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Carbohydrates electrocatalytic oxidation using CNT–NiCo-oxide modified electrodes

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ABSTRACT

A new sensor for an amplified electrochemical detection of carbohydrates is proposed, where carbohydrates are oxidized by CNT–NiCo-oxide composite in basic solutions. Cyclic voltammograms of the modified electrode show a stable and well defined redox couple in alkaline media due to the synergy of Ni(II)/Ni(III) system with Co(II)/Co(III). The modified electrode shows excellent electrocatalytic activity towards monosaccharides oxidation at reduced overpotential in alkaline solutions. Six monosaccharides were determined amperometrically at the surface of this modified electrode with high sensitivity over a wide range of concentrations, from 0.02 up to 12.12 mM. Low detection limit of 5 μM for glucose could be obtained.

1. Introduction

Electrocatalytic oxidation of carbohydrates is of great interest in many areas, ranging from analytical applications in food industry and medical diagnosis to wastewater treatment. Sustained efforts to understand and achieve the enzyme less detection of glucose have been made since the early study of the glucose electrochemistry [1]. The electrooxidation of glucose and some other monosaccharides have been studied on various metals such as platinum [1,2], copper [3–5], nickel [6,7] and gold [8–11] and also on modified surfaces such as ruthenium dioxide [12], nickel oxide [13–15], cobalt oxide [16,23–25], alloy [17,18] and metallic complexes such as cobalt phthalocyanine [19].

In most cases for carbohydrates analysis, capillary electrophoresis as well as liquid chromatography is used for separation of neutral carbohydrates and coupled up with different detection systems. As most carbohydrates are uncharged and do not contain any chromophore or fluorophore, the separation process requires the total ionization of carbohydrates, which can be accomplished only in strong alkaline solutions (carbohydrates have pK values ranging from 12 to 14). For this reason, the oxidation of carbohydrates in alkaline media is of great interest and it is especially compatible with the use of a metallic electrode as an electrochemical detector. Among metallic electrodes, particularly nickel electrode has received more attention for the electrooxidation of saccharides in alkaline media in the constant-potential application method. Fleischmann et al. [7] investigated the oxidation of alcohols and amines on a Ni electrode, proposing the mechanism which involves the electron-transfer mediation by a $Ni(OH)_2/NiOOH$ redox couple in the oxide film at electrode surface. This mechanism has been supported by Berchmans et al. [14] and Luo et al. [20], reporting the anodic oxidation of glucose at Ni electrodes in alkaline media. In addition, Robertson [21] suggested that the reaction might be dependent on the concentrations of OH^- ions, which would influence the Ni surface state. You et al. [22] reported the response of Ni nanoparticles dispersed in disordered graphite-like carbon to sugars. According to their report, Ni–graphite material enhances the sensitivity to sugars of at least 1 order compared with those of bulk Ni and show good reproducibility with a relative standard deviation of 1.75% for 40 consecutive injections of glucose in a flow system.

Cobalt on the other hand, has emerged as a possible alternative material for detection systems for carbohydrates. Shadjou et al. [23] investigated the electrocatalytic oxidation of some carbohydrates on nanoparticles of cobalt hydroxide electrodeposited on glassy carbon electrode in alkaline solutions. Mannino et al. [24] showed that cobalt(II, III) oxide mixed with carbon paste, greatly reduces the overvoltage for the oxidation of various biologically important compounds, such as sugars. Cataldi et al. [25] have demonstrated the electrocatalytic oxidation of sugars in alkaline solution at Co-oxide-based glassy carbon electrodes, proposing an oxidation mechanism of Co(II) to Co(III) in terms of hydrous cobalt oxides for the anodic oxidation of carbohydrates.

There have been reported several studies which employed Ni oxide or Co oxide modified electrodes for the oxidation of sac-

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charides in alkaline media, however there is no example in the literature that employed a combination of those two metal oxides for the purpose of carbohydrates oxidation. Mixed oxides are often used to adjust the electrode properties through synergetic effects arising from the intimate electronic interaction of the components as such IrO_2 entrapped inside PbO_2 [26] or mixed PbIrOx [27] which have been shown to display enhanced catalytic activity towards the electrooxidation of carbohydrates compared to the monoxide. One of the most promising materials in alkaline electrolyte is the mixed Ni and Co oxides, which have been reported to exhibit interesting electrocatalytic activities, making them attractive for O_2 evolution [28,29]. It has been proved that among many additives used in the nickel hydroxide electrodes, cobalt is especially important because it provokes a shift of Ni(II)/Ni(III) redox potential towards less positive values [30–33]. The electrocatalytic activity of these mixed metal oxides composited with carbon nanotubes (CNT) material has been previously studied by our group [34] in connection with insulin electrochemical detection.

The purpose of the present work is the detailed investigation of carbohydrates oxidation on CNT–NiCo-oxide composite in alkaline solution. It is well known that high-surface-area CNT when combined with metal nanoparticles or metal oxide can improve the performance of the final material. Generally, nanomaterials, possessing unique optical and electrical properties due to electron and photon confinement are receiving great attention as matrices for catalyst immobilization and to improve the sensitivity and stability of sensors. The electrocatalytic oxidation of carbohydrates on this type of electrode is attractive because of the interest and need in sensitive and stable sugar sensors for medical and food industry, as well as sugar–oxygen fuel cell application. The expectation of a synergistic electrocatalytic benefit from the combined properties of the components resulted in the motivation for the study of mixed metal oxide electrodes.

2. Experimental part

2.1. Reagents

Nickel cobalt mixed oxide nanopowder with a linear formula (NiO)(CoO) 1 of 1 (<150 nm, 99%), Nickel(II) oxide nanopowder (<50 nm particle size, 99.8%), Cobalt(II) oxide (≥99.99%) and sodium hydroxide pellets (NaOH) were supplied by Sigma–Aldrich. Multiwall carbon nanotubes (MWNT, 6–13 nm diameters and 2.5–20 μm length, 99.8% purity) were purchased from Sigma–Aldrich and use as received, without any further purification. The Nafion 5% solution was provided by Fluka.

Fructose was purchased from Merk. All the other carbohydrates are provided by UPM Finland and produced by MP Biomedicals USA (D-galactose anhydrous) and Across Organics USA (D-mannose, D-xylose, α-D-glucose and L-arabinose).

2.2. Apparatus and methods

Cyclic voltammetry and amperometry methods were used to investigate the electrocatalytic properties of the nickel–cobalt oxides composite. All experiments were carried out using a PalmSens Instrumentation potentiostat (Palm Instrument BV, The Netherlands) connected to a PC. The electrochemical measurements of carbohydrates were carried out in NaOH 0.1 M, in a conventional electrochemical cell of 3 mL volume, using a three-electrode system with a planar configuration of a screen printed electrode (SPE), fabricated and purchased from Biosensor Laboratory, University of Florence, Italy. The working carbon based electrode is of 3 mm diameter.

Amperometric measurements were performed at a constant applied potential of +0.35 V vs Ag/AgCl in 0.1 M NaOH. When a stable baseline was reached, a few microlitres of a standard solution of carbohydrate were injected into a cell filled with 3 mL of 0.1 M NaOH solution, and the steady state current due to direct oxidation of the sugar was measured.

All solutions used in this work were prepared with double distilled water. All electrochemical experiments were carried out at room temperature and the potentials were referred to Ag/AgCl.

2.3. Preparation of mixed oxide composite material

As reported in a previous work [34] the coating composite was prepared by dispersing 4.5 mg of Ni–Co mixed oxide (or single NiO, CoO respectively) together with 8 mg of MWNT into 1 mL aqueous solution of Nafion 2%, with the aid of stirring and ultrasonic bath for 10 min. 2 μL of the resulting mixture was pipetted onto the SPE working surface and allowed to dry 1 h at room temperature then kept at 4 °C until used. The electrodes have been denoted as CNT–NiCo-oxide/Nafion composite having a composition of 16 μg CNT and 9 μg Ni–Co oxide per electrode. For the preparation of simple CNT composite electrodes, the CNT powder was added to Nafion solution to obtain a concentration of 8 mg/mL following the same protocol of stirring and ultrasonication for 10 min, then coating the working electrode with 2 μL of the CNT/Nafion mixture.

3. Results and discussions

Preliminary cyclic voltammetry experiments were performed to study the electrochemical behavior of glucose on the screen printed electrodes coated with CNT–NiCo-oxide/Nafion composite. The results have been compared to those obtained for electrodes modified by simple CNT/Nafion composite. Fig. 1A shows the cyclic voltammogram obtained for CNT/Nafion composite electrode in 0.1 M NaOH solution without (dotted line) and with 1.5 mM glucose (solid line). No faradaic response was observed within −0.2 to +0.5 V potential window and the oxidation process of glucose starts at potentials more positive than +0.55 V. However, when CNT are composited with NiCo-oxide, the modified electrode produces a peak-shaped voltammogram even in the absence of glucose, as shown in Fig. 1B (dotted line). As previously reported [34], the anodic and cathodic peaks appeared at +0.25 (±0.02) V and +0.14 (±0.02) V vs Ag/AgCl, can be attributed to the Ni(II)/Ni(III) and Co(II)/Co(III) couples, which are overlapping and give raise to a single pair of sharp peaks. The results are in agreement to the reported effect of adding Co to the Ni oxide [30–32] when the redox potential of Ni(II)/Ni(III) is shifted towards less positive values compared to only Ni oxide, the potential difference between the oxidation and reduction peaks is reduced and the reversibility of the process is amplified. A significant increase in the anodic peak current at +0.3 V is observed in the presence of 1.5 mM glucose (Fig. 1B, solid line) confirming the electrocatalytic effect of NiCo-oxide.

In alkaline medium, a nickel oxide electrode is covered by a nickel(II) hydroxide layer, which is electrochemically oxidized to a nickel(III) oxyhydroxide layer, according to the reaction [14,35]:

$$Ni(OH)_2 + OH^- \rightarrow NiOOH + H_2O + e^- \quad (1)$$

Analogous, a cobalt oxide material is covered by a cobalt(II) hydroxide layer, which is gradually converted to Co(III) oxyhydroxide specie [36]:

$$Co(OH)_2 + OH^- \rightarrow CoOOH + H_2O + e^- \quad (2)$$

The Co oxide redox chemistry occurs in the same potential range as the Ni(II)/Ni(III) transition and therefore the corresponding peaks cannot be resolved separately, as they overlap and give

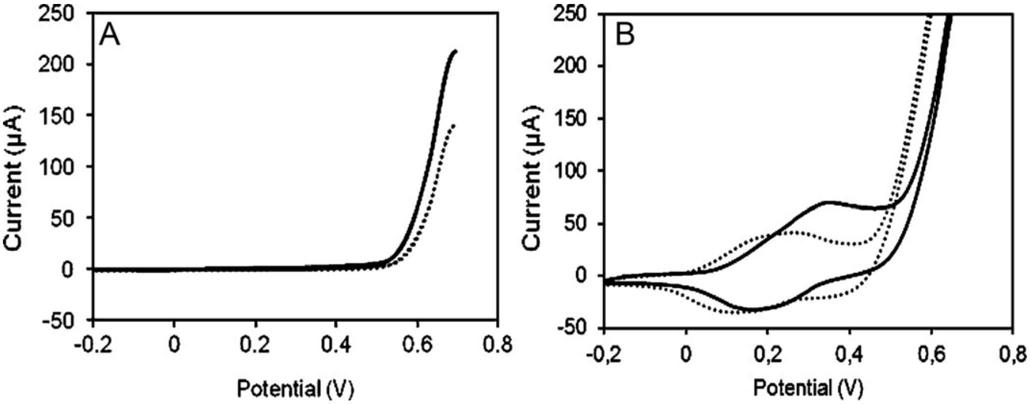

Fig. 1. Cyclic voltammograms of (A) CNT/Nafion electrode and (B) CNT–NiCo-oxide electrode in 0.1 M NaOH before (dotted line) and after (solid line) the addition of 1.5 mM glucose. Scan rate: 20 mV/s.

raise to only one pair of sharp peaks [37]. This Ni(III) and Co(III) layer can oxidize carbohydrates, thereby being reduced to Ni(II) and Co(II) and reoxidized electrochemically by the applied potential, thus giving an increased current signal. The monosaccharides can be oxidized at NiOOH/CoOOH region (0.25 V vs Ag/AgCl) by the mechanism:

$$\mathrm{NiOOH} + \mathrm{R_1R_2CHOH} \rightarrow \mathrm{Ni(OH)_2} + \mathrm{R_1R_2C^{\bullet}OH}$$
$$\mathrm{CoOOH} + \mathrm{R_1R_2CHOH} \rightarrow \mathrm{Co(OH)_2} + \mathrm{R_1R_2C^{\bullet}OH}$$
$$\mathrm{R_1R_2C^{\bullet}OH} \rightarrow \text{products}$$

Ni(III) and Co(III) act as strong oxidants, reacting with the carbohydrate molecules by subtracting a hydrogen atom to yield a radical. Further reaction of the radical with additional surface sites results in product formation. A similar mechanism was explained by other authors for oxidation of carbohydrates on Ni [38] or Ni complexes [39] electrodes. As reported in the literature, gluconolactone and gluconic acid [40,41] were detected as the main products of oxidation of glucose. In addition, formate and oxalate [42] were reported as oxidation products.

It is reported [16,23] that cobalt hydroxide (oxide) modified glassy carbon electrodes are catalytically active for carbohydrates in alkaline solution with the electrooxidation around 500 mV vs Ag/AgCl or 530 mV vs SCE. The electrooxidation of carbohydrates at Ni oxide modified electrodes has been shown to carry out around 450–550 mV vs Ag/AgCl [15,22,38,40]. In our work, the catalytic oxidation of carbohydrates takes place at 300 mV vs Ag/AgCl, probably explained by the synergy between the two metal oxides in addition to the high surface area of CNT, which entangle with the oxide particles resulting in a uniform dispersion. The synergistic effect between multicomponent electrocatalysts has been previously exploited as a good opportunity for the development of new electrocatalysts with enhanced activity and/or stability [26,27,43,44]. This effect is explained as an amplification of the properties of pure components when an intimate homogeneous mixing of the components is achieved. In this work, the glucose response at mixed Ni–Co-oxides has proved to be significantly higher compared with simple monoxide (NiO and CoO) electrodes and this was attributed to the synergy between the Ni-sites and Co-sites in the anodic response mechanism. Also, the voltammetric response for glucose appears at significantly lower potential compared with NiO or CoO electrodes as they are presented in Fig. 2, which shows the voltammograms of CNT-monoxide films in the absence and presence of glucose. The shape of voltammogram and peaks potential were typical for nickel oxide/hydroxide electrodes (Fig. 2A, dotted line) and the presence of glucose give raise to an increase of the current peaks, with an oxidation peak potential at 550 mV (solid line). At CNT–CoO electrode (Fig. 2B), the presence of glucose resulted in an increase of the anodic current, while the cathodic current decreased. The low reversibility of $\mathrm{Co(OH)_2}$ electrodes was already reported by other authors [16,23]. However, CoO considerably increases the peak height and decreases the peak potential for resulted NiCo-oxide when compared to the same amount of NiO used for modification of electrode.

The dependence of the peak current response with the scan rate has been studied for 1.5 mM glucose at the CNT–NiCo-oxide composite electrode in the 10–300 mV/s range. The peak current is proportional to the square root of the scan rate, indicating that monosaccharide oxidation is a diffusion-limited process, which correspond with previous reports referring to Ni electrodes [22,38].

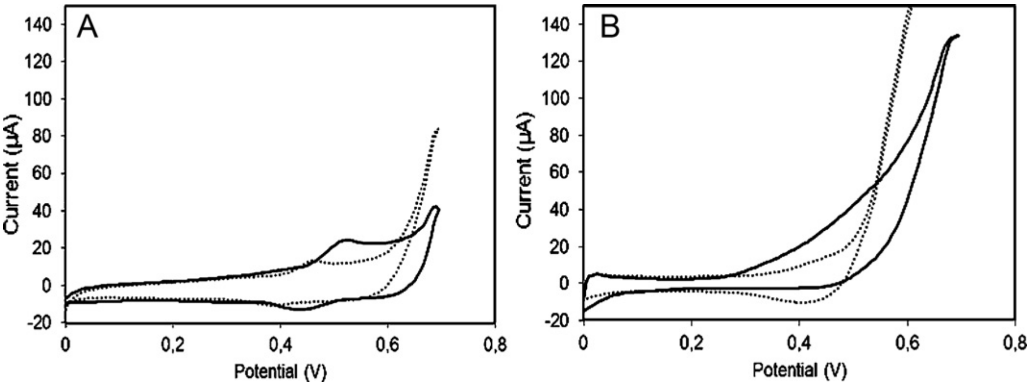

Fig. 2. Cyclic voltammograms of (A) CNT–NiO/Nafion and (B) CNT–CoO/Nafion electrodes in 0.1 M NaOH before (dotted line) and after (solid line) the addition of 1.5 mM glucose. Scan rate: 20 mV/s.

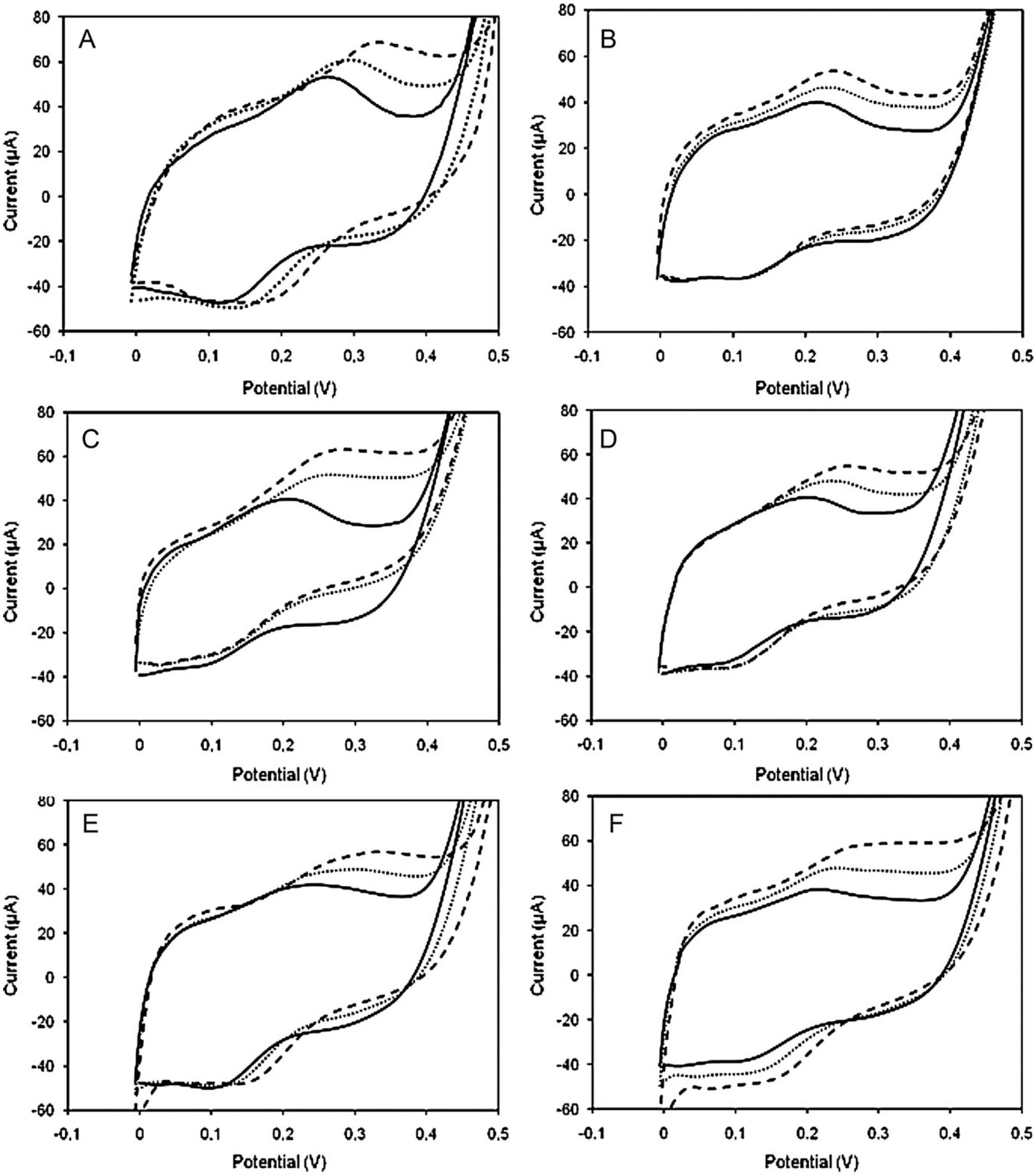

Fig. 3. Voltammetric oxidation of 0.5 (dotted line) and 1 mM (dashed line) glucose (A), fructose (B), arabinose (C), xylose (D), galactose (E) and mannose (F) at CNT–NiCo oxide composite electrode in 0.1 M NaOH electrolyte. Scan rate: 20 mV/s.

Electrooxidation of other different monosaccharides at CNT–NiCo-oxide modified electrodes in alkaline media has been studied by cyclic voltammetry technique, scanning the potential in a 0–0.5 V window.

Fig. 3 shows typical voltammetric curves at CNT–NiCo oxide composite electrodes in 0.1 M NaOH aqueous solutions in the presence of 0.5 and 1 mM monosaccharides. The studied compounds included the aldohexose type monosaccharides such as glucose, galactose, mannose and aldopentose type monosaccharides such as arabinose and xylose as well as ketohexose like fructose. In all cases, addition of monosaccharide to the blank NaOH causes a notable enhancement of the anodic current, starting at potential ca. 0.2 V and the peak currents increased with raising the concentration of monosaccharide, as shown in Fig. 1A–F. Therefore, the CNT–NiCo-oxide composite electrode exhibits electrocatalytic performance for oxidation of monosaccharides.

As reported, many glucose sensors based on metal and alloy electrodes usually lose their activity because of being poisoned by oxidation products or because of the leaching of catalyst from electrode surface. The electrocatalytic stability of CNT–NiCo-oxide

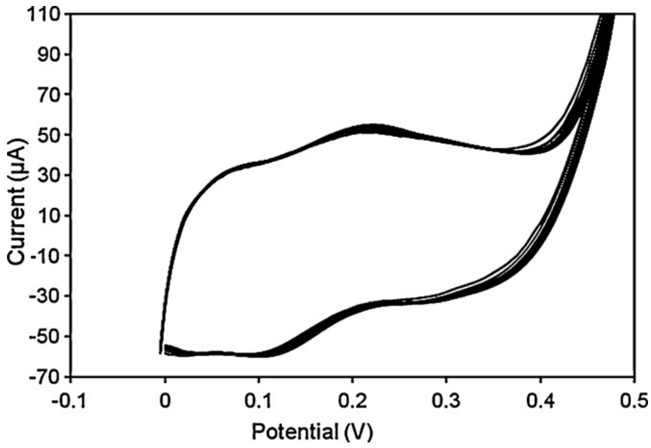

Fig. 4. Consecutive 15 cyclic voltammograms recorded for CNT–NiCo-oxide electrode in 0.1 M NaOH at the scan rate of 20 mV/s..

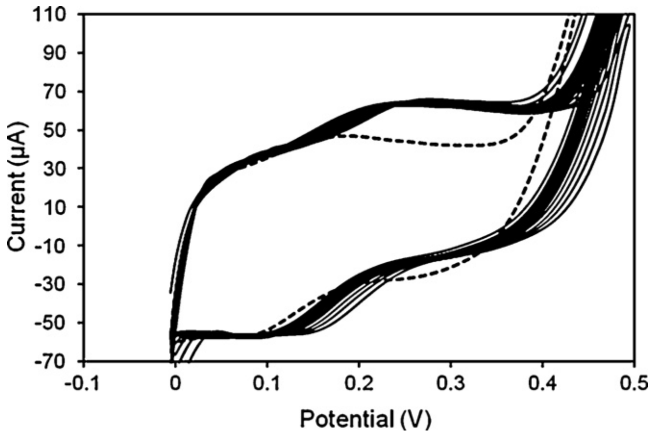

Fig. 5. Stability of voltammetric response of CNT–NiCo-oxide electrode for 1 mM xylose in NaOH 0.1 M. Cycles number from 1 to 15. Dashed line: initial cyclic voltammogram in NaOH 0.1 M. Scan rate of 20 mV/s.

electrodes has been investigated in NaOH electrolyte solution, as well as in the presence of monosaccharide. Fig. 4 presents 15 consecutive cyclic voltammograms (CV) of a CNT–NiCo-oxide electrode in 0.1 M NaOH solution recorded at a potential sweep rate of 20 mV/s. The very slight growth of anodic current with the number of potential scans indicate a gradual conversion of Ni^{2+} to Ni^{3+} and Co2+ to Co3+, generating the oxide hydroxide layer. This change is more significant for the first 3 cycles and then the peak current is stabilized.

Fig. 5 presents the stability of electrocatalytic activity of modified CNT–NiCo oxide electrode in monosaccharides oxidation process, evaluated by repetitive scanning in 0.1 M NaOH solution containing 1 mM xylose. No decrease in electrocatalytic response can be seen during 15 consecutive cycles. The value of current remains constant as the initial value, suggesting the stability of electrocatalyst which is not passivated during continued cycling in monosaccharide solution.

On the basis of the voltammetric results described above, it appears that amperometric detection of carbohydrates by CNT–NiCo oxide composite is effectively possible. The amperometric calibration for four hexoses (glucose, mannose, galactose and fructose) and two pentoses (arabinose and xylose) were carried out using the proposed electrochemical system and applying a potential of 0.35 V, more positive than anodic peak potential in order to obtain a good sensitivity. Amperometric calibrations were done in stirred solution by successive addition of different concentrations of monosaccharide in NaOH 0.1 M electrolyte. A very fast current response was obtained within a few seconds (4 s) upon each injection, indicating that the composite electrode has a fast response to tested carbohydrates.

The intensity of the current response for all six monosaccharides is proportional to the respective concentration with a linearity divided on two ranges of concentrations. The calibration plots and detection limits obtained for these six monosaccharides are summarized in Table 1.

Note that the detection limit of glucose (for signal/noise = 3) is lower than that reported earlier at Co oxide-MWCNT glassy carbon electrode [16], Ni oxide-MWNT [39] or CNT-modified electrode [40], even at applying a lower potential when compared to mentioned papers. The fast response of CNT–NiCo oxide electrodes makes them highly suitable for monitoring carbohydrate compounds in flow through systems. The analytical performances of the proposed sensors for monosaccharides compared favorably with other modified sensors previously reported in the literature (Table 2).

From a detailed comparison between the magnitude of the catalytic current and the molecular structure of the carbohydrates we can conclude that the responses do not distinguish hexoses from pentoses. The linear range for each monosaccharide was over 3 orders of magnitude. From the linearity of current response it is evident that no electrode fouling occurred due to the oxidized product of sugars on the surface even after successive addition of sugars in increased concentrations.

The operational stability of the amperometric response of CNT–NiCo-oxide electrode was investigated by continuously measuring the amperometric signal to 0.2 mM glucose for about 20 min, applying a 0.35 V constant potential. The current response was stable for approximately 1 min followed by a decay of 30% in the following 20 min, this can be attributed to the decrease in concentration of glucose due to the its oxidation at the surface of the modified electrode.

Table 1
Analytical parameters of CNT–NiCo-oxide electrodes for electrochemical detection of monosaccharides.

Monosaccharide		Sensitivity (μA/mM)	Specific sensitivity (μA/mM × cm²)	LOD (μM)	Linear range (mM)	R^2
Hexose	Glucose	4.63 ± 0.22	66.15 ± 3.1	5	0.01–0.93	0.9906
		1.08 ± 0.01	15.43 ± 0.14		0.93–12.12	0.9985
	Mannose	1.9 ± 0.17	27.15 ± 2.4	12	0.02–0.93	0.9902
		0.49 ± 0.006	7.01 ± 0.08		0.93–12.12	0.9905
	Galactose	4.43 ± 0.37	63.29 ± 5.2	5.4	0.01–0.93	0.9915
		1.11 ± 0.04	15.86 ± 0.57		0.93–12.12	0.9991
	Fructose	2.5 ± 0.08	35.72 ± 1.1	9.5	0.02–0.675	0.9888
		1.08 ± 0.009	15.43 ± 0.12		0.675–12.12	0.9994
Pentose	Arabinose	3.8 ± 0.21	53.83 ± 2.9	6.3	0.01–0.675	0.9899
		0.9 ± 0.004	12.86 ± 0.05		0.675–12.12	0.999
	Xylose	3.57 ± 0.1	51 ± 1.4	6.7	0.01–0.5	0.9898
		0.65 ± 0.005	9.29 ± 0.07		0.5–12.12	0.9983

Table 2
Analytical parameters of different electrode modifications for sugars sensors compared with proposed sensors in this work.

Electrode modifications	Detection technique	Sensitivity	LOD	Linear range	Ref.
MWCNT/NiO-glassy carbon electrode	Cyclic voltammetry; peak current at +0.6 V vs Ag/AgCl	13.7 μA mM^{-1}	0.16 mM glucose	0.2–12 mM	[45]
CNT – glassy-carbon electrodes	Amperometric detection at +0.45 V	26 μA mM^{-1}	10 μM galactose	–	[46]
Freestanding SWCNT film	Amperometry at +0.6 V	248.6 μA mM^{-1} cm^{-2}	0.01 mM	0.01–2.16 mM	[47]
Nickel particle/poly(1-naphtylamine) carbon paste electrode	Cyclic voltammetry; peak current at +0.45 V vs Ag/AgCl	38.98 μA mM^{-1}	6 μM glucose	0.04–1 mM	[48]
Nickel hydroxide – glassy carbon electrode	Flow injection analysis, potentiostatic conditions of +0.45 V vs Ag/AgCl	13.8 mA mM^{-1} cm^{-2}	3.4 μM glucose	–	[15]
Nickel electrode	Flow injection analysis applied potential of +0.55 V vs Ag/AgCl	1.09 μA mM^{-1}	0.04 mM glucose	0.1–2.5 mM	[40]
Cobalt oxide/MWCNT glassy carbon electrode	Flow injection amperometric measurements at +0.5 V vs Ag/AgCl	34.19 μA mM^{-1}	0.07 mM glucose	0.15–5 mM	[16]
CNT–NiCo-oxide screen printed electrode	Constant potential amperometric detection at 0.35 V vs Ag/AgCl	66.15 μA mM^{-1} cm^{-2}	5 μM glucose	0.01–12.12 mM	This work

When the stability of CNT–NiCo-oxide electrode was evaluated for repetitive amperometric measurements of 0.2 mM glucose, applying 0.35 V constant potential and rinsing the electrode and cell between measurements, the results are remarkably better: the amperometric response displays a decrease of 5% after 10 consecutive assays (from 1.75 μA for the first amperometric measurement to a current of 1.67 for the 10th measurement). The reproducibility of 5 different electrodes was 2.33% at 0.2 mM glucose ($1.72 \pm 0.04\,\mu$A). The CNT–NiCo-oxide composite could be stored at 4 °C for up to 5 months and then used to prepare the modified electrodes without affecting the sensitivity to glucose. This behavior demonstrates that the proposed electrodes can be used for repetitive detection of glucose, recommending them as suitable for use in flow systems. On the other hand, the simple and reproducible method used for preparation of the electrodes, offer a very interesting and facile alternative for the easy construction of novel disposable electrochemical detectors in connection with screen-printed electrodes.

4. Conclusions

This article described a novel electrode consisting of nickel and cobalt mixed oxide particles dispersed in a Nafion polymer in combination with CNT, used as a very effective sensor for constant potential amperometric detection of carbohydrates. The synergy between mixed metallic oxide and CNT provides a marked decrease in overpotential for the oxidation of carbohydrates on the working electrode. The electrode was electrocatalytically active around 300 mV vs Ag/AgCl in the presence of carbohydrates. The amperometric detection of six monosaccharides was performed by applying a 350 mV potential, which is lower than other reported potentials used for amperometric detection of carbohydrates, but sufficient to obtain a good sensitivity of the modified electrodes. The fast response of CNT–NiCo oxide electrodes make them highly suitable for monitoring carbohydrate compounds in flow through systems.

The very simple and sensitive reported electrodes can be used as sensitive amperometric detector in high-performance liquid chromatography (HPLC), based on the oxidation of carbohydrates at the active CNT–nickel–cobalt oxide electrode in combination with anion exchange chromatography, if separation of carbohydrates is needed. The electrode may also be used as a detector in capillary electrophoresis or as a sugar sensor for analytical applications in some environments. Future efforts will aim at exploiting the attractive electrocatalytic action of CNT–NiCo oxide electrodes for monitoring these compounds following chromatographic and/or electrophoretic separations.

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