

Nonenzymatic glucose sensor with high performance electrodeposited nickel/copper/carbon nanotubes nanocomposite electrode

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ABSTRACT

The uniform and homogeneous carbon nanotubes thin film was electrophoretically deposited and decorated with nickel (Ni) and copper (Cu) nanostructures for Ni/Cu/CNTs nanocomposite electrode as a sensor for enzyme free glucose detection. The CNTs film on fluorine-doped tin oxide (FTO) glass confined the growth of Ni and Cu nanoparticles by electrochemical deposition through cyclic voltammetry (CV). The fabricated nanocomposite electrode replaced the expensive glassy carbon electrode in efficiency. The electrocatalytic glucose oxidation behavior of sensing electrode was analyzed by amperometric measurements and cyclic voltammetry in the presence of alkaline medium. The fabricated nanocomposite electrode exhibited higher sensitivity $1836.5 \mu\text{A mM}^{-1} \text{cm}^{-2}$, fast response time of 1 s, linear wide range of concentration (0.02 mM–4.5 mM) and low glucose detection value of $2.0 \mu\text{M}$. The simple fabrication process of sensing electrode makes Ni/Cu/CNTs an efficient nanocomposite for efficient glucose detection with high reproducibility.

1. Introduction

In latest years, biosensors demand is growing significantly in biomedical and food productions, in clinical quantifiable diagnostics and several environmental applications [1,2]. The sensitive, fast and reliable glucose biosensors are critical for monitoring of food items and diabetes [3]. The enzyme, glucose oxidase, based amperometric electrochemical glucose biosensors have extensively been examined for glucose level detection in food stuff and blood for better electrocatalytic response and improved sensitivity [4,5]. Immobilized enzyme sensors, however, have some disadvantages such as instability due to presence of intrusive chemicals and changes in the pH and temperature of the sample. To overcome these drawbacks, an alternative approach has been proposed that is determined by the direct electrochemical oxidation of glucose using nonenzymatic glucose sensors [6]. Therefore, efforts have been turned to determine an electrocatalyst to limit the drawbacks of enzymatic glucose biosensors by direct electrocatalysis.

Recently, significant research studies have revealed the extensive applications of nanostructured materials. Nanostructured materials having large aspect ratios and superior electrocatalytic activities have been incorporated in the synthesis of nonenzymatic biosensors for significant physical and chemical analytical performance [7–10].

Different noble metals, such as (Ag, Pt) and metal alloys (Ag-Pt) [11,12], some transition metals and their oxides (Ni, Fe, Cu, CuO, CO_3O_4 , Mn_3O_4) [10,13–16] and perovskite based metallic nanocomposites, for example, $\text{LaNi}_{0.5}\text{Ti}_{0.5}\text{O}_3$ [17], $\text{LaNi}_{0.6}\text{CO}_{0.4}\text{O}_3$ [18], $\text{LaNiO}_3\text{-AgO}$ [19] have been incorporated in nonenzymatic glucose detection because of their remarkable activities as an electrocatalyst. However, expensive noble metals and its alloys are not affordable and therefore are not suitable for large scale production of nonenzymatic glucose sensors [20].

Among several nanomaterials, Copper (Cu) and Nickel (Ni) nanoparticles offer great potential in many applications such as pharmaceutical industry [21], biocatalysis [22] and biosensor [23,50]. Cu and Ni are categorized as efficient electrical conductors at low over potential. The large surface areas and chemical properties of Ni and Cu nanoparticles provide high adsorption rates and strong interaction of elements in glucose sensors. Carbon nanotubes (CNTs) have been an attractive material for high electroanalytical performance due to high chemical stability and surface to volume ratio [24,25,48,49]. CNTs being the supporting matrix play a crucial role in catalyst technology. Therefore, in an attempt to improve functions of catalysts such as stability, electrocatalytic activity and simple preparation, strategies has been focused on the electrochemical fabrication of nanocatalysts on a

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nanostructured support [26–28]. The integration of Cu and Ni with CNTs can play an important role in nonenzymatic glucose sensors. The Ni/Cu nanoparticles provide excellent catalytically active sites with enhanced electron transfer rates through carbon nanotubes [29,30]. However pure Ni and Cu nanoparticles are difficult to fabricate and offer reduced stability due to easy oxidization in air.

Electrophoretic deposition has been used in this project to form CNTs coated thin films [31]. Different simple and inexpensive techniques have been utilized to prepare Cu and Ni nanoparticles with different shapes and sizes, including sol-gel [32], electrodeposition [33], thermal decomposition of organic complexes [34] and chemical reduction [35]. However, these methods are suffering from some limitations of long and costly processes as well as complexity. In the current study, electrophoretic deposition (EPD) has been utilised to develop a simple method to synthesize CNTs based nanocomposites providing strong adhesion and elimination of oxidization of Cu and Ni that has not been reported previously. In this way, Ni and Cu nanoparticles were loaded sequentially on electrophoretically deposited CNTs electrode by a simple electrodeposition. The obtained nanocomposite offered uniform and homogeneous coatings of nanoparticles and characterized with different techniques. The prepared nanocomposite material exhibited wide stability range, high electrocatalytic activity, sensitivity and selectivity precisely for Glucose.

2. Materials and methods

Purified multiwalled carbon nanotubes of diameter ~20 nm, length ~30 μm were purchased from Jinzhou Ltd. China. The chemicals utilised in experiment, sodium dodecyl sulphate (SDS), nickel sulphate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$), nickel Chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), boric acid (H_3BO_3), copper sulphate (CuSO_4), sodium hydroxide (NaOH), potassium ferrocyanide ($\text{K}_4[\text{Fe}(\text{CN})_6]$), glucose, uric acid (UA) and ascorbic acid (AA) were purchased from Merck India. The reagents used were nitric acid (HNO_3), sulphuric acid (H_2SO_4) and deionized (DI) water.

The carbon nanotubes were modified through functionalization with carboxylic acid (COOH) by sonicating at 60 $^\circ\text{C}$ for 6 h in the acid mixture of $\text{HNO}_3/\text{H}_2\text{SO}_4$ (1:3/50 ml). This suspension was mixed in deionized water and centrifuged for 30 min at 8500 revolutions per minute. This procedure was repeated many times for neutral pH solution. Then resulted neutral suspension was then dried for 24 h at 20 $^\circ\text{C}$ to provide carboxylic acid (COOH) functionalized MWCNTs named as COOH-CNTs. To achieve the most dispersed and stable solution for electrophoretic deposition, COOH-CNTs were mixed in the solution of anionic surfactant sodium dodecyl sulphate (SDS). Electrophoretic deposition (EPD) has been performed by using DC voltage power supply. The DC voltage (32 V/cm) was applied for deposition time of 3 min at room temperature. During EPD, in two electrodes cell, the working electrode was FTO substrate and counter electrode was of graphite. These two electrodes were placed parallel to each other at a constant distance in the EPD cell. DC voltage was then applied between electrodes and electrophoresis happened. The CNTs deposited on FTO substrate. This electrode was washed with DI water for removal of contaminants and then dried under ambient conditions. The prepared electrode was ready for Cu electrodeposition. The electrochemical Copper deposition was carried in mixture of Sulphuric acid and copper sulphate (Cu_2SO_4) [0.85 M Cu_2SO_4 + 0.55 M H_2SO_4] using cyclic voltammetry. The voltage scan rate was fixed 100 mV/s from 0.5 to -0.6 V. The Cu/CNTs/FTO electrode fabricated by electrophoretic deposition was also utilized for electrodeposition of nickel through cyclic voltammetry. The nickel (Ni) electrodeposition was carried out in boric acid solution of nickel sulphate and nickel chloride [1 M $\text{Ni}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ + 0.2 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ + 0.5 M H_3BO_3] at 100 mV/s scan rate. The voltage was varied from 0.5 to 1.1 V. Cyclic voltammetry for deposition was repeated 30 times during Cu and Ni electrodeposition for the highly reproducible and sensitive electrodes fabrication. The

highly uniform and homogeneous Ni electrodeposition was performed on electrophoretically deposited CNTs electrode. The fabricated nanocomposite Ni/Cu/CNTs substrate was kept used for electrocatalytic glucose detection.

Ni/Cu/CNTs electrode was characterized through XRD 2001 Bruker diffractometer. The ultraviolet visible (UV-Vis) spectrophotometer recorded the absorption spectrum of sensing electrode. The morphology of nanocomposites was analyzed by scanning electron microscopy (SEM; JSM-6480 L V). To study the electrochemical catalytic properties, amperometric measurements and cyclic voltammetry was performed using Princeton 263 A work station. Three electrodes configuration was used. The counter electrode was graphite, reference electrode was saturated calomel and carbon nanotubes based nanocomposites electrodes were used as working electrode.

3. Results and discussion

In this project, COOH-CNTs were noncovalently functionalized with Sodium Dodecyl Sulphate (SDS) for improved dispersion, followed by electrophoretic deposition of such CNTs on the FTO electrode (CNTs/FTO). Uniform and homogeneous Cu and Ni nanoparticles based thin films were then sequentially deposited on the CNTs/FTO using simple electrochemical deposition. SDS, like other polymers, has a polar side chain with negative charge, which helps to attract the positively charged Cu^{2+} and Ni^{2+} ions, enabling the formation of Ni/Cu/CNTs hybrid composites. In the presence of oxygen and moisture, corrosion of materials takes place and involves oxidation at anodic site and reduction at cathodic site. Corrosion Inhibitors protect materials against corrosion. The surfactant act as inhibitors and reduces corrosion on metallic materials. Surfactant inhibitors offer advantages of high efficiency, low price and low toxicity [36–38]. These properties are attributed to their strong capability to influence the properties of surfaces and interfaces. Sodium dodecyl sulfate (SDS) has been found to be effective corrosion inhibitor for copper and nickel [39]. The use of the SDS in this project as a solubilizing agent provides corrosion inhibition for nickel and copper. Ni electrodeposition over Cu has also increased the corrosion resistance of copper and its uniform layer provided an efficient physical protection to Cu and hence the morphology of Ni/Cu/CNTs electrode stays stable for longer period of time. No oxidation peaks of Cu and Ni has been observed in XRD analysis.

The UV-VIS analysis of nanocomposite Ni/Cu/CNTs electrode was performed using radiations 200 nm–900 nm. Fig. 1 shows the absorbance spectrum of successively electrodeposited Ni and Cu film on electrophoretically deposited CNTs substrate. The optical absorbance peaks around 340 nm and 527 nm confirmed the presence of nickel (Ni) and copper nanostructures (Cu) respectively. The peak around 207 nm shows the optical properties of graphite respectively.

The CNTs, Ni/CNTs, Cu/CNTs, Ni/Cu/CNTs composite electrodes characterized by SEM is shown in Fig. 2. The small particles of diameter

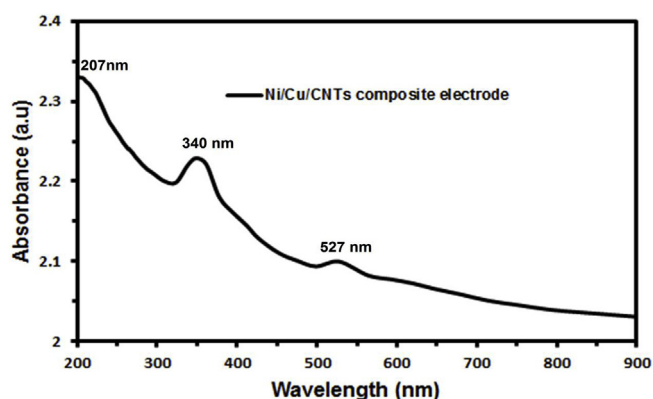


Fig. 1. UV-VISIBLE spectrograph of Ni/Cu/CNTs electrode.

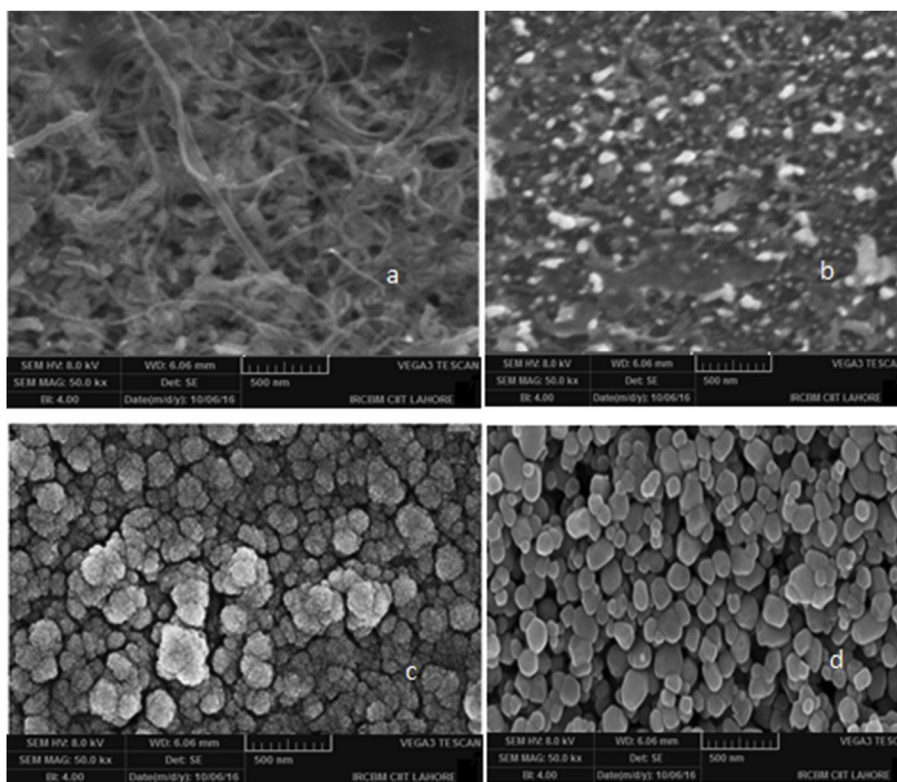


Fig. 2. SEM images of (a) CNTs (b) Ni/CNTs (c) Cu/CNTs (d) Ni/Cu/CNTs electrode.

20 nm are corresponding to Ni and the large particles of diameter 70 nm are corresponding to Cu. The large Cu nanoparticles size indicates agglomeration of uniformly sized Cu nanoparticles. As the size proliferates, some neighboring particles in random distribution combine resulting in aggregation. It depends on the fact that as Cu deposition occurred before Ni, so Cu had enough space to be deposited on the surface of CNTs electrode. Therefore, larger Cu nanoclusters have been originated in the Ni/Cu/CNTs nanocomposite. These images indicate the successful sequential electrodeposition of nickel (Ni) and copper (Cu) on CNTs electrodes. These Cu and Ni nanoparticles provide Ni/Cu/CNTs nanocomposite electrodes having more porous structure in comparison to the Cu/CNTs and Ni/CNTs electrodes. This nanocomposite electrode provides a perfect interface for high performance non-enzymatic electrochemical glucose sensor, since smaller nanoparticles size facilitates the manipulation of high surface area, large electrocatalytic activity and active transfer of electrons from the electrocatalyst to conductive substrate. Fabrication of efficient sensing electrodes needs growth of nanostructures directly on the surface of electrode for seamless connection of nanostructures with electrode to promote fast electro transfer [40]. Herein, an inexpensive and easy technique to attach nanostructure on electrode surface has been adapted. We have directly grown CNTs on FTO substrate by low cost electrophoretic deposition and decorated with Cu and Ni nanoparticles (Ni/Cu/CNTs/FTO electrode) to increase the electrochemical activity of glucose oxidation through higher surface area and direct electron surface. Morphological structure of Ni and Cu modified directly grown CNTs confirmed that the CNTs are seamlessly connected to the electrode surface and uniformly decorated with Cu and Ni nanoparticles.

The Energy dispersive X-ray spectroscopy (EDX) analysis of the Ni/Cu/CNTs electrode in Fig. 3 shows the mixture contains carbon, copper, nickel, and oxygen. The little oxygen is from covalent (COOH) functionalization of the carbon nanotubes. The appearance of Sn is due to FTO glass substrate.

The XRD determination confirmed the crystal structure of Ni/Cu/CNTs nanocomposite electrode as shown in Fig. 4. The X-ray diffraction

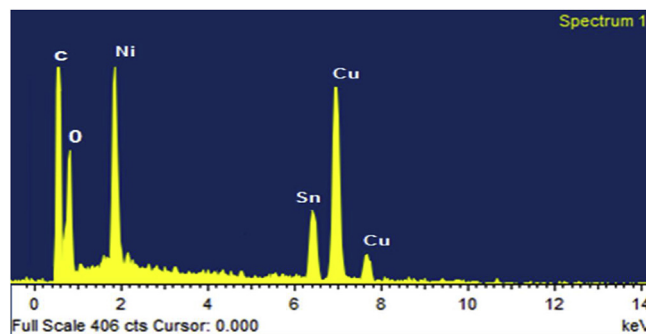


Fig. 3. EDX analysis of Ni/Cu/CNTs electrode.

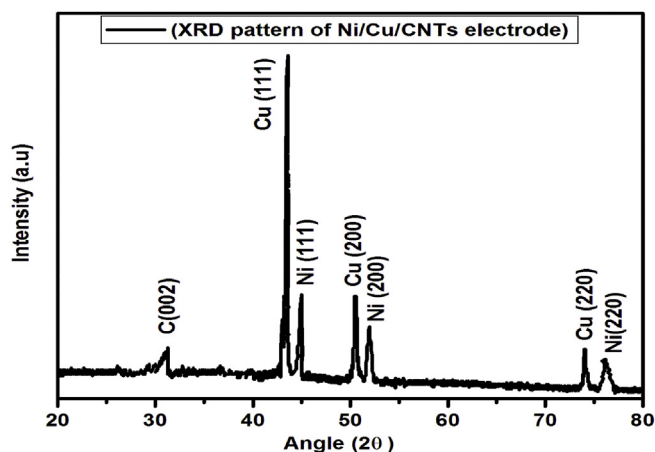


Fig. 4. X-ray diffraction Pattern of Ni/Cu/CNTs electrode.

Table 1
Net current for glucose oxidation with different Ni:Cu ratio using Ni/Cu/CNTs nanocomposite electrode.

Ni:Cu	I _a (μA/cm ²)
20:80	632.5
30:60	827.6
50:50	1002.7
60:30	751.5
80:20	543.6

graph specifies FCC Ni lattice structure with three peaks at 44.70 {111}, 51.76 {200}, and 76.11{220} and peaks at 43.32, 50.59 and 73.85 corresponds to FCC lattice structure of Cu [41]. The XRD peak at 31.4 corresponds to CNTs plane [002] [42]. These outcomes show the successful metallic Cu and Ni electrodeposition on electrophoretically deposited CNTs based electrodes. XRD results signify that in the Ni/Cu/CNTs/FTO nanocomposite the Cu and Ni are separate particles. This might indicates a compact structure formation in Ni/Cu/CNT hybrid composites. It represents more incorporation of amounts of the Nickel (Ni) and copper (Cu) on CNTs modified electrode in compact hybrid structure. This can accomplish that the large aspect ratio of the CNTs assisted the sequential electrodeposition of Cu and Ni nanoparticles.

The electrocatalytic performance of Ni/Cu/CNTs hybrid composite electrode depends on the Ni/Cu ratio. This ratio was optimized by varying scan segments of cyclic voltammetry for different amounts of Cu and Ni to be electrodeposited. The deposition occurred for each ratio of scan segments. Each composite was analyzed for the glucose electrocatalytic oxidation in the presence of 0.5 mM glucose. The anodic oxidation current (I_a) by different composites was estimated as shown in Table 1 The ratio of 50:50 for Ni/Cu provided highest current towards glucose oxidation. This result suggests that this optimised ratio provided an active Ni/Cu/MWCNT composite.

Fig. 5 represents compared voltammograms of carbon nanotubes based FTO electrodes decorated with Ni and Cu nanoparticles in electrolyte of 0.5 mM K₃Fe(CN)₆ and 0.1 M KCl. Potassium chloride (KCl) is utilized as electrically conducting solution known as electrolyte. Potassium ferrocyanide is an important redox system which is selected for its highly surface sensitive electrochemical response. The fabricated electrodes were placed in electrochemical cell as working electrodes. The cyclic voltammetry was conducted at 50 mV/s scan rate from -0.2–0.4 V. The single electron reversible redox mechanism of potassium Ferrocyanide has been analyzed. This strong voltammetric response of Ferrocyanide for CNTs modified electrode is ascribed to high

surface to volume fraction and high catalytic activity. In Fig. 5 for Ni/Cu/CNTs sensing electrode, the current density magnitude was higher as compared to the Cu/CNTs, Ni/CNTs and CNTs modified electrode. The voltammograms showed that Nickel (Ni) and Copper (Cu) were efficiently immobilized on CNTs surface offering the conduction paths for electron between analyte and surface of electrode such as at the nanoscale electrode. The combined Ni and Cu nanoparticles on CNTs electrode has increased the magnitudes of Peak current I_p and decreased the Peak separation (ΔE_p) in comparison to the other nanocomposite electrodes. This designates that the Cu and Ni nanoclusters have also increased the electroactive surface area.

The active surface area was calculated from the Randles–Sevcik equation ($I_p = 2.69 \times 10^5 n^{3/2} AC\nu^{1/2}D^{1/2}$), where I_p is the Redox peak current (A), *n* is the electron transfer number (= 1), *A* is the surface area of the electrode (cm²), *D* is the diffusion coefficient (0.76 × 10⁻⁵ cm²/s), *C* is the concentration of electroactive species (K₃Fe(CN)₆, M/L), and *ν* is the scan rate (V/s).

The electroactive surface areas of nanocomposite electrodes Ni/Cu/CNTs, Ni/CNTs and Cu/CNTs have been calculated to be 2.89 cm², 1.60 cm², 1.32 cm² respectively [38]. These areas were calculated through Randles–Sevcik equation. The active surface area of Ni/Cu/CNTs electrode is higher as compared to other electrodes.

The electrocatalysis of glucose oxidation for CNTs, Cu/CNTs, Ni/CNTs and Ni/Cu/CNTs nanocomposite substrate has been examined by cyclic voltammetry in alkaline solution (Fig. 6a,b,c). The analysis was performed with and without glucose in NaOH solution (0.1 M) at 20 mV/s. The potential was varied between 0 and 0.9 V. The presence of alkaline solution is required to enhance the electrocatalysis of Cu and Ni for oxidation of glucose. Fig. 6(a and b,c) demonstrates that without glucose, no reduction or oxidation peaks appear for CNTs, Cu/CNTs, Ni/CNTs, Ni/Cu/CNTs electrode. When glucose (0.5 mM) was added in alkaline solution, redox peak current was significantly increased for all electrodes except CNTs electrodes. These results indicates that Cu and Ni nanoparticles exhibit excellent electrocatalytic activity towards glucose and CNTs electrode provide high conductivity to increase the electron surface rate. In the presence of glucose, the Cu/CNTs, Ni/CNTs and Ni/Cu/CNTs modified electrodes had net currents of 436 μA/cm², 990 μA/cm² and 1002 μA/cm² respectively. With glucose, the Ni/Cu/CNTs nanocomposite electrode had higher current density as compared to other fabricated electrodes. This higher current magnitude is ascribed to higher CNTs conductivity and bimetallic nanoparticles incorporation. The structure of CNTs-based electrode has been found steric and offered high conductive area to deposit the Ni and Cu electroactive nanoparticles [46].

The redox peak current for Ni/Cu/CNTs is higher as compared to

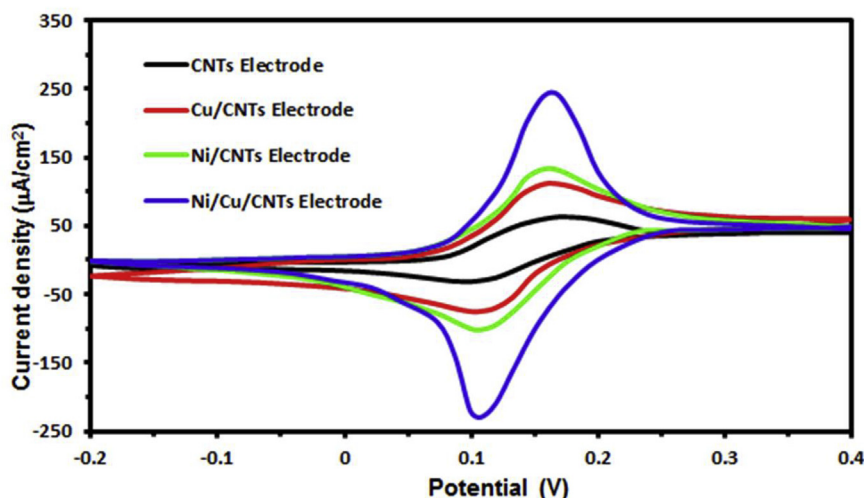


Fig. 5. Cyclic Voltammograms of CNTs, Cu/CNTs, Ni/CNTs and Ni/Cu/CNTs electrodes.

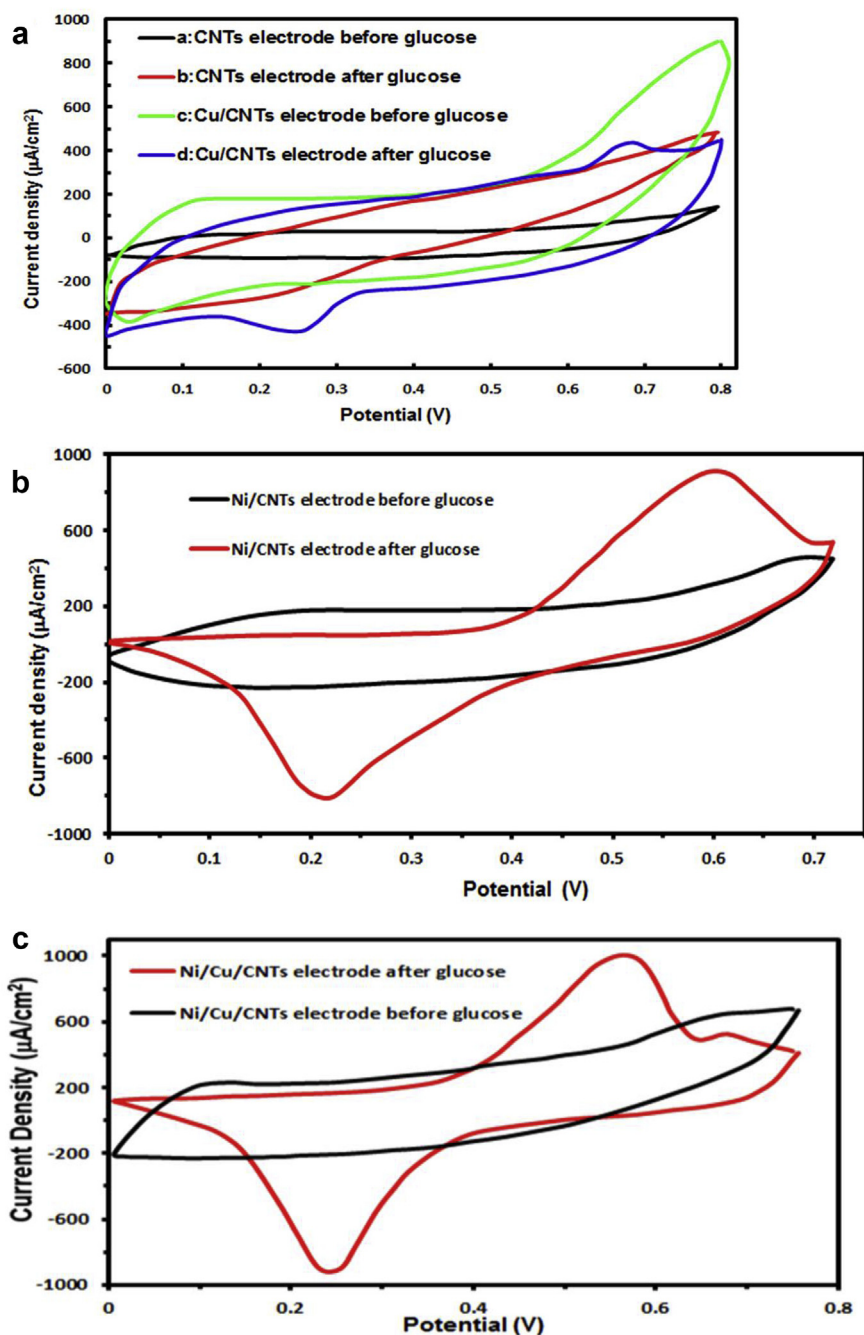


Fig. 6. a)Cyclic Voltammogram of Cu/CNTs electrode after and before adding 0.5 mM glucose. b)Cyclic Voltammogram of Ni/CNTs electrode after and before adding 0.5 mM glucose. c)Cyclic Voltammogram of Ni/Cu/CNTs electrode after and before adding 0.5 mM glucose.

Fig. 5 because the large amount of glucose concentration has been added in electrolyte for glucose oxidation. Current density is directly proportional to glucose concentration. The observed oxidation peak currents at over potential 0.67 and 0.55 V corresponds to the oxidation of glucose for the transition of Cu (II) to Cu (III) and Ni(II) to Ni(III) respectively [43–45]. This specifies that the Ni and Cu nanoparticles in the sensing electrode provide good electroactive catalytic behavior towards glucose oxidation.

Cyclic voltammogram of nanocomposite Ni/Cu/CNTs electrode was also observed in solution of glucose and NaOH (0.1 M) at variable scan rates 20, 60, 80, 100 and 150 mV/s. The scan rates were varied in fixed voltage range 0–0.8 V as shown in Fig. 7. As the scan rate was increased, peak currents increased to higher value. Figure shows the linear variation of square roots of scan rate with reduction peak

currents (cathodic) i_c and oxidation peak currents (anodic) i_a indicating the surface controlled electrochemical reactions through glucose adsorption. The correlation coefficient $R^2 \sim 0.961$ for oxidation and 0.971 for reduction has been calculated.

Glucose detection response was monitored using amperometric measurements in which a current is measured at constant voltage in three electrode electrochemical cell.

The solution pH is also an important factor in determining the activity of nonenzymatic glucose sensors towards glucose oxidation. Table 2 shows the pH-dependent response of the Ni/Cu/CNTs electrode with pH values ranging from 10 to 14. The pH value was varied by varying NaOH concentration in solution. The oxidation potential shifts negatively with increasing pH. As the concentration of NaOH increases, pH increases and anodic peak current increases until the pH reaches 13.

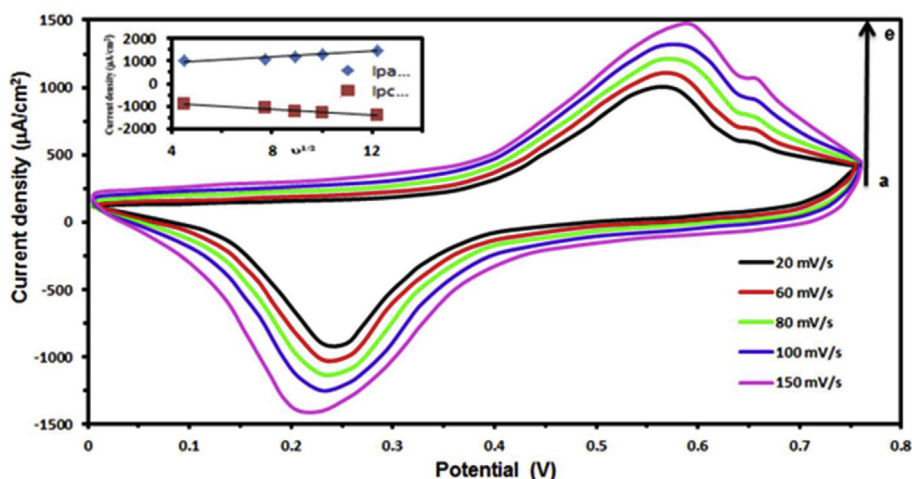


Fig. 7. Cyclic Voltammograms of Ni/Cu/CNTs nanocomposite electrode at various scan rates. Inset: Plot of peak currents with the square root of scan rate.

Table 2
Anodic peak currents under different pH conditions.

pH	I _a (µA/cm ²)
10	200.5
11	423.5
12	856.4
13	1002.7
14	950.6

For further increase in pH, oxidation current decreases. The higher concentration of NaOH would destabilize the substrate materials. Thus pH 13 (0.1 M NaOH) was selected as optimized value for highest glucose oxidation current and it suggests the high performance of the Ni/Cu/CNTs electrode in hydroxide-rich solution [47].

Fig. 8 reveals amperometric current signals of Ni/Cu/CNTs nanocomposite at the optimal voltage ~ 0.55 V. The varying concentration of glucose has been added with continuous intervals in alkaline solution (0.1 M NaOH). As the glucose was added, a rise in current was detected. The current signal then acquires a steady state value in almost 1 s as shown in Fig. 8. The response time was found to be varied between 1 s and 2 s. This indicates an enormously fast reaction of Ni/Cu/CNTs sensing electrode towards oxidation due to rapid glucose flow to electrode. The electrophoretically deposited Carbon nanotubes based electrode has increased the electro conductive performance.

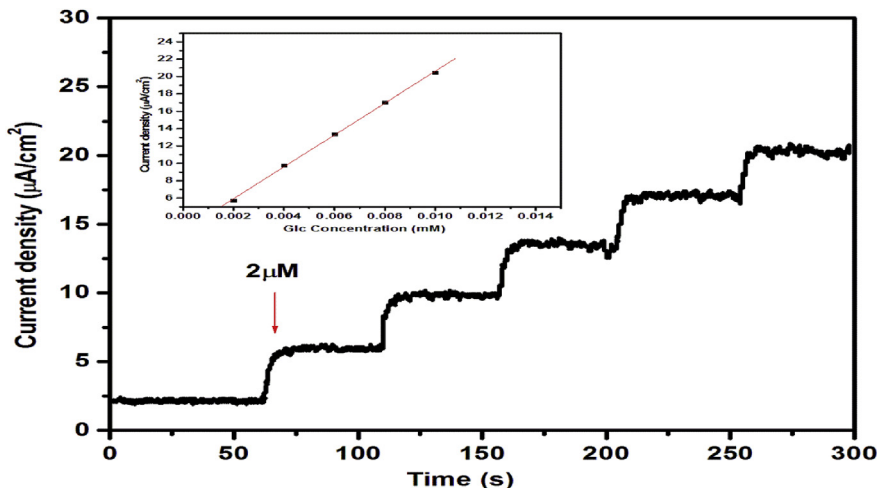


Fig. 8. Current versus time plot of Ni/Cu/CNTs nanocomposite for variable glucose concentrations. Inset: Plot of Current and glucose concentration.

The linear plot of current density ($\mu\text{A}/\text{cm}^2$) and varying glucose concentrations (mM) has been shown in inset of Fig. 8. This inset provides correlation coefficient R^2 0.999. Sensitivity of the electrode indicates the change in current signal by varying the analyte concentration, therefore the slope of inset curve of Fig. 8 evaluated the sensitivity. The slope equation for the linear curve is $y = 1836.5x + 2.259$ providing the sensitivity of the Ni/Cu/CNTs electrode to be $1836.5 \mu\text{A mM}^{-1} \text{cm}^{-2}$. The limit of detection was found using ($\text{LOD} = 3 \cdot \text{sd}/m$) where sd is standard deviation of blank sample and m represents calibration sensitivity that was calculated ($1836.5 \mu\text{A mM}^{-1} \text{cm}^{-2}$) from the slope of linear plot of current versus concentration. The standard deviation was measured by running CV for 10 times with modified electrode in the absence of glucose in electrolyte. The 10 values of current of blank was measured at 0.6 V potential where glucose gets oxidised. Standard deviation was calculated for these 10 values. Lowest limit of glucose concentration to be detected is 2.0 μM .

Reproducibility of electrode has been evaluated by fabricating five consecutive Ni/Cu/CNTs nanocomposite electrodes having identical experimental conditions. The current reactions were investigated in electrolyte solution of glucose and NaOH (0.5 mM: 0.1 M). The generated current has been evaluated for these electrodes. The relative standard deviation (RSD) of five measurements of each electrode was found 3.6%. The current evaluation of successive 5 electrodes contributes RSD of 4.9%. Thus Ni/Cu/CNTs electrode offers excellent

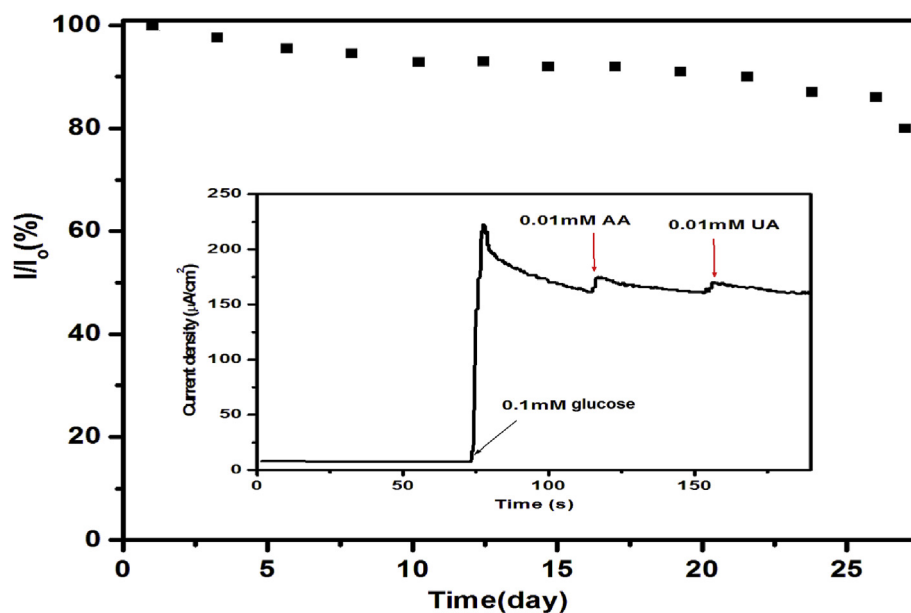


Fig. 9. Stability evaluation of Ni/Cu/CNTs electrode. Inset: Interference response of Ni/Cu/CNTs electrode.

reproducible current during enzyme free glucose measurements. Fig. 9 displays the stability evaluation of nanocomposite Ni/Cu/CNTs electrode. The stability performance of sensing electrode has been analyzed by examining the detection response to glucose solution, after successive 2 days. The oxidation of nanocomposite Ni/Cu/CNTs electrode was observed by storing in air. It has been evaluated that the net magnitude of current persevered about 90% after 25 days. This ensures a good stability of nanocomposite electrode.

Some easily oxidizable chemicals like uric acid (UA) and ascorbic acid (AA) provides intrusive current values which are the main drawbacks in the nonenzymatic glucose detection. Even though these interfering species of uric acid and ascorbic acid are in lower quantity as compared to glucose in regular blood serum sample, however these produce comparable responsive current signals. This phenomenon is ascribed to more number of transfers of electrons [39]. The comparison of current signals of 0.01 mM intrusive species and 0.1 mM glucose is shown in the inset of Fig. 9. A substantial response has been detected for glucose oxidation in comparison to AA and UA. Thus the interfering species has shown negligible response. This determines that the Ni/Cu/CNTs nanocomposite is highly active towards glucose irrespective of interfering compounds.

To consolidate finally, the nonenzymatic glucose sensor based on Ni/Cu/CNTs electrode presents attractive features, like high sensitivity, improved stability, strong reproducibility, and tiny response time. Thus Ni/Cu/CNTs nanocomposite is attractive material for electrochemical glucose sensor for the continuous glucose measurements. The enzyme free glucose analysis literature shows that this electrode is competitive for operative low cost glucose determination with high sensitivity and low values of over-potential and detection limit.

4. Conclusion

Enzyme free electrochemical glucose sensor has been established by successive electrodeposition of Cu and Ni nanoparticles on CNTs based electrode. The CNTs electrode was fabricated on FTO substrate thorough electrophoretic deposition. The fabricated Ni/Cu/CNTs electrode exhibited fast response time of approximately 1 s, high stability and reproducibility. Sensitivity $1836.5 \mu\text{A}/\text{mM}^{-1}\text{cm}^{-2}$ was fairly high by the electrode. The glucose detection by electrode offered linear range (0.02–4.5 mM). The lowest value of glucose concentration ($2 \mu\text{M}$) has been detected. This value of higher sensitivity is ascribed to the

increased electrocatalysis by successful uniform successive electrodeposition of metallic nanoparticles (Ni and Cu) on CNTs thin films based substrate. The low cost CNTs coated FTO substrate can be replaced with expensive glassy carbon electrode (GCE) for effective glucose determination. This project offers an encouraging technique to integrate the electrophoretically deposited CNTs electrodes for potential applications in several industries.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jpjcs.2018.04.015>.

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