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Direct growth of ternary copper nickel cobalt oxide nanowires as binder-free electrode on carbon cloth for nonenzymatic glucose sensing

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ABSTRACT

A new binder free electrode based on ternary copper nickel cobalt oxide nanowires grown on the carbon cloth ($CuNiCoO_4$ NWs@ carbon cloth) was prepared and characterized by field emission scanning electron microscopy (FE-SEM), x-ray diffraction (XRD), Energy-dispersive X-ray spectroscopy (EDX), and cyclic voltammetry (CV). The prepared electrocatalyst was directly used for electrochemical sensing of glucose without using enzyme. The effect of different parameters such as potential scan rate, switching potential, and glucose concentration on the electrochemical oxidation of glucose was investigated. The results showed that such an electrode presents excellent catalytic activity toward the oxidation of glucose in aqueous alkaline solution. Under optimum conditions, the potential application of the electrode was evaluated by applying it to the analytical determination of glucose concentration. The results revealed that the electrocatalytic current increased linearly with the glucose concentration in the range from 0.02 to 1.4 mM with a low detection limit of 6.5 μM and good sensitivity of as high as 1782 $\mu A\, mM^{-1}\, cm^{-2}$. Selectivity investigations demonstrate that the $CuNiCoO_4$ NWs@CC electrode could be used for selective detection of glucose in the presence of interfering species. Real sample analysis shows reasonable RSD values implying negligible matrix effect in determination of glucose in human serum samples.

1. Introduction

Rapid, sensitive, selective and reliable glucose sensing is important for wide variety of industries and sciences such as food industry, biotechnology, environmental, and clinical monitoring [1]. So far, various glucose sensors have been established based on optical, acoustic, electronic, fluorescent, electrochemical methods and et cetera [2]. Between these glucose sensors, electrochemical sensors are of high great importance because of their high sensitivity, specific selectivity and low cost [3]. Since Clark's and Lyon's work on enzyme glucose biosensor in 1962 [4], determination of glucose attracted particular attention. Commercialized sensors for glucose monitoring utilized enzymes such as glucose oxidase, which adheres particularly to b-D-glucose and then it catalyzes the glucose oxidation to hydrogen peroxide and D-glucono-δ-lactone. The transduce signal is originates form the oxidation of hydrogen peroxide that is produced in the presence of sensing element (enzyme) [1, 5, 6]. Although, these sensors show high sensitivity and selectivity toward glucose oxidation [5, 7, 8], but, they usually suffered from short lifetime and their efficiency are simply affected by the changes in pH values, humidity of the media, temperature, the enzyme immobilization techniques and the attendance of toxic chemicals during measurements [9–11].

Recently, electrochemical methods have attracted increasing attention for determination of glucose and other analytes [12–15]. However, Non-enzymatic glucose sensors of noble metals such as Pd [16], Au [17] and Pt [18] or their corresponding amalgams [19, 20] widely utilized for glucose measurement. However, these electrode materials have high costs which limits their wide applications in various field of sciences. Hence, many attempts have been done to design new and cost-effective catalyst materials. In this regard, one component-based transition metal oxides such as Co_3O_4 [21], NiO [1, 22], Cu_2O [23] or binary metal oxides and hydroxides such as CuO_x-CoO_x

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[24], Cu_2O/NiO_x [25], $Ni_xCo_{2x}(OH)_{6x}$ [26], $NiCo_2O_4$ [27, 28] have been attracted an extensive attention.

Commonly, in a typical electrochemical nonenzymatic glucose sensor, the electrocatalysts are produced in the form of nanoparticles, and then immobilized on conductive substrates by definite usually non-conductive and electrochemically inactive polymeric binders. The existence of the polymeric binders in the electrochemical nonenzymatic glucose sensor not only enhances the series resistance values but also blocks the active sites of the catalyst and hinders the electrolyte ions diffusion to the surface of the catalyst, eventually results in a significantly reduced electrocatalytic activity and poor performance of the sensor. However, using binder-free electrocatalysts grew directly on the surface of conductive substrates could overwhelmed such problems [1, 29–31]. However, to the best of our knowledge, there is no report on the preparation of ternary metal oxides for glucose sensing in alkaline media.

In this work, $CuNiCoO_4$ nanowires constructed on carbon cloth electrode ($CuNiCoO_4$ NWs@CC) as nonenzymatic glucose sensor were proposed for the first time. The ternary metal oxide nanowires uniformly covered the carbon cloth surface and formed three-dimensional heterostructures. Due to the presence of more active catalytic sites, the resulting nanowires showed a high performance for the non-enzymatic determination of glucose. The electrochemical and electrocatalytic behaviors of the ternary metal oxide nanowires toward the oxidation of glucose were evaluated by cyclic voltammetry and hydrodynamic amperometry methods. The results showed that this new ternary metal oxide could be an excellent candidate for electrocatalytic oxidation of glucose in alkaline media.

2. Experimental

2.1. Materials

The copper nitrate trihydrate ($Cu(NO_3)_2{\cdot}3H_2O$), cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$), nickel nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$), ammonium fluoride (NH_4F) and urea ($CO(NH_2)_2$) were purchased from Merck Chemicals Company. All used aqueous solutions were made up in deionized (DI) water. All the chemicals used in the experiments were of analytical grade without further purification.

2.2. Synthesis of $CuNiCoO_4$ NWs@CC

The growth of $CuNiCoO_4$ NWs arrays on CC was performed using a facile hydrothermal synthesis method that combined with a calcination procedure. Before deposition process, a piece of commercial CC substrates was ultrasonically cleaned in acetone, deionized water and ethanol, respectively and dried in an oven. Then, a reaction solution including 1 mM of $Cu(NO_3)_2{\cdot}3H_2O$, 1 mM of $Ni(NO_3)_2{\cdot}6H_2O$, 1 mM of $Co(NO_3)_2{\cdot}6H_2O$, 6 mM of ammonium fluoride (NH_4F) and 15 mM urea ($CO(NH_2)_2$) in distilled water was prepared under constant magnetic stirring for 30 min. After putting a piece of cleaned CC (1 cm × 1 cm), a portion of 70 mL of the prepared solution was transferred into 100 mL Teflon-lined stainless steel autoclave and the temperature was maintained at 120 °C for 6 h. After the autoclave spontaneously cooled to room temperature, in order to remove residual reactants and free debris, the CC that covered with mixed metal (Cu, Ni, Co) carbonate hydroxide precursor film was carefully rinsed with de-ionized water and absolute ethanol in succession. Then, the prepared carbonate hydroxide precursor was dried using vacuum at 60 °C for 12 h. Finally, the precursor sample was put in a quartz tube furnace and thermal annealing was performed at 350 °C (2 °C min^{-1}) in argon atmosphere for 2 h, which a full transform of precursor to hierarchical structure of Cu-Ni-Co ternary oxide ($CuNiCoO_4$) supported on CC was occurred in this step.

2.3. Materials characterizations

The crystallographic structure of the prepared samples was investigated by X-ray diffraction (XRD) equipped with Cu Kα radiation (λ: 1.78901 Å). The microstructure and chemical composition of the samples were determined by using a field-emission scanning electron microscope (FE-SEM) that equipped with an energy-dispersive X-Ray spectrometer (EDX) (TESCAN). All of the electrochemical measurements were performed on Autolab PGSTAT101 at the room temperature.

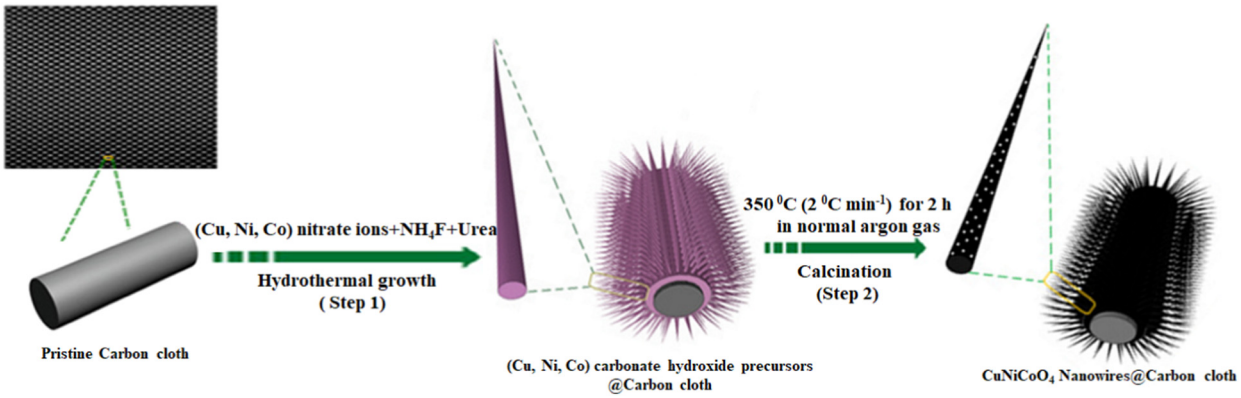
2.4. Electrochemical studies

Electrochemical performance of the as-synthesized hierarchical nanostructured electrode was studied in aqueous solution of NaOH (0.1 M) with three electrode cell configuration which $CuNiCoO_4$ NWs@CC was directly used as a working electrode, a platinum plate as a counter electrode, and a Ag/AgCl (3.5 M KCl) as a reference electrode. Cyclic voltammetry (CV) tests were done to study the oxidation behavior of glucose at the $CuNiCoO_4$ NWs@CC. Amperometric response of glucose sensor was measured in a stirred medium. Before adding glucose solutions and concentration measurements, the background current was allowed to fall to a steady value.

3. Results and discussion

3.1. Characterization of $CuNiCoO_4$ NWs@CC

The nano-architecture active materials were prepared using a simple two-step synthesis strategy (Scheme 1) containing directly growth of mixed Cu-Ni-Co precursors on CC by hydrothermal reaction



Scheme 1. The schematic overview of $CuNiCoO_4$ NWs@carbon cloth fabrication.

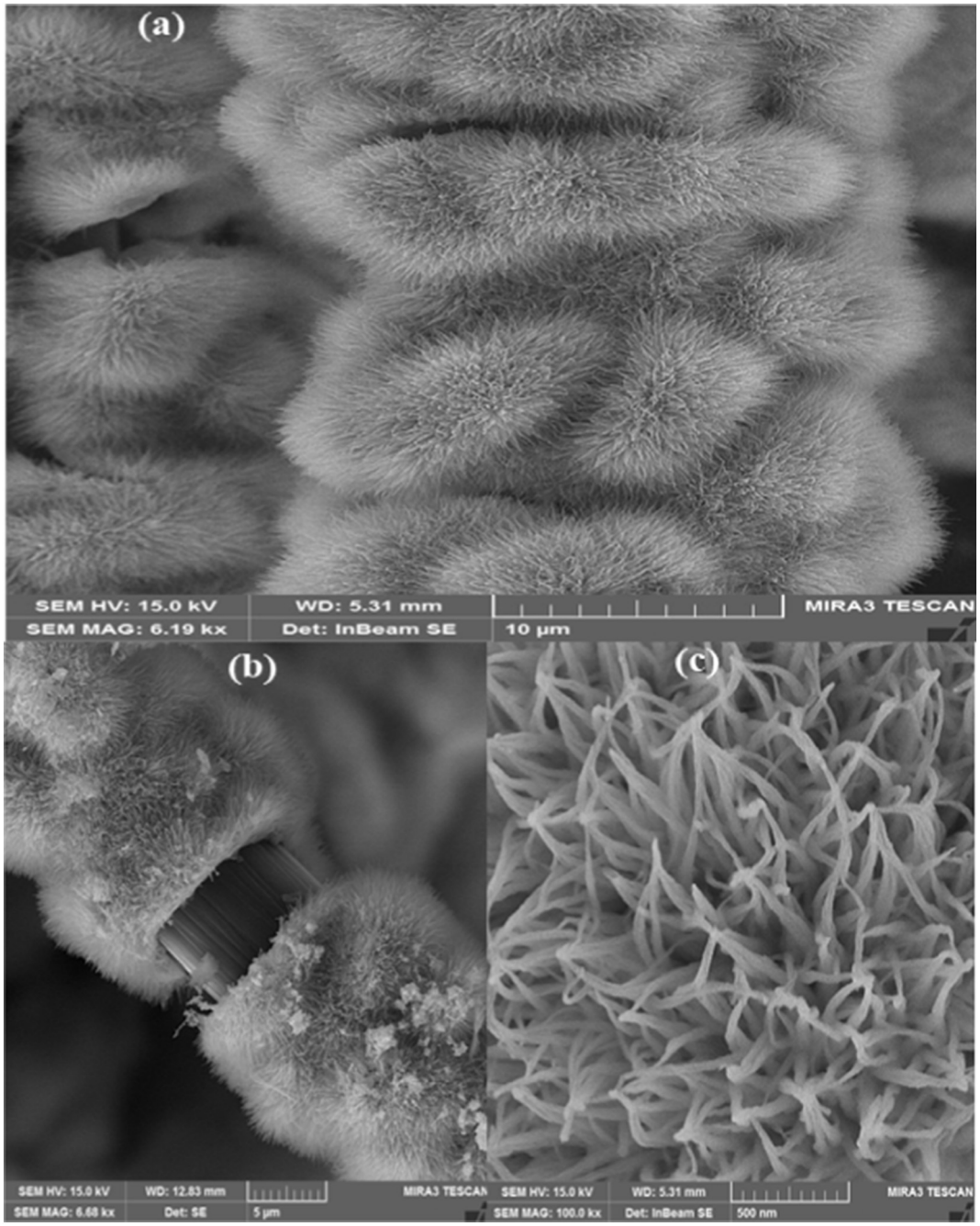


Fig. 1. The FE-SEM images of the $CuNiCoO_4$ NWs@CC at various magnifications.

at 120 °C for 6 h and subsequently thermal treatment of basic mixed Cu-Ni-Co carbonate hydroxide precursors during annealing treatment in argon atmosphere at 350 °C for 2 h to obtain porous $CuNiCoO_4$ NWs nanostructures.

The FE-SEM technique was used to investigate the morphology and microstructure of $CuNiCoO_4$ NWs@CC and its related images were shown in Fig. 1. As we can see in Fig. 1(a), the FE-SEM images confirmed that a compact $CuNiCoO_4$ NWs with a high density and well-ordered orientation are grown uniformly and vertically on the surface of CC. In addition, as shown in Fig. 1(b), the three-dimensional nano networks of $CuNiCoO_4$ NWs were directly formed on the surface of CC with a strong adhesion, which enhanced the physical and electrical contact between active electrode material and carbon cloth substrate and also stability of the entire electrode. Moreover, these kinds of nanowires structures and their orientations can be shortening the diffusion and electron transport path in the electrochemical reaction [31–34]. The higher magnified FE-SEM image of electrode revealed the detailed information about the final $CuNiCoO_4$ NWs on the surface of

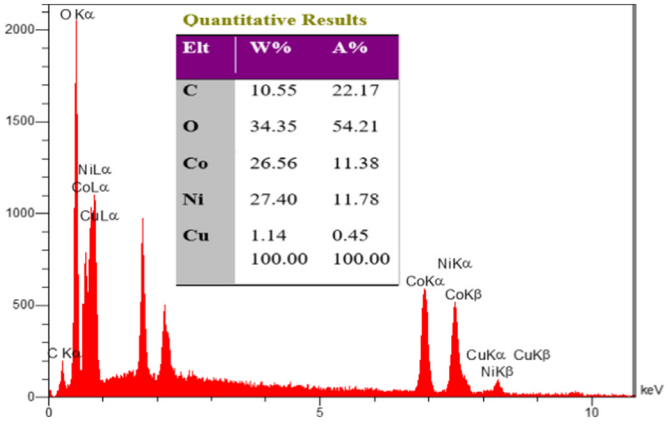


Fig. 2. The EDX analysis of obtained $CuNiCoO_4$ NWs@CC.

CC (Fig. 1c). Fig. 1c indicate that the nanowire arrays have been fabricated in the form of accumulated nanowire with around 6 μm in length and 50–110 nm in diameter (Fig. 1c). Therefore, the unique structure of $CuNiCoO_4$ NWs@CC can provide excellent electrochemical performance and high specific surface area with the high utilization of electrode material in electrochemical sensing.

Furthermore, the EDX analysis was confirmed the presence of C, O, Cu, Ni and Co elements in the hierarchical $CuNiCoO_4$ NWs@CC (Fig. 2). The peak from carbon mainly originates from the carbon cloth substrate and also from hydrolysis of urea at elevated temperatures. Also, the inset of Fig. 2 shows local weight and atomic percentages of various elements in the $CuNiCoO_4$ NWs@CC.

The EDX mapping analysis was further used for characterization of hierarchical $CuNiCoO_4$ NWs. This technique was similarly confirmed the presence of C, O, Cu, Ni and Co elements with the uniform distribution on $CuNiCoO_4$ NWs@CC without self-aggregation (Fig. 3).

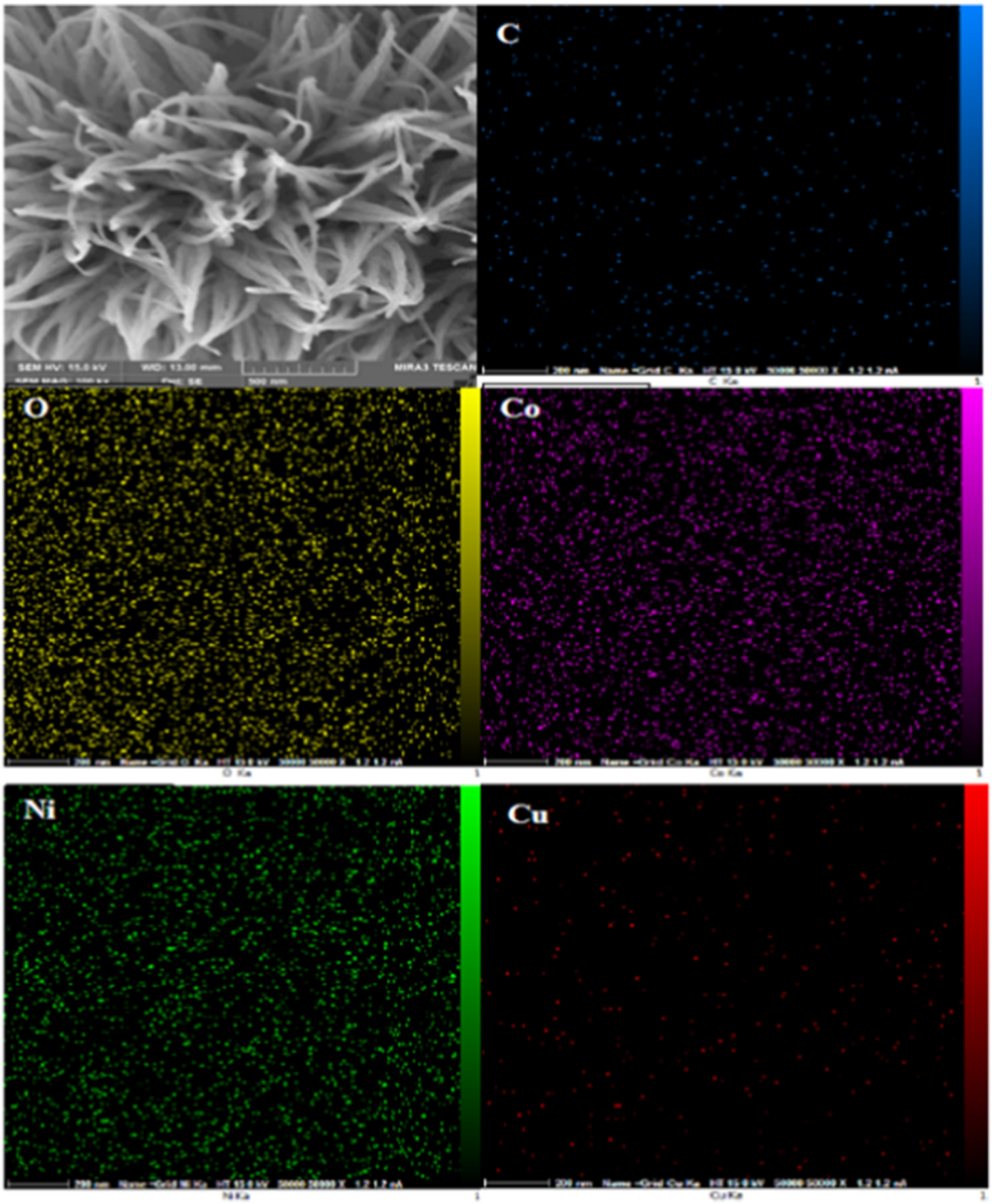


Fig. 3. The FE-SEM image and corresponding EDX elemental mappings of Ni, Co, Cu, C and O for the $CuNiCoO_4$ NWs@CC.

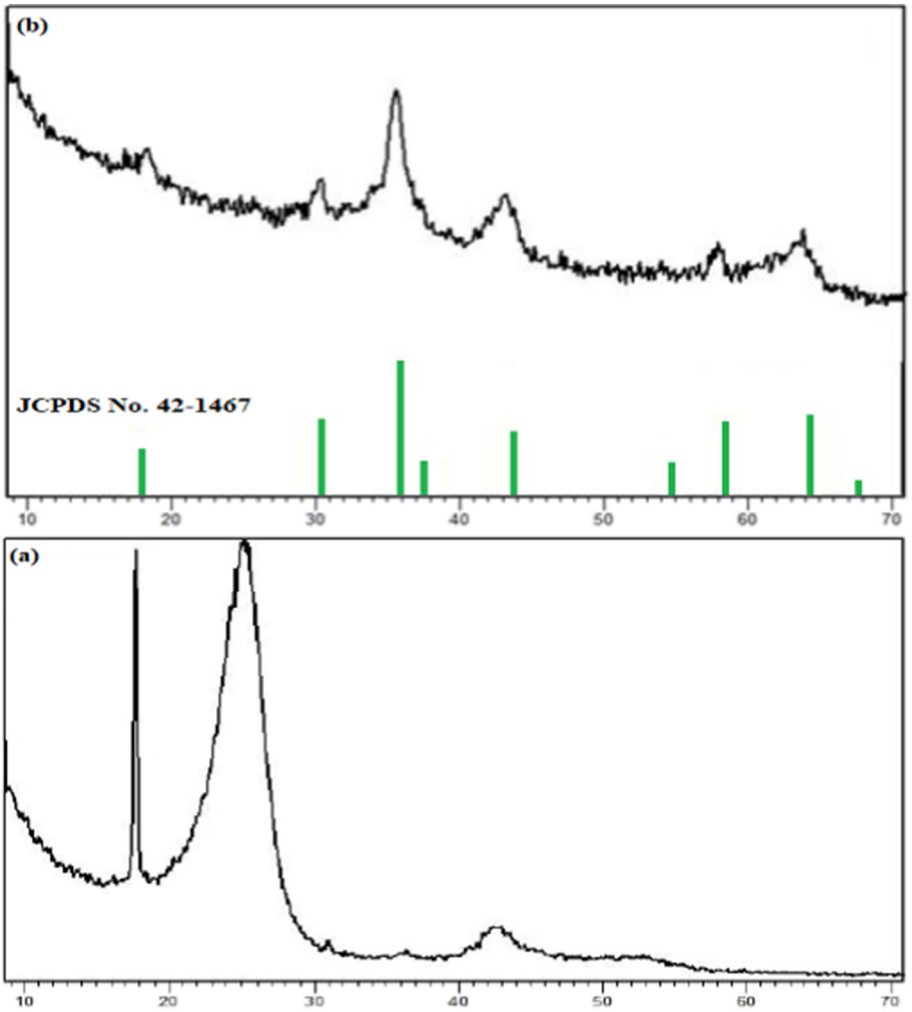


Fig. 4. The XRD patterns of (a) carbon cloth and (b) $CuNiCoO_4$ NWs@CC.

The crystallographic structure of prepared $CuNiCoO_4$ NWs@CC was determined using X-ray diffraction (XRD). As shown in Fig. 4(a), two main peaks around 25° and 43° were clearly observed for CC that are related to the (002) and (100) reflections of graphite, respectively [29]. The diffraction peaks of $CuNiCoO_4$ NWs deposited on CC are well matched with the cubic spinel Co_3O_4 structure phase of space group Fd3m (JCPDS No. 42-1467) [35–37]. The obtained results confirmed that the pure $CuNiCoO_4$ ternary oxide nanowires were obtained by substitution of cobalt atoms with copper and nickel without deterioration of structure. In addition, the XRD pattern does not show any additional peaks, indicating that high purity $CuNiCoO_4$ NWs@CC nanostructures have been formed during the annealing process.

3.2. Electrochemical characterization of CuNiCoO4 NWs@CC

The material characterizations confirmed that the $CuNiCoO_4$ NWs structure has been successfully prepared on the surface of the CC electrode with a hierarchical core/shell structure, which can be making it as an ideal binder free electrode in the electrochemical sensing. To study the characteristic behavior of CC supported $CuNiCoO_4$ NWs nanostructure electrode for electrochemical sensing, the electrochemical behavior of the electrode was first studied using CV measurements in 0.1 M NaOH as a supporting electrolyte (Fig. 5a). As shown in Fig. 5a, a pair of strong redox peaks was observed in the CV response of ternary $CuNiCoO_4$ NWs@CC as an electrode material that it may be originates from the reversible reactions of Co^{2+}/Co^{3+}, Ni^{2+}/Ni^{3+}, Cu^{2+}/Cu^{3+} and Co^{3+}/Co^{4+} redox pairs in 0.1 M NaOH electrolyte and the mechanism of redox reactions can be take placed as follows:

$$CuNiCoO_4 + OH^- + H_2O \leftrightarrow CoOOH + CuOOH + NiOOH + e^- \quad (1)$$

$$CoOOH + OH^- \leftrightarrow CoO_2 + H_2O + e^- \quad (2)$$

which two electrons are involved in the redox reaction. Furthermore, the peak currents were increased with increasing the scan rate (Fig. 5a) and a good linear dependence of both anodic and cathodic peak currents intensity were observed against the square root of scan rate (Fig. 5b), suggesting the electrochemical redox reaction was controlled by the diffusion of hydroxide ions on the surface of $CuNiCoO_4$ NWs@CC. In addition, by increasing the scan rate, the E_{pc} and E_{pa} of these electrodes shift to more negative and positive potentials, respectively (Fig. 5b), which indicates quasi-reversible nature of the redox reaction [37, 38].

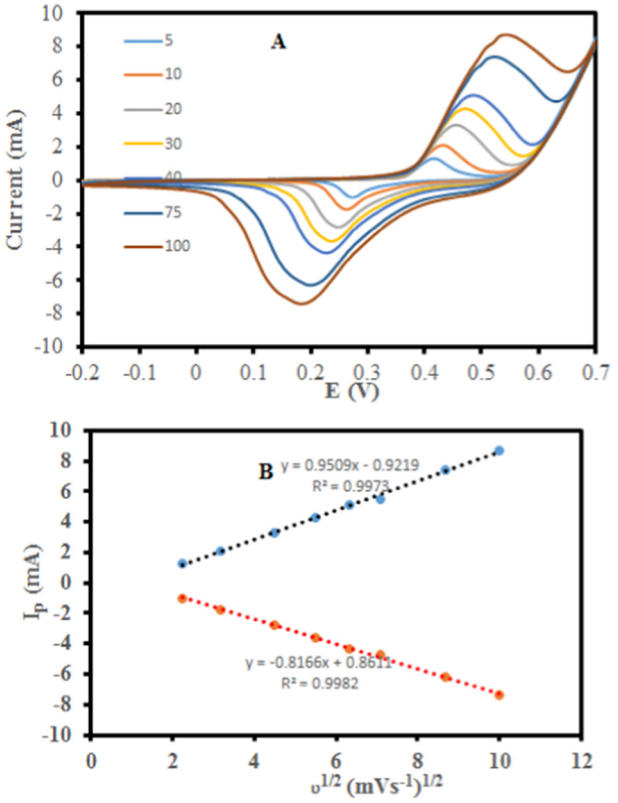


Fig. 5. a) CVs of $CuNiCoO_4$ NWs@CC in 0.1 M NaOH at different scan rate: 5, 10, 20, 30, 40, 75 and 100 mV s^{-1}, b) plot of anodic and cathodic peak currents against the square root of potential sweep rate.

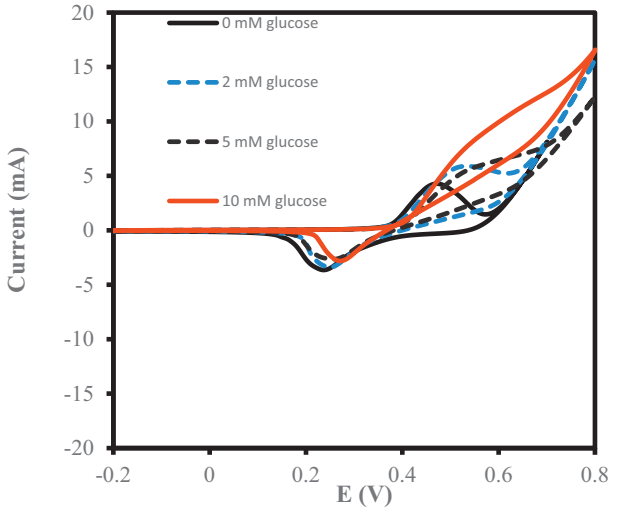


Fig. 6. CVs of $CuNiCoO_4$ NWs@CC electrode in 0.1 M NaOH in the absence (0 mM glucose) and presence of 2 mM, 5 mM and 10 mM glucose at a sweep rate 30 mV s^{-1}.

3.3. Electrocatalytic oxidation of glucose

The potential application of $CuNiCoO_4$ NWs@CC was evaluated for electrooxidation and detection of glucose. Fig. 6 shows the CV curves of the $CuNiCoO_4$ NWs@CC electrode in the 0.1 M NaOH solution with the concentrations of 0 mM (black line), 2 mM (blue dashed line), 5 mM (black dashed line) and 10 mM (red dashed line) glucose, respectively.

As we mentioned, the CV curve of $CuNiCoO_4$ NWs@CC electrode in blank alkaline solution shows a pair of redox peaks at about +024 and

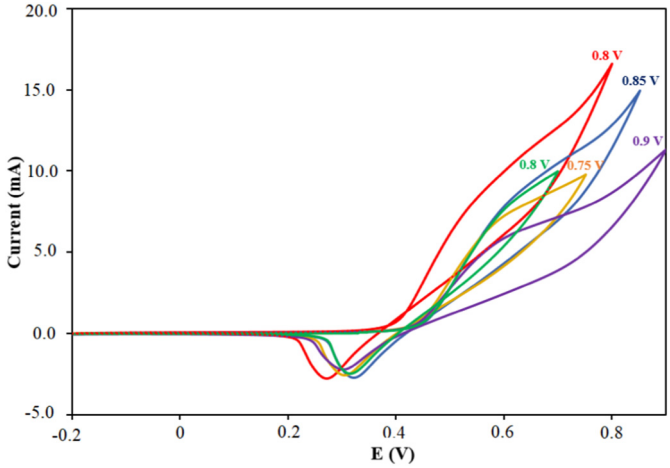


Fig. 7. CVs of $CuNiCoO_4$ NWs@CC electrode in 0.1 M NaOH in the presence of 10 mM glucose at a scan rate 30 mV s^{-1} in various switching potential ranging from 0.6 V to 0.9 V.

+0.48 V for cathodic an anodic peaks, respectively, which corresponds to the redox reactions of active electrode materials including copper, nickel and cobalt species. The addition of glucose to the alkaline electrolyte causes distinct increase of the oxidation currents and decrease in the reduction currents. It is also must be mentioned that higher concentration of glucose results in more increase in catalytic oxidation currents. The oxidation of glucose at the $CuNiCoO_4$ NWs@CC electrode in alkaline medium is generally containing a multi-step procedure, whereas strongly oxidizing Ni(III), Cu(III), and Co(IV) species (NiOOH, CuOOH and CoO_2, respectively) could act as heterogenous electrocatalyst for electrocatalytic oxidation of glucose. First of all, Cu(II), Ni (II) and Co(III) are electrochemically oxidized to higher oxidation states of Cu(III), Ni(III) and Co(IV) species and then these species could mediate electrocatalytic oxidation of the glucose and convert glucose to the main product of gluconolactone and by-products such as and gluconic acid. Furthermore, the anodic peak current shows a distinct shift in positive potential direction by successive addition of glucose, demonstrating a kinetic limitation in the reaction of glucose oxidation. The reaction equations which involves in electrocatalytic oxidation of glucose are as follows:

$$NiO + OH^- \leftrightarrow NiOOH + e^- \quad (3)$$

$$CoO + OH^- \leftrightarrow CoOOH + e^- \quad (4)$$

$$CoOOH + OH^- \leftrightarrow CoO_2 + H_2O + e^- \quad (5)$$

$$CuO + OH^- \leftrightarrow CuOOH + e^- \quad (6)$$

$$NiOOH + \text{glucose} \leftrightarrow NiO + OH^- + \text{gluconolactone} \quad (7)$$

$$CoO_2 + \text{glucose} \leftrightarrow CoOOH + OH^- + \text{gluconolactone} \quad (8)$$

$$CuOOH + \text{glucose} \leftrightarrow CuO + OH^- + \text{gluconolactone} \quad (9)$$

To determine the potential limit required to sufficiently oxidize the glucose on the surface $CuNiCoO_4$ NWs@CC electrode, the effect of switching potential was studied from 0.6 V to 0.9 V (Fig. 7). The highest oxidation peak current is visible at switching potential of 0.8 V. In the other hand, the value of the oxidation peak current increased to its maximum value as the switching potential was extended from 0.6 to 0.8, demonstrating the complete oxidation reaction of glucose and maximum electro-catalytic activity of our electrode in this potential. Thus, this potential was selected as optimized switching potential for further electrochemical investigations.

The CVs of the $CuNiCoO_4$ NWs@CC electrode in 0.1 M NaOH solution containing 10 mM glucose at various scan rates of 5, 10, 20, 30, 40, 50, 75 and 100 mV s^{-1} were showed in Fig. 8A. It was seen from

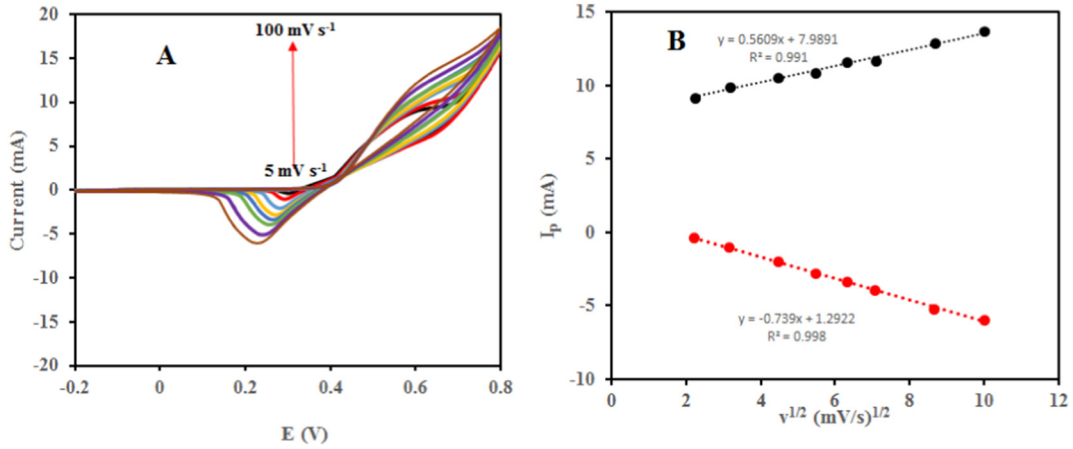


Fig. 8. A) CVs of $CuNiCoO_4$ NWs@CC in 0.1 M NaOH containing 10 mM glucose at different sweep rates: 5, 10, 20, 30, 40, 50, 75 and 100 mV s^{-1}, B) plots of anodic and cathodic peak currents versus the square root of potential sweep rate.

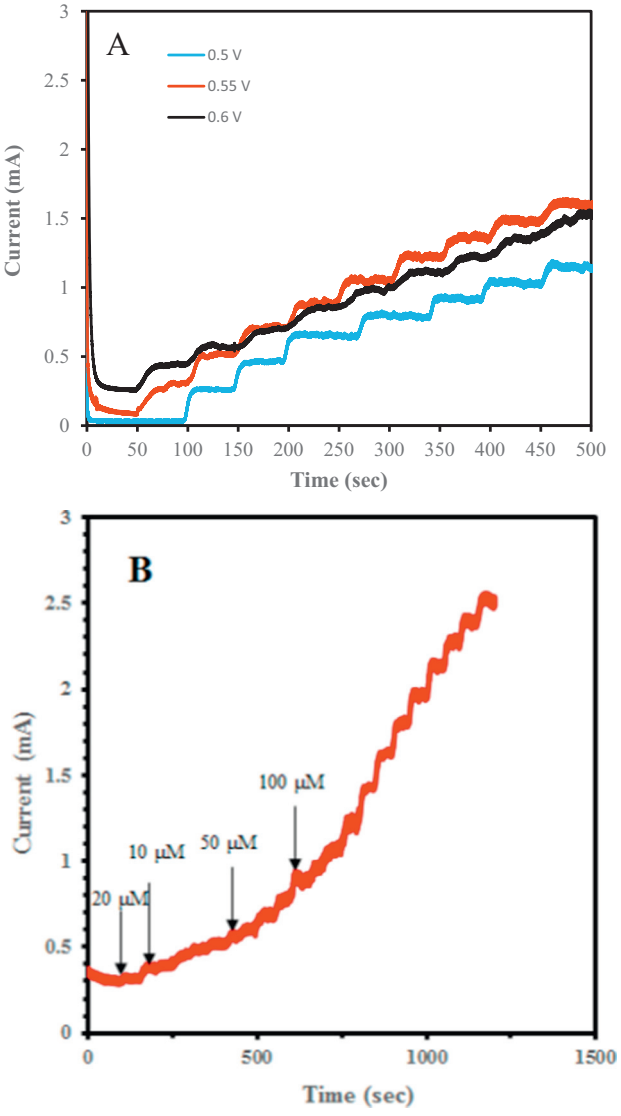


Fig. 9. A) Current response of $CuNiCoO_4$ NWs@CC electrode during successive addition of 100 µM glucose at various operating voltages, B) amperometric response of $CuNiCoO_4$ NWs@CC electrode by successive injection of various concentrations of glucose into the stirred NaOH electrolyte.

Fig. 8A, that by increasing the scan rate, the anodic peak potential shifted toward more positive potentials and the peak currents of glucose oxidation were enhanced correspondingly. Fig. 8B demonstrates that the anodic and cathodic peak currents increases linearly with the square root of the scan rate, demonstrating that the electrochemical catalytic oxidation of glucose on the surface of $CuNiCoO_4$ NWs@CC electrode is a diffusion-controlled redox reaction at these scans rates.

3.4. Amperometric determination of glucose

The potential application of the proposed electrode material for determination of glucose was evaluated using amperometric technique. Since the sensitivity of a glucose sensor greatly depends on the applied potential, an amperometric signal was investigated on the $CuNiCoO_4$ NWs@CC electrode for the successive addition of 100 µM glucose into 0.1 M NaOH every 50 s under the potentials range from 0.5 V to 0.60 V, as shown in Fig. 9. A. It was obviously seen that the anodic currents increased gradually from 0.5 V to 0.55 V, and then decreased. It established that high potentials could increase current responses due to

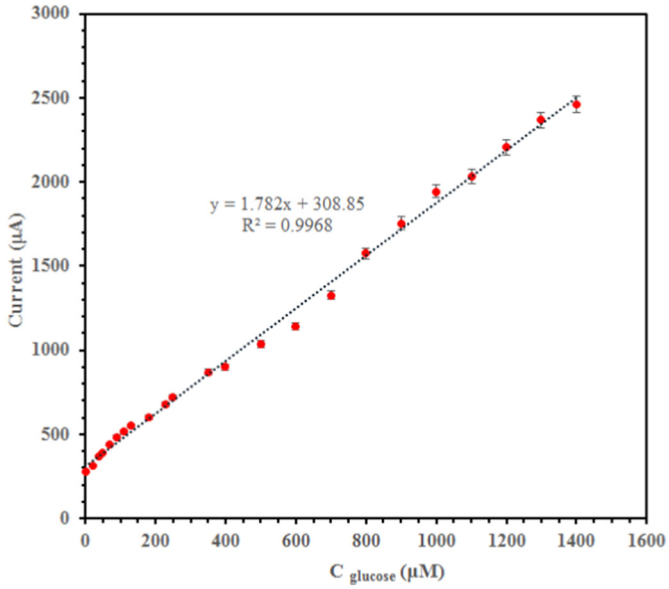


Fig. 10. The calibration curve of amperometric current response vs glucose concentration for $CuNiCoO_4$ NWs@CC electrode.

Table 1
Electrochemical performance comparison of $CuNiCoO_4$ NWs@carbon cloth electrode with other nonenzymatic cobalt based glucose sensors.

Electrode material	Potential (V)	Sensitivity ($\mu A\,mM^{-1}\,cm^{-2}$)	Linear range (mM)	LOD (μM)	Reference
Co_3O_4/3DGF	+0.58	3390	Up to 80 μM	0.025	[39]
Co_3O_4 nanofiber	+0.59	36	Up to 2.04 mM	0.97	[40]
CoOOH nanosheets	+0.40	341	0.03–0.7 mM	30.9	[29]
CuOx-CoOx/graphene	+0.50	507	0.005–0.570	0.5	[24]
Co_3O_4/PPy/NF	+0.60	2920	0.002 to 0.70	0.74	[41]
		590	0.70 to 5.0		
Co LDH/carbon cloth	+0.5	1280	0.001–0.10	0.50	[42]
$CuNiCoO_4$ NWs@CC	+0.55	1782	0.02–1.4	6.5	This work

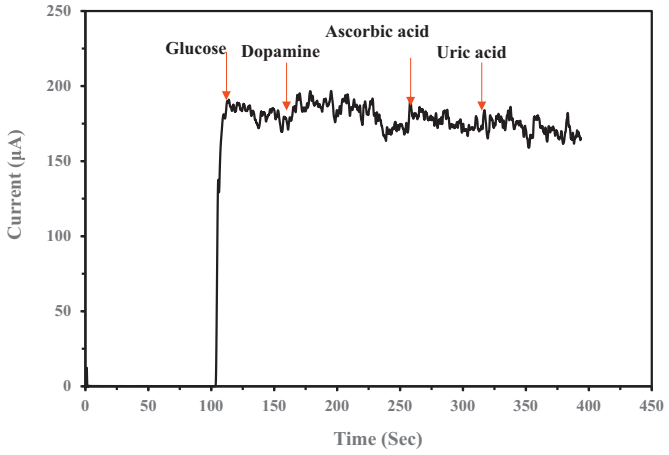


Fig. 11. Amperometric response of the $CuNiCoO_4$ NWs@CC electrode toward the addition of glucose (0.1 mM) and various interfering species (0.1 mM) including dopamine (DA), uric acid (UA) and ascorbic acid (AA) in 0.1 M NaOH.

the increased amount of electrocatalyst (high oxidation states of active materials as mentioned before). However, using higher potential than 0.55 V, could produce some intermediates, which maybe interacted with the active electrode material, thereby results in the drastic reduction of catalytic current [38]. Meanwhile, the strong and irreversible adsorption of intermediates could poisoned the electrode surface and hinder the glucose electrooxidation. As a result, the highest current response was observed at +0.55 V.

Fig. 9B shows successive addition of different concentrations of glucose into the NaOH electrolyte while the solution is stirred. The electrolyte solution was strongly stirred to ensure good mixing of analyte with the electrolyte to obtain a homogeneous glucose concentration through the entire of solution. The amperometric currents show a stepwise increase in responses with a stepwise addition of glucose concentrations.

The error bars were used for the determination of the standard deviations at each injected concentration. The glucose sensor shows a linear range of 0.02 to 1.4 mM and a sensitivity of 1782 $\mu A\,mM^{-1}\,cm^{-2}$. The LOD is evaluated to be 6.5 μM based on the signal-to-noise ratio of 3 (S/N = 3) (Fig. 10). Table 1 summarizes the performance comparison between the $CuNiCoO_4$ NWs@CC electrode with other cobalt based non-enzymatic glucose sensors. As seen from Table 1, analytic performance of the prepared $CuNiCoO_4$ NWs@CC electrode is superior in terms of liner range, sensitivity, potential and detection limit, which can be comparable to, or even better than that of glucose non-enzyme sensors reported recently.

3.5. Selectivity of the CuNiCoO4 NWs@CC

The selectivity of the $CuNiCoO_4$ NWs@CC electrode is one of the important parameters for evaluation of non-enzymatic glucose sensor because the interfering species usually coexist with glucose, such as dopamine (DA), uric acid (UA) and ascorbic acid (AA). Fig. 11 shows the significant current response by the addition of 0.1 mM glucose, while no remarkable current response with the addition of interfering species. These results demonstrate that the $CuNiCoO_4$ NWs@CC electrode can be used for selective detection of glucose in the presence of interfering species and high catalytic activity of $CuNiCoO_4$ NWs@CC electrode toward glucose sensing.

Table 2
Recovery tests for glucose determination in human serum samples.

No	Spiked (μM)	Found[a] (μM)	RSD (%) n = 3	Recovery (%)
1	300	291.6	4.35	97.2
2	400	423.6	3.85	105.9
3	600	616.8	2.87	102.8

[a] Average of three replicate measurements (rounded).

3.6. Real sample analysis

As an example of a practical use, the as-prepared $CuNiCoO_4$ NWs@CC electrode was also used for determination the glucose concentration in the human serum samples. For this purpose, the discrete amount of human serum sample has been diluted by addition of NaOH solution. The corresponding results of recovery were found to be in the range of 97.2–105.9% and the obtained relative standard derivations (RSD) of three additions were presented in the Table. 2. These results indicate that the $CuNiCoO_4$ NWs@CC electrode can be applied for determination of glucose concentration in human serum samples.

4. Conclusions

We have successfully fabricated a binder free electrode based on ternary copper nickel cobalt oxide nanowires grown on the carbon cloth ($CuNiCoO_4$ NWs@CC) and applied it for nonenzymatic glucose detection. The new prepared sensor shows excellent electrocatalytic activity for glucose oxidation in aqueous NaOH solution. At the $CuNiCoO_4$ NWs@CC electrode, there is a linear relation between the glucose concentration and the oxidation current. It was observed that the prepared electrode could detect glucose concentration with high sensitivity and selectivity. Real sample analysis shows negligible matrix effect on the detection of glucose in human serum samples. This work provides a promising new platform for the investigation of the application of binder-free ternary metal oxides in electrocatalysis and the manufacturing of attractive sensor in the future.

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