Detection of Several Carbohydrates Using Boron-doped Diamond Electrodes Modified with Nickel Hydroxide Nanoparticles

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In this work the electrooxidations of glucose, galactose, mannose, rhamnose, xylose and arabinose are studied at a nickel hydroxide nanoparticle modified boron-doped diamond electrode and compared to an unmodified electrode. These carbohydrates are very important in the second-generation ethanol production process. Nickel hydroxide modified boron-doped diamond was characterized by scanning electron microscopy and energy dispersive X-ray. Electrochemical impedance spectroscopy was employed to study the interface properties of surface-modified electrodes in the absence and presence of the carbohydrates. Limits of detection were $5.3 \times 10^{-5}$, $6.8 \times 10^{-5}$, $2.7 \times 10^{-4}$, $6.9 \times 10^{-4}$, $8.8 \times 10^{-4}$ and $2.6 \times 10^{-4}$ mol L$^{-1}$ for glucose, galactose, mannose, rhamnose, arabinose, xylose, respectively.

Keywords Carbohydrates, nickel nanoparticles, modified boron-doped diamond electrode, voltammetry

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Introduction

The search for new materials with electrocatalytic characteristics and the study of their applications such as a fuel cell catalyst, electrocatalyst for organic synthesis and in analytical approaches has received considerable interest in recent years. In electroanalysis, electrocatalytic materials have been used as a modifier of electrodes for the development of sensors and detectors for organic and inorganic compounds due to their superior properties, which are significantly different from conventional electrodes, e.g., glassy carbon, boron doped diamond (BDD) or platinum. There are several types of materials with electrocatalytic properties used as an electrode modifier, among them enzymes and DNA in biosensors and metal and metal oxide nanoparticles (NPs), for example, for determination of inorganic and organic compounds. The electrode modification with metal or metal oxide NPs increases surface coverage and catalytic activity of the electrode. With a greater number of active sites there is considerable improvement in the signal-to-noise ratio, and the modification requires minimal amounts of modifying materials which reduces the cost of electrode preparation. Thus, these properties make nanomaterials suitable for electroanalytical applications.

Metals commonly used for NPs are gold, silver, and platinum, but also metals such as palladium, ruthenium, nickel, copper, bismuth and iridium are used. Several studies have been devoted examining the electrocatalytic potential of nickel in several applications. Nickel nanoparticles (NiNPs), in the form of hydroxide or oxide, have been utilized in the study of oxygen-evolution reactions and the oxidation of organic compounds, such as glucose, alcohol, amino acids, ascorbic acid, neurotransmitters and drugs, and inorganic compounds. Especially in the determination of glucose, nickel modified electrodes have been extensively studied mainly in biological samples and have shown to be a good alternative to enzymic sensors, which in spite of showing great selectivity and high sensitivity, are thermally and chemically unstable. Nickel hydroxide or oxide NPs exhibit remarkable electrocatalytic capability for glucose oxidation and other compounds due to the effect originating from the redox couple of Ni(OH)$_2$/NiO(OH) on the electrode surface in as alkaline medium. Surface modification with NiNPs can be done by various chemical routes, such as sol-gel, electrodeposition and electrophoretic deposition, among others. Among them, electrodeposition is convenient because it involves the direct formation of NPs on the electrode surface. In addition to being a simple technique, electrodeposition may occur at room temperature and is possible to control size and coverage of electrodeposited nanostructures by monitoring deposition parameters such as deposition time, deposition potential and metallic ion concentration.

Furthermore, the choice of the substrate electrode is important because interaction between NPs and the electrode surface must be favored, background current must be low and the material has to show good electrical conductivity and physical robustness. Many substrates have been already used for NiNP modification, such as BDD, glassy carbon, graphene, polymer modified electrodes, carbon nanotube, graphite, TiO$_2$ nanowire electrode, as well as gold. Among them, BDD is attractive because it shows many required features, and it is stable in a wide potential window, shows low chemical reactivity, it is resistant in various corrosive solutions and is also an excellent platform to promote nanoparticle formation instead of films due to the irregularity of its surface. In this study we have associated the ability of NiNP to oxidize...
carbohydrates with the fact that BDD has attractive features as an electrode and provides the easy formation of NPs. The great majority of past research has focused on glucose oxidation, and to our knowledge, few works have studied other carbohydrates, like sucrose, xylose, lactose, fructose, maltose, arabinose and rhamnose.\textsuperscript{17,44,46–49} Recently, our group studied the kinetics of electrooxidation of different carbohydrates at a glassy carbon electrode modified with carbon nanotubes decorated with nickel oxy-hydroxide.\textsuperscript{17} A our interest is to study the electroanalytical characterization of BDD electrodes modified with nickel hydroxide for future determination of these carbohydrates in lignocellulosic material of sugar cane, which are important in the second-generation ethanol production.\textsuperscript{50,51} Therefore, the main goal of the present paper is the fabrication and the characterization of BDD electrodes modified with nickel hydroxide nanoparticles (Ni(OH)\textsubscript{2}/BDD) and its use in the electrooxidation of glucose, galactose, mannose, rhamnose, arabinose and xylose, the main carbohydrates present in the lignocellulosic material of sugar cane.

\section*{Experimental}

\subsection*{Reagents and chemicals}
All reagents used in this study were of analytical grade and all solutions were prepared using water from the Milli-Q system at a resistivity no less than 18.2 M\textOmega\,cm\textsuperscript{-1} at 25 °C. The electrochemical measurements on the behavior of a BDD electrode were performed in 0.50 mol L\textsuperscript{-1} H\textsubscript{2}SO\textsubscript{4}. The solution used to modify the BDD by electrodeposition was 1.0 × 10\textsuperscript{-3} mol L\textsuperscript{-1} NiCl\textsubscript{2} in sodium acetate buffer solution (pH 4.0). The passivation of the BDD electrodes was performed with phosphate buffer (pH 7.0), 0.10 mol L\textsuperscript{-1} NaOH and sodium acetate (pH 4.0). For the studies of electrochemical detection of carbohydrates, 0.10 mol L\textsuperscript{-1} NaOH was used. The stock solutions of carbohydrates were prepared in 0.10 mol L\textsuperscript{-1} NaOH at concentrations of 0.05 mol L\textsuperscript{-1}.

\subsection*{Apparatus}
Electrochemical measurements were performed on a potentiostat/galvanostat model of AUTOLAB PGSTAT 30 controlled by GPES 4.9 software. The working electrodes were constituted by plates of boron-doped diamond with an area of 1 cm\textsuperscript{2}, and resistivity of 0.02 to 0.18 \textOmega\,cm, prepared by chemical vapor deposition technique by ElementSix\textsuperscript{8}. The area was restricted to 0.16 cm\textsuperscript{2} in the electrochemical experiments. The reference electrode was Ag/AgCl (in saturated KCl) and the counter electrode was a platinum wire. All results were obtained using a conventional single-compartment cell.

\subsection*{Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS)}
Morphological characterization of BDD electrode and modified BDD electrode was performed by scanning electron microscopy and energy dispersive X-ray spectroscopy using a electron emission field effect (FEG-SEM), Model JSM 7500F by JEOL.

\subsection*{BDD treatments}
The BDD electrode was subjected to anodic and/or cathodic treatments in 0.50 mol L\textsuperscript{-1} H\textsubscript{2}SO\textsubscript{4}. In anodic treatment a potential of 3.0 V (vs. Ag/AgCl) was applied for 30 s and in the cathodic treatment the potential was –3.0 V (vs. Ag/AgCl) for the same interval time.

\section*{Results and Discussion}

\subsection*{Effect of pretreatments on the electrochemical response of the BDD}
Cathodic and anodic pretreatments are simple and quick ways to activate the BDD electrode surface and due to gas evolution during these pretreatments, adsorbed particles on the electrode surface are removed, promoting its cleaning. Moreover, the physical and chemical properties of the BDD are affected by the polarizations. In the anodic pretreatment in acid solutions the diamond surface is oxidized and intense oxygen evolution is observed, consequently oxygen terminations are formed. These terminations are hydrophilic with positive electron affinity and low conductivity. On the other hand, during the cathodic pretreatment, intense hydrogen evolution occurs and the BDD surface is reduced, forming hydrogen terminations, which are hydrophobic with negative electron affinity and high conductivity.\textsuperscript{52}

Regarding the influence of BDD preconditioning, we have studied the influence of anodic, cathodic and both pretreatments of BDD electrodes in the electrochemical detection of glucose using linear sweep voltammetry (LV). The anodic and cathodic pretreatments were performed at 3.0 V and –3.0 V (vs. Ag/AgCl), respectively. Both were carried out for 30 s in 0.50 mol L\textsuperscript{-1} H\textsubscript{2}SO\textsubscript{4}. BDD electrode cyclic voltammograms in an acid medium after the polarizations (not shown) showed a clean surface, with very low capacitive resistance and absence of any faradaic processes, between –0.75 and 2.35 V. Figure 1 shows responses for BDD in NaOH solution after different pretreatments in the presence of 1.5 × 10\textsuperscript{-3} mol L\textsuperscript{-1} of glucose. On the untreated BDD surface, no faradaic response was observed. However, when BDD is first undergone anodic pretreatment for surface cleaning\textsuperscript{33–35} and being subjected to cathodic pretreatment, the peak current for glucose oxidation increases dramatically and the oxidation peak becomes better defined. This improvement of the electrochemical response may be attributed to the formation of a hydrophilic and conductive surface due to cathodic pretreatment.\textsuperscript{56} Limit of detection (LOD), linear range, correlation coefficient (R) and amperometric sensitivities (SA) for the BDD electrode were calculated and are shown in Table 1. The catalytic superiority of BDD after two polarizations (anodic then cathodic polarization) compared to an electrode that received just one polarization or no pretreatment is confirmed by means of the
In order to improve analytical response to carbohydrates, the pretreated BDD electrode was modified with NiNP. BDD electrodes anodically and cathodically pretreated were modified with metallic NiNP by electrodeposition. The parameters for nickel modification of electrodeposition time, solution of electrodeposition and pH for oxidation of metallic nickel were studied in order to achieve a better response to glucose oxidation. The optimal parameters were determined to be a 1.0 \times 10^{-3} \text{ mol L}^{-1} \text{NiCl}_2 solution in acetate buffer (pH 4.0) and a reduction potential of –1.2 V (vs. Ag/AgCl) applied for 300 s. After, the nickel modified BDD electrodes were washed and placed in 0.10 mol L^{-1} NaOH solution. Metallic nickel can be electro-oxidized to nickel hydroxide at approximately –0.8 V (vs. SCE) in alkaline and aerated solution. There are two possible phases of nickel hydroxide, the hydrated \( \beta \)-Ni(OH)\(_2\), and the anhydrous \( \alpha \)-Ni(OH)\(_2\). The \( \alpha \)-Ni(OH)\(_2\) is the catalytic active form favored in high electrolyte concentration.\(^{32}\) This form is oxidized to \( \beta \)-Ni(OH)\(_2\) at approximately –0.8 V in alkaline solutions, according to Eq. (1).\(^{34}\) Figure 2 shows the first and the thirtieth scan of Ni(OH)\(_2\) modified BDD electrode, Ni(OH)\(_2\)/BDD, in NaOH solution. The redox couple with \( E^0 = 0.410 \text{ V} \) refers to the process Ni(II)/Ni(III). An increase of anodic and cathodic peak currents is observed with successive scans; this is due to the entry of OH\(^-\) species into the structure of Ni(OH)\(_2\) NPs.\(^{35}\)

\[
\text{Ni(OH)}_2 \rightleftharpoons \text{NiO(OH)} + \text{H}^+ + \text{e}^-
\]  

Chemical and morphological characterization of the BDD and nickel hydroxide modified BDD surface

The Ni(OH)\(_2\)/BDD electrode was characterized by the techniques of scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). The SEM was employed to observe the morphologic aspects of the modified electrodes. Figure 3 shows SEM images with 10000 times magnification EDS spectra of unmodified BDD and Ni(OH)\(_2\)/BDD.

Figure 3A shows the BDD electrode surface is irregular and exhibits plateaus in its extension. According to the EDS spectrum, only carbon was identified on the BDD substrate. Figures 3C and 3D show the effective electrode modification with isolated and agglomerated hydroxide nickel spherical NPs, with size ranging from 44 to 90 nm in diameter. The chemical characterization proves the existence of nickel through the peaks at approximately 0.8 and 7.6 keV, and of oxygen through the peak at 0.5 keV, which are expected to modification with nickel hydroxide.

Electrochemical oxidation of glucose

In order to evaluate the electrocatalytic activity of nickel hydroxide nanoparticles toward the electrooxidation of glucose, cyclic voltammograms using Ni(OH)\(_2\)/BDD in 0.10 mol L\(^{-1}\) NaOH in the absence and presence of 1.0 \times 10^{-3} \text{ mol L}^{-1} \text{glucose} were obtained and are shown in Fig. 4. This figure shows that Ni(OH)\(_2\)/BDD in an alkaline medium (dashed line) presents two distinct peaks, with \( E^0 = 0.410 \text{ V} \) (vs. Ag/AgCl), corresponding to the redox couple Ni(OH)\(_2\)/Ni(OH)\(_3\). However, with the addition of 1.0 \times 10^{-3} \text{ mol L}^{-1} \text{glucose}, an increase of the anodic current peak and a shift of peak potential to more positive values are observed, in addition to the disappearance of the cathodic peak related to the reduction of Ni\(^3+\) to Ni\(^2+\), which is due to the regeneration of the Ni(OH)\(_2\) species during the glucose oxidation reaction. This fact indicates the irreversible oxidation of glucose, and a conversion of the Ni(OH)\(_2\) in Ni(OH)\(_3\).\(^{37}\) The anodic peak shift can be attributed to the diffusion limitation of glucose at the electrode surface. When voltammetric behaviors

![Fig. 1](image1.png)  
Fig. 1 Linear voltammograms obtained for BDD electrode after cathodic pretreatment (I), anodic pretreatment (II), without pretreatment (III) and after anodic and cathodic pretreatments (IV) in presence of 1.5 \times 10^{-3} \text{ mol L}^{-1} \text{glucose in 0.10 mol L}^{-1} \text{NaOH. Scan rate of 50 mV s}^{-1}.  

![Fig. 2](image2.png)  
Fig. 2 First (dashed line) and thirtieth (solid line) scans for Ni(OH)\(_2\)/BDD electrode in 0.10 mol L\(^{-1}\) NaOH; scan rate of 100 mV s\(^{-1}\).  

Table 1 Analytical parameters of linear range, linearity, sensitivity and LOD for glucose using BDD electrode after different pretreatments

<table>
<thead>
<tr>
<th>BDD pretreatment</th>
<th>Linear range/mol L(^{-1})</th>
<th>SA/A L mol(^{-1})</th>
<th>R</th>
<th>LOD(\gamma)/mol L(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>No treatment</td>
<td>9.8 \times 10^{-4} - 10.3 \times 10^{-3}</td>
<td>0.002</td>
<td>0.999 1 4.2 \times 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>Cathodic</td>
<td>2.4 \times 10^{-3} - 9.0 \times 10^{-3}</td>
<td>0.002</td>
<td>0.9990 3.8 \times 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>Anodic</td>
<td>1.5 \times 10^{-3} - 11.5 \times 10^{-3}</td>
<td>0.001</td>
<td>0.9952 1.0 \times 10^{-3}</td>
<td></td>
</tr>
<tr>
<td>Anodic and cathodic</td>
<td>4.9 \times 10^{-4} - 11.5 \times 10^{-3}</td>
<td>0.006</td>
<td>0.9998 2.6 \times 10^{-4}</td>
<td></td>
</tr>
</tbody>
</table>

a. LOD = 3 \times SD/slope.
of glucose at Ni(OH)$_2$/BDD and pretreated BDD are compared, a shift around 0.11 V for more cathodic potential is observed using the modified electrode, in addition to the pronounced increase of the peak current.

These results point to the catalytic effect of the nickel hydroxide nanoparticle that greatly facilitated the oxidation of glucose. Figure 5 shows the analytical response of glucose using unmodified pretreated BDD and Ni(OH)$_2$/BDD electrodes after successive additions of glucose. For the Ni(OH)$_2$/BDD, the peak current was linearly proportional to glucose concentration in the range between $1.3 \times 10^{-4}$ and $3.9 \times 10^{-3}$ mol L$^{-1}$, with $R$ of 0.9999 and SA and LOD of
values in literature based on electroanalytical methods employing nickel modified electrodes (Table 2).58–66 Taking into account the differences between the techniques employed and the oxidation processes, increase of anodic peak current and a shift of anodic peak potential to more positive values, in addition to a decrease of cathodic peak current. The electrooxidation reactions of carbohydrates follow the same mechanism, that is, the oxidation of galactose leads to galanolactone, arabinox to arabinonalactone, rhamnose to rhaminonalactone and xylose to xylonolactone.69

Electrochemical oxidation of other carbohydrates

Ni(OH)2/BDD was used for the electrochemical studies of galactose, mannose, rhamnose, xylose and arabinose, the most important carbohydrates present in the lignocellulosic material of sugar cane. The voltammetric behavior of these carbohydrates was studied at Ni(OH)2/BDD in 0.10 mol L−1 NaOH. All carbohydrates showed a similar voltammetric response, with re-oxidation processes, increase of anodic peak current and a shift of anodic peak potential to more positive values, in addition to a decrease of cathodic peak current. The electrooxidation reactions of carbohydrates follow the same mechanism, that is, the oxidation of galactose leads to galanolactone, arabinose to arabinonalactone, mannose to mannonalactone, rhamnose to rhaminonalactone and xylose to xylonolactone.69

The influence of concentration of each carbohydrate in the voltammetric behavior of Ni(OH)2/BDD was investigated at 50 mV s−1 in 0.10 mol L−1 NaOH. Successive additions of 0.05 mol L−1 of each carbohydrate were performed Figure 8 shows the analytical curves for glucose, galactose, mannose, arabinose, rhamnose and xylose. These curves were obtained by peak current measuring. In Table 3, the values of LOD, linear range, SA and R for carbohydrates are presented. The highest SA value for glucose when compared to other carbohydrates can be explained because the ring hemiacetal form of glucose has more OH groups available in relation than other carbohydrates due to the stereochemistry of these molecules. On the other hand, mannose showed the lowest SA and the worst LOD due to a lower number of hydroxyl groups
available for oxidation, which contributes to a decrease in the electrochemical response. This contributes to an increase of adsorption on the electrode surface and the kinetics of reaction.

Recovery studies were carried out in order to evaluate the method. Recovery average values were of (96.1 ± 3.4) % for glucose, (97.6 ± 1.7) % for galactose, (97.5 ± 2.4) % for mannose, (97.6 ± 5.3) % for rhamnose, (99.3 ± 1.1) % for arabinose and (97.8 ± 0.83) % for xylose.

Table 3 Analytical parameters of linear range, linearity, sensitivity and LOD for different carbohydrates at Ni(OH)2/BDD electrode

<table>
<thead>
<tr>
<th>Carbohydrates</th>
<th>Linear range/mol L⁻¹</th>
<th>SA/ A L mol⁻¹</th>
<th>R</th>
<th>LOD/ mol L⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glucose</td>
<td>1.3 × 10⁻⁴ – 3.9 × 10⁻³</td>
<td>0.053</td>
<td>0.9999</td>
<td>5.3 × 10⁻⁵</td>
</tr>
<tr>
<td>Galactose</td>
<td>1.3 × 10⁻⁴ – 3.9 × 10⁻³</td>
<td>0.029</td>
<td>0.9983</td>
<td>6.8 × 10⁻⁴</td>
</tr>
<tr>
<td>Mannose</td>
<td>1.3 × 10⁻⁴ – 5.8 × 10⁻³</td>
<td>0.002</td>
<td>0.9985</td>
<td>2.7 × 10⁻⁴</td>
</tr>
<tr>
<td>Rhamnose</td>
<td>1.3 × 10⁻⁴ – 2.4 × 10⁻³</td>
<td>0.019</td>
<td>0.9992</td>
<td>6.9 × 10⁻⁴</td>
</tr>
<tr>
<td>Arabinose</td>
<td>1.3 × 10⁻⁴ – 2.8 × 10⁻³</td>
<td>0.039</td>
<td>0.9991</td>
<td>8.8 × 10⁻⁵</td>
</tr>
<tr>
<td>Xylose</td>
<td>1.3 × 10⁻⁴ – 2.2 × 10⁻³</td>
<td>0.024</td>
<td>0.9999</td>
<td>2.6 × 10⁻⁴</td>
</tr>
</tbody>
</table>

a. LOD = 3 × SD/slope.

available for oxidation, which contributes to a decrease in the electrochemical response. This contributes to an increase of adsorption on the electrode surface and the kinetics of reaction.

Recovery studies were carried out in order to evaluate the method. Recovery average values were of (96.1 ± 3.4) % for glucose, (97.6 ± 1.7) % for galactose, (97.5 ± 2.4) % for mannose, (97.6 ± 5.3) % for rhamnose, (99.3 ± 1.1) % for arabinose and (97.8 ± 0.83) % for xylose.

Fig. 7 Cyclic voltammograms of Ni(OH)2/BDD electrode in 0.10 mol L⁻¹ NaOH in the absence (dashed line) and in the presence of 1.0 × 10⁻³ mol L⁻¹ glucose, galactose, arabinose, mannose, rhamnose and xylose (solid line). Scan rate of 50 mV s⁻¹.

Fig. 8 Dependency between peak current and concentration of glucose (I), arabinose (II), galactose (III), xylose (IV), rhamnose (V) and mannose (VI) in 0.10 mol L⁻¹ NaOH, using Ni(OH)2/BDD electrode.
Impedance studies for the Ni(OH)₂/BDD electrode

Electrochemical impedance spectroscopy (EIS) is an efficient tool for studying the interface properties of surface-modified electrodes. The diameter of the semicircle in the Nyquist diagram is usually equal to the charge-transfer resistance ($R_\text{ct}$), which controls the charge-transfer kinetics of the redox process at the electrode interface.\(^7\)

EIS experiments were performed in the frequency range from 100 kHz to 10 mHz, at an amplitude of 5 mV and potential of 0.46 V. First, Ni(OH)₂/BDD was compared to unmodified BDD, in 0.10 mol L⁻¹ NaOH the $R_\text{ct}$ was 251.3 kΩ for BDD, a value much bigger than for hydroxide nickel modified electrode, offering limited resistance to charge transfer, hence promoting a very fast electron exchange rate. In other words, Ni(OH)₂/BDD exhibits a higher catalytic activity, promoting greater interaction of the glucose molecule on the Ni(OH)₂/BDD surface than on the unmodified diamond electrode, and these results were confirmed through cyclic voltammetric studies. $R_\text{ct}$ values for all carbohydrates, in the same concentration, were: 1.34 kΩ for rhamnose and arabinose, 1.48 kΩ for galactose, 1.62 kΩ for xylose and 2.18 kΩ for mannose.

Conclusions

The proposed BDD electrode modification method with nickel hydroxide NPs was efficient and simple. MEV images and EDS spectra showed the effective modification of a BDD electrode with nickel hydroxide NPs. The voltammetric behavior of glucose, galactose, mannos, rhamnose, arabinose and xylose in an alkaline medium was studied. When compared to a bare BDD electrode after different pretreatments, the Ni(OH)₂/BDD showed higher sensitivity and lower limit of detection for glucose. Thus, the Ni(OH)₂/BDD holds great potential for employment as an electrochemical detector of carbohydrates in the lignocellulosic material of sugar cane.

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