the electrochemical methods, chemically modified electrodes are preferred by the present day researchers [11]. In recent years, chemical modification of electrodes has been done by using various transition metal oxides (ZnO , Co_3O_4 , NiO , Cu_2O and CuO) [12-16]. These metal oxides are high stable, environmentally compatible, possess valuable electronic and magnetic properties with good catalytic ability. Among the transition metal oxides, CuO as a p-type semiconductor (band gap=1.2 eV) in particular, has received more attention for the construction of enzyme less H_2O_2 sensor. Due to its distinct electrical, mechanical and thermal properties, CuO is effectively applicable in sensors, electronics, catalysis, batteries and field emission devices. So far, various CuO nanostructures with diverse morphologies were reported formerly, including nanosheet, nanowire, nanorod and nanoflower in the determination of H_2O_2 [16-18].

Carbon nanotubes are formed by the hexagonal arrangement of graphene sheets. They are cylindrical in shape with large surface area which provides more number of reactive sites for the generation of faradic current [19]. Relative to single walled carbon nanotubes (SWCNTs), multi walled carbon nanotubes (MWCNTs) possess incomparable electrical, structural, thermal, optical and mechanical properties [20]. Though, MWCNTs have very low dispersion in aqueous medium, its surface can be altered by oxidation to increase the adsorption and dispersion ability [21]. In order to increase the hydrophilicity of surface, some of the method was used to induce various functional groups on the surface of MWCNTs. This functionalized MWCNTs provide number of anchoring site for the deposition of various metal and metal oxide than that of only MWCNTs [22].

As the conductance and electrochemical activity of MWCNTs is higher, this work involves the preparation and fabrication of CuO nanoberry covered *f*-MWCNTs modified GCE ($CuONBs/f$ -MWCNTs/GCE) for the sensitive amperometric determination of H_2O_2 . Surface morphological studies, elemental and crystal structure analysis were carried out using field emission scanning electron microscopy (FESEM), energy-dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD) techniques. Electrochemical method of reducing H_2O_2 was performed at our modified fabricated electrode. An excellent electro-reduction of H_2O_2 was evident from the calculated values of wide linear range, low limits of detection and high sensitivity for $CuONBs/f$ -MWCNTs/GCE. These valued parameters are in close agreement with the related H_2O_2 sensors of the previous literatures. The highly

selective nature and better practicability further support the good electrocatalytic activity of our fabricated electrode.

2. EXPERIMENTAL

2.1 Reagents and apparatus

MWCNTs (powder, <20 μm), copper (II) nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$), hydrogen peroxide (H_2O_2), sodium dihydrogen phosphate (NaH_2PO_4), sodium phosphate dibasic (Na_2HPO_4) and all other chemicals were purchased from Sigma Aldrich at ACS-certified reagent grade and used without any further purification. The supporting electrolyte, 0.05 M (PB) phosphate–buffer (pH 7) solution was prepared with sodium dihydrogen phosphate and sodium phosphate dibasic and used for all the electrochemical measurements. Prior to each experiment, all the solutions were deoxygenated with pre-purified N_2 gas for 15 min unless otherwise specified. Double distilled water (conductivity $\geq 18 \text{ M}\Omega \text{ cm}^{-1}$) was used throughout the electrochemical experiments.

2.2 Characterization

CHI 6171D work station with a conventional three electrode cell was utilized to perform the electrochemical studies (Cyclic voltammetry). A modified GCE of area 0.071 cm^2 , saturated $\text{Ag}|\text{AgCl}$ (saturated KCl) and Pt wire were applied as working electrode, reference electrode and counter electrode, respectively. Analytical rotator AFMSRX (PINE instruments, USA) and rotating disc glassy carbon electrode (RDE, area 0.21 cm^2) were employed in the amperometric studies. Field emission scanning electron microscopy (FESEM) and energy dispersive X-ray (EDX) spectroscopy were performed using Hitachi S4700 and HORIBA EMAX XACT. X-ray diffraction (XRD) studies were done with Rigaku D/maxB, DMX-2200.

2.3 Preparation and fabrication of $\text{CuO}/f\text{-MWCNTs}/\text{GCE}$.

CuONBs was synthesized by the precipitation method as previously reported [23]. In brief, 0.05 M copper nitrate was dissolved in double distilled water and it was stirred for 10 min to get a homogenous solutions. Then, aqueous solution of 0.05 M ammonium carbonate was slowly added in to the beaker containing 0.05 M copper nitrate. After adding ammonium carbonate, the solution of copper nitrate was converted in to copper hydroxide precipitate. This precipitate was dried at 90°C . The obtained dried precipitate was calcinated at 400°C for 6 h to convert copper hydroxide in to copper oxide. The preparation of $f\text{-MWCNTs}$ was done by using the earlier reported procedure as follows [24]: Crude MWCNTs (0.5 g) and 0.4 M aqueous solution of HCl (60 ml) were mixed together in a beaker and sonicated for 4 h. 3:1 concentration of 60 ml concentrated $\text{H}_2\text{SO}_4/\text{HNO}_3$ was gradually added by stirring the above mixture. Later, the mixture was refluxed for 4 h and cooled to room temperature. 400 ml double distilled water was used to dilute the mixture and filtered until the pH of

the mixture becomes 7. The solid *f*-MWCNTs product was dried at 70 °C for 12 h and further utilized in CuONBs/*f*-MWCNTs nanocomposite preparation.

The prepared copper oxide (1mg/ml) was mixed with the aqueous solution of *f*-MWCNTs (1 mg/ml) and sonicated for 30 min to get CuONBs/*f*-MWCNTs nanocomposite. The surface of glassy carbon electrode (GCE) was polished with 0.05 μm alumina slurry using a Buehler polishing kit, cleaned and dried. Then 8 μl of CuONBs/*f*-MWCNTs nanocomposite was drop cast onto the pre-cleaned GCE, dried at ambient conditions and used for electrochemical experiments. For the control, CuO and *f*-MWCNTs modified GCEs were also individually fabricated.

3. RESULT AND DISCUSSION

3.1 Characterization of CuONBs/*f*-MWCNTs nanocomposite

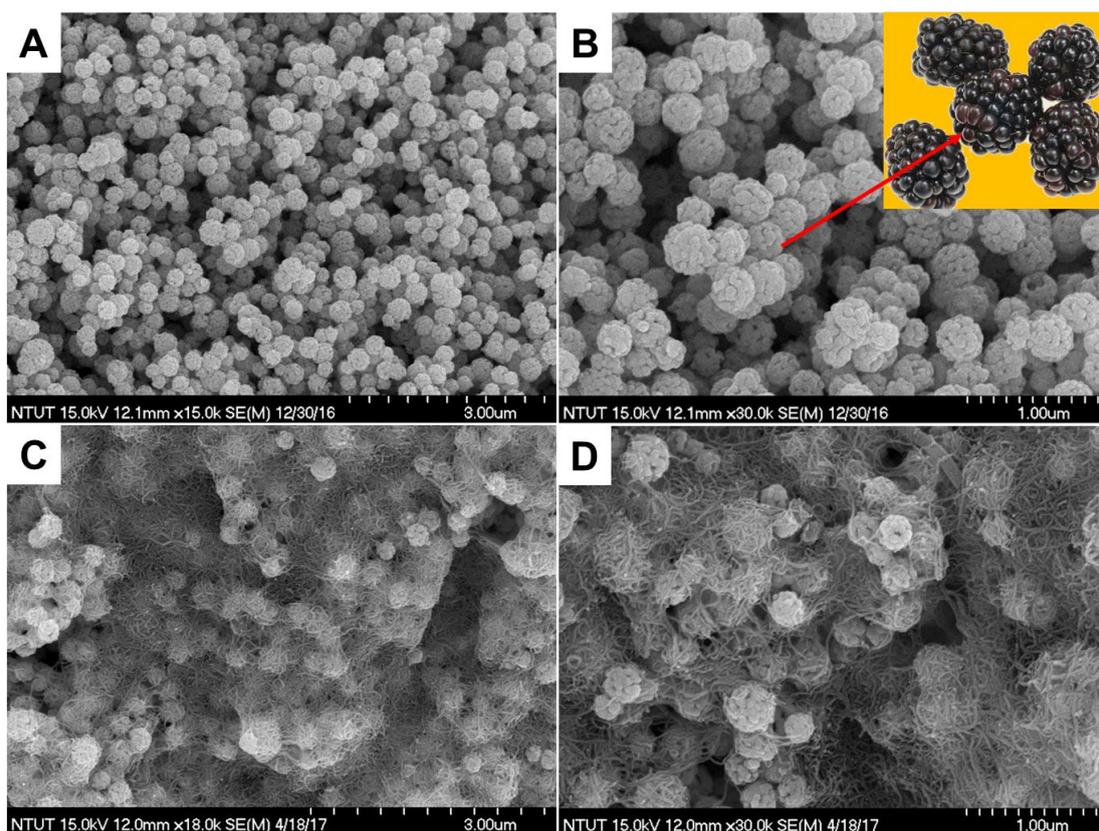


Figure 1. FESEM image of CuONBs (A&B) and CuONBs/*f*-MWCNTs (C&D).

The morphology of the prepared nanocomposite was characterized by field emission scanning electron microscopic (FESEM) technique. FESEM images of CuONBs and CuONBs/*f*-MWCNTs are presented in Figure 1 (A–D). The Figures 1A&1B shows the FESEM images of copper oxide at higher and lower magnifications. Figure (1A&B) shows the highly dense berries like nanoparticles with a diameter of 200 ± 50 nm. MWCNTs covered copper oxide nanoberries was observed for CuONBs/*f*-

MWCNTs. This indicates that the $-\text{COOH}$ functional group of MWCNTs is ready to accept the copper oxide nanoparticles on its wall. Moreover, the elemental composition of the prepared CuONBs/*f*-MWCNTs was studied by energy dispersive x-ray spectroscopy (EDX) and their results are given in Figure 2A. EDX spectrum of CuONBs/*f*-MWCNTs showed signals for the elements: carbon, oxygen and copper with their weight percentages of 28.18, 29.84 and 41.98, respectively. The observation of high weight percentage (41.98) for copper, apparently revealed the higher loading of copper oxide in to MWCNTs.

Figure 2B shows the X-ray diffraction (XRD) pattern observed for CuONBs/*f*-MWCNTs. For copper oxide, nine different diffraction peaks were obtained at the 2θ values of 32.74° , 35.93° , 39.02° , 48.97° , 53.28° , 62.28° , 67.77° , 68.31° and 75.91° with their corresponding crystal planes at (-110), (-111), (111), (-202), (020), (-113), (-311), (-211) and (222), respectively. The obtained XRD pattern of CuONBs was in concordance with the previously reported crystalline copper oxide [25]. Moreover, a broad diffraction peak at 24° (002) was also appeared indicating the graphitic network of carbon nanotubes [26]. From the XRD results, the formation of CuONBs decorated *f*-MWCNTs was clearly exposed.

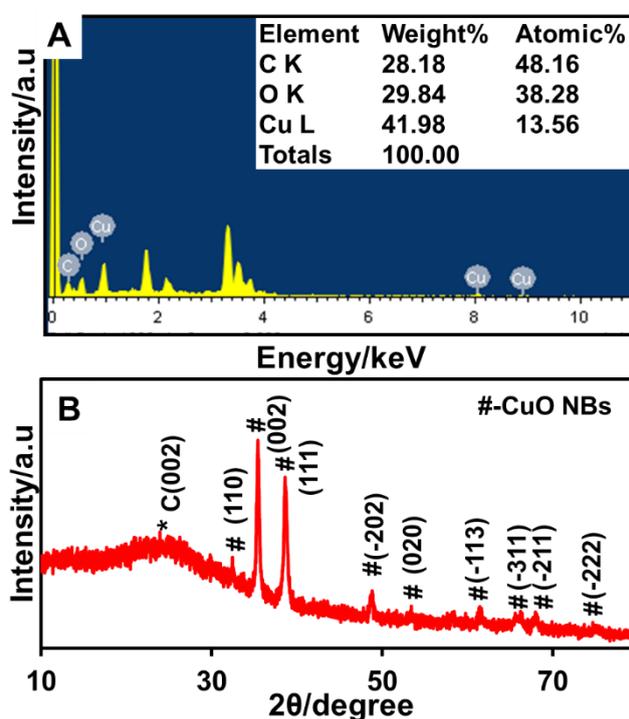


Figure 2. EDX (A) and XRD (B) spectrum CuONBs/*f*-MWCNTs.

3.2 Electro-reduction of H_2O_2 at various modified electrodes

The CVs for the electro-reduction of H_2O_2 in 0.05 M PB (pH 7) solution at bare, CuO, *f*-MWCNTs and CuONBs/*f*-MWCNTs modified GCEs for the presence of 2 mM H_2O_2 were given in Figure 3. The bare GCE exhibited no considerable peak current response towards reduction of 2 mM H_2O_2 indicating its poor electron transfer kinetics (For sake of clear plotting, figure is not given). The

good electrocatalytic activity of CuO/GCE was exposed from the enhanced cathodic peak at -0.217 V (peak current= $120.92 \mu\text{A}$). But, a low cathodic response at -0.77 V was shown by *f*-MWCNTs/GCE with a peak current value of $309 \mu\text{A}$. CuONBs/*f*-MWCNTs/GCE displayed a well-defined cathodic peak (peak current= $0.252 \mu\text{A}$) at the potential of -0.34 V which is 2 folds higher than CuO/GCE and many folds higher than *f*-MWCNTs/GCE and bare GCE. The decreasing order of the modified electrodes in the electro-reduction of H_2O_2 is CuONBs/*f*-MWCNTs > CuO NBs > *f*-MWCNTs > bare (unmodified). This higher performance of CuONBs/*f*-MWCNTs can be due to the several functional groups present in *f*-MWCNTs holding more CuO and so the composite offers high surface area and numerous catalytic sites for the reduction of H_2O_2 at CuONBs/*f*-MWCNTs/GCE.

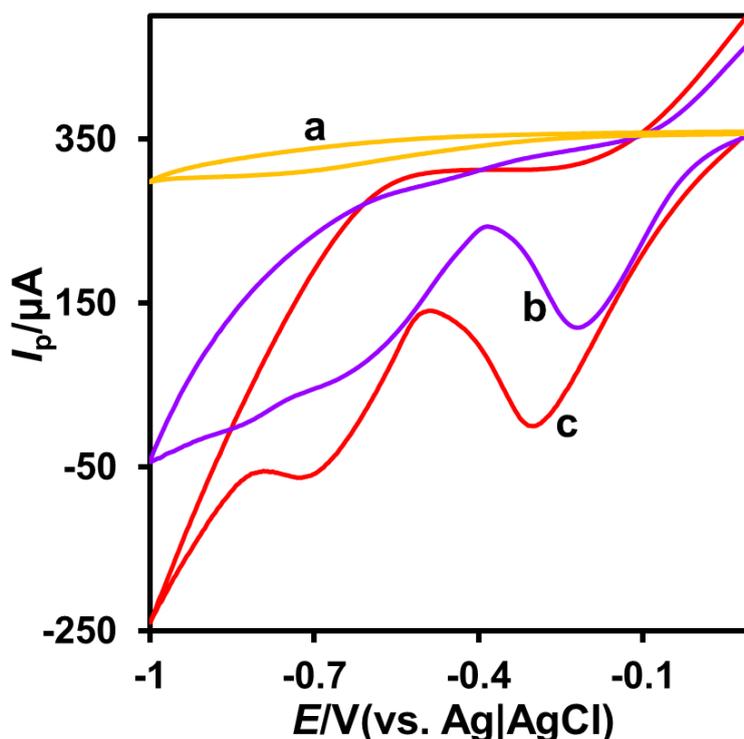


Figure 3. CVs obtained at *f*-MWCNTs (a), CuO (b) and CuONBs/*f*-MWCNTs (c), films modified electrodes in 0.05 M PB (pH 7) solution in the presence of 2 mM H_2O_2 [scan rate= 50 mVs $^{-1}$]

3.3 Effect of scan rate

The CVs for the effect of scan rate at CuONBs/*f*-MWCNTs modified GCE in 0.05 M PB (pH 7) solution containing 2 mM H_2O_2 were displayed in Figure 4A. The CVs were taken in the varying scan rate from 0.1 V/s to 0.5 V/s. Each increase in the scan rate value from 0.1 V/s to 0.5 V/s correspondingly exhibited an increase in the cathodic peak current response and additionally a potential shift was observed in the negative direction. The calibration plot (Figure 4B) represents the linear relationship between cathodic peak current and square root of scan rate. Thus, the overall reaction of H_2O_2 reduction at CuONBs/*f*-MWCNTs/GCE is a diffusion controlled process [27].

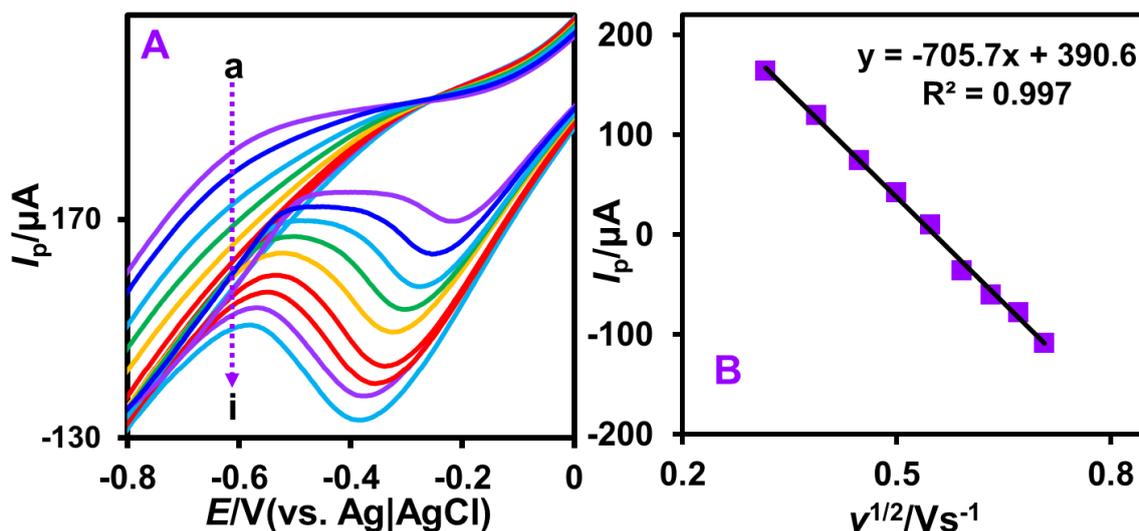


Figure 4. (A) CVs obtained at CuONBs/*f*-MWCNTs/GCE in 0.05 M PB (pH 7) solution at different scan rates (0.1 to 0.5 V s⁻¹) in the presence of 2 mM H₂O₂. (B) Calibration plot between I_p vs $v^{1/2}$.

3.4 Amperometric *i*-*t* determination of H₂O₂ at CuONBs/*f*-MWCNTs/GCE

The amperometric *i*-*t* response for the determination of H₂O₂ at CuONBs/*f*-MWCNTs/GCE in 0.05 M PB (pH 7) solution at rotation speed of 1500 rpm was displayed in Figure 5A. The applied potential for the amperometric measurement was fixed to be -0.3 V. The immediate cathodic peak current response exhibited by CuONBs/*f*-MWCNTs modified GCE for each addition of H₂O₂ was stable and also 98.2 % of the steady state response current was achieved within a time period of 3 s. An increase in cathodic peak current was observed for each consecutive addition of H₂O₂ with increasing concentration (5, 50 and 500 μM). The distinguishable peaks appeared for the addition of different H₂O₂ concentrations can be visualized from the Figure 4A. Standard error (n=3) bar was used for fitting the calibration plot between $j/\text{mA cm}^{-2}$ and [H₂O₂]. The calibration plot (Figure 5B) shows the linear dependency between cathodic peak current response and concentration of H₂O₂. The calculated values of linear range, LOD (limits of detection) and sensitivity for our fabricated electrode were found to be 5 μM–10.5 mM, 0.78 μM and 1100 μA mM⁻¹cm⁻², respectively. The LOD value was evaluated by using the equation: $\text{LOD} = 3s_b/S$ (Here, s_b =standard deviation of blank signal and S =sensitivity) [28]. The valued electroanalytical parameters namely linear range, LOD and sensitivity were quite comparable with the formerly reported electroanalytical parameters of the H₂O₂ sensors (Table 1). The calculated LOD and linear range of modified are quite compared with formerly reported copper and copper oxide based nanomaterial modified electrodes. Notably, the obtained sensitivity of our modified electrode achieved several times higher compared to other copper and copper oxide based nanomaterial modified electrodes [15,18, 27, 29-34]. From this observation, it concludes that our fabricated CuONBs/*f*-MWCNTs/GCE showed an excellent electrocatalytic ability towards the determination of H₂O₂.

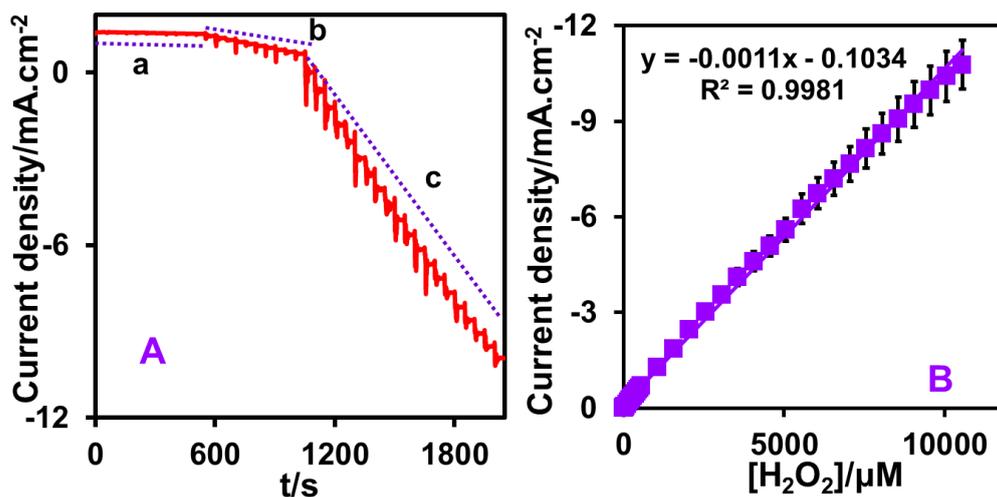


Figure 5. (A) Amperograms obtained at CuONBs/*f*-MWCNTs nanocomposite modified rotating disk electrode upon the successive additions of 5, 50 and 500 μM H₂O₂ into 0.05 M PB (pH 7) solution. Working potential = − 0.3 V. (B) Calibration plot of I_{pa} vs [H₂O₂].

Table 1. Comparison of electroanalytical parameters towards the determination of H₂O₂ at CuONBs/*f*-MWCNTs/GCE with other films modified electrodes.

| Modified Electrode | Linear range(mM) | Sensitivity (μA mM ⁻¹ cm ⁻²) | LOD (μM) | Ref. |
|--|------------------|--|-------------|--------------|
| Heart/dumbbell-like CuO | 0.01–0.9 | 72.9 | 4 | |
| Grass-like CuO | 0.01–0.9 | 80.4 | 5.5 | [27] |
| Aggregate CuO | 0.01–0.4 | 8.7 | 6 | |
| CuO nanorod | 0.1–0.8 | 150 | 0.22 | [29] |
| CuO NPs | 0.001– 2.5 | 392.99 | 0.5 | [30] |
| Cu/Porous silicon | 0.50–3.78 | – | 0.27 | [31] |
| PVP stabilized CuNPs | 0.008– 0.07 | – | 3.4 | [32] |
| SCuO-nanoflower | 0.042–40 | 88.4 | 0.167 | [18] |
| Carbon quantum dots/ octahedral Cu ₂ O | 0.02– 4.3 | 0.298 | 8.4 | [33] |
| Cu ₂ O/Graphene nanosheets | 0.3–7.8 | – | 20.8 | [15] |
| Cu ₂ O/Nafion | 0.002–0.35 | – | 1.3 | [34] |
| CuONBs/ <i>f</i> -MWCNTs | 0.005–10.5 | 1100 | 0.78 | This work |

3.5 Repeatability, reproducibility and stability

The studies for repeatability and reproducibility were also done by cyclic voltammetry method. Single CuONBs/*f*-MWCNTs modified GCE was used to perform six measurements repetitively in 0.05 M PB (pH 7) solution. The concentration of H₂O₂ were fixed as 0.05 mM and 50 mV/s. Our modified electrode showed an acceptable repeatability with 2.9% of relative standard deviation (RSD). So as to examine the reproducing behavior, six CuONBs/*f*-MWCNTs/GCEs were constructed and tested in the similar conditions as mentioned earlier. An appreciable reproducibility along with the RSD of 3.3%

was achieved by our proposed sensor. It reveals that the by-products formed during oxidation or reduction reactions does not affect the reproducibility of CuONBs/*f*-MWCNTs/GCE during its repeated usage. In order to test the stability of CuONBs/*f*-MWCNTs/GCE, it was stored in 0.05 M PB (pH 7) solution at 4 °C for a month after performing the everyday experiment for the detection of H₂O₂. The amperometric response for the electro-reduction of H₂O₂ at CuONBs/*f*-MWCNTs modified GCE displayed 95.2% of the initial response current throughout its storage period. Thus, CuONBs/*f*-MWCNTs/GCE possess a considerable storage as well as operational stability.

3.6 Selectivity studies

The selectivity experiment of CuONBs/*f*-MWCNTs/GCE was carried out in the presence of various biologically interfering molecules (0.1 mM) such as dopamine, uric acid, glucose, fructose, nitrite, ascorbic acid and nitrate. CuONBs/*f*-MWCNTs/GCE exhibited an enhanced cathodic peak current response towards the electro-reduction of 0.05 mM H₂O₂. On the other hand, no obvious peak current response was observed for other interfering agents due to the probable detection of H₂O₂ at low potential value. Therefore, our fabricated electrode is highly selective towards H₂O₂ even in the presence of various interfering biomolecules.

3.7 Real sample analysis

The demonstration of practical feasibility for CuONBs/*f*-MWCNTs modified GCE was done in urine and blood serum samples of humans. This analysis was performed in the same experimental conditions as mentioned earlier in section 3.4. The valued recovery results (Table 2) for the human urine and blood serum samples by using the standard addition method were 97.92%, 99.04%, 98.24% and 99.24, respectively. These evaluated recovery values were fairly satisfactory and the RSD is very low compared to the fixed tolerable limit of H₂O₂. This validates the better feasible practicality of our proposed fabricated electrode.

Table 2. Determination of H₂O₂ in human urine and serum samples

| Samples | Added (μM) | Found ^a (μM) | Recovery (%) | RSD ^b (%) |
|-------------|------------|-------------------------|--------------|----------------------|
| Human urine | 50 | 48.96 | 97.92 | 2.9 |
| | 100 | 99.04 | 99.04 | 2.83 |
| Human serum | 50 | 49.12 | 98.24 | 2.78 |
| | 100 | 99.23 | 99.24 | 2.54 |

4. CONCLUSIONS

In summary, CuONBs/*f*-MWCNTs/GCE, a highly sensitive amperometric sensor for the detection of H₂O₂ was successfully fabricated through a simple electrochemical approach. FESEM, XRD and EDX techniques were employed to validate the surface morphology, crystal structure and

elemental composition of the prepared composite. The results of cyclic voltammetry and amperometric i-t technique reveals the superior electrocatalytic ability of CuONBs/f-MWCNTs/GCE towards reduction of H₂O₂. The calculated electroanalytical parameters namely a wide linear range, low LOD and high sensitivity also support the excellent electrocatalytic behavior of CuONBs/f-MWCNTs modified GCE. The sensitive determination of H₂O₂ in real samples demonstrates the better practical feasibility of our fabricated electrode. Therefore, CuONBs/f-MWCNTs/GCE can be used as a promising platform for the near future applications including optics, biosensors and electronics.

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