Prussian Blue Modified Carbon Nanotube Paste Electrodes: A Comparative Study and a Biochemical Application

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ABSTRACT

Prussian Blue modification of Single Walled Carbon Nanotubes and the successive assembling of paste electrodes is presented in this article for the first time. The electrochemical feature of such electrodes have been fully evaluated with CV and amperometric experiments. Prussian Blue Nanotube Paste electrodes showed a high sensitivity towards hydrogen peroxide with a LOD of $7.4 \times 10^{-6}$ M. They also proved to possess a strong stability even at

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basic pHs (i.e., pH 9 and 10) demonstrating no significant loss of
signal after three days of continuous work. In addition, the loading
in the paste mixture of glucose oxidase has brought to a sensitive tool
for the detection of glucose in a range between 0.1 and 50 mM.

**Key Words:** Prussian blue; Nanotubes; Nanotube paste electrode;
Hydrogen peroxide; Glucose oxidase; Glucose.

**INTRODUCTION**

Carbon nanotube is a novel carbon material discovered by Iijima in
1991[1] and it has been found to have excellent electrode performances.[2]
Single walled carbon nanotubes constitute a new form of molecular
diameter metallic semiconducting wire. Their high conductance, tensile
strength, and chemical stability have attracted much attention[3] and
interest for many applications.[4–8] Single wall carbon nanotubes, reported
for the first time in 1993 were firstly studied and characterized as electrode
material by two research groups.[9–11] The electrodes were obtained casting
a film of single wall carbon nanotubes on a glassy carbon electrode and
were found to have an electrochemical activity towards some biomolecules
such as dopamine, epinephrine, and ascorbic acid.

In a recent article by our research group an extended study of the
electrochemical properties of carbon nanotubes paste electrodes has been
presented.[12] Paste electrodes were constructed mixing single walled
carbon nanotubes with mineral oil. Performances of carbon nanotube
paste were evaluated studying the parameters of cyclic voltammetry
towards several electroactive molecules. Due to their high surface
area,[13,14] single walled carbon nanotubes required a higher amount of
mineral oil (40%) in respect of what observed with graphite (34%)[22] and
glassy carbon (20%)[20] in the assembling of paste electrodes. Moreover,
electrodes showed an enhanced electroactivity towards hydrogen per-
oxide, dopamine, NADH oxidation in respect of classic graphite based
paste electrodes.[12] This behavior together with the compatibility with
biological tissues makes the nanotubes suitable for the development
of new chemical sensors and biosensors. Nowadays the largest number
of biosensors are based on the use of oxidase enzymes that catalyze the
oxidation of a substrate with the consequence reduction of O2 to hydro-
gen peroxide. A rapid, interference free, and precise detection of H2O2
(whose concentration is proportional to the substrate concentration)
is then always required to give an accurate measure of the enzymatic
substrate which represents in much cases the analyte. For this reason
Prussian Blue, a selective catalyst of the H$_2$O$_2$ reduction, has been fully investigated during last decade.[15–18] The modification of an electrode surface with a layer of PB makes in fact it possible to measure H$_2$O$_2$ at low applied potential (around 0.0 V) and to greatly decrease any electrochemical interference, as demonstrated in a previous article.[19]

In this work, we report for the first time the modification of single walled carbon nanotube powder with Prussian Blue and the successive assembling of composite electrode for H$_2$O$_2$ detection. The electrochemical behavior of these probes has been fully characterized by cyclic voltammetry in terms of surface charge, peak currents, formal potential, and $\Delta$Ep. Amperometric experiments have been carried out to evaluate the H$_2$O$_2$ response and analytical parameters such as detection limit, linear range, RSD, and sensitivity have been evaluated. A comparison with PB modified graphite electrodes is also presented. This is in our knowledge the first article reporting the direct modification of carbon nanotubes with an electrochemical mediator. An application obtained by simply loading aliquots of oxidase enzyme in the paste mixture is also presented.

**EXPERIMENTAL**

**Apparatus**

Amperometric measurements were carried out using a VA 641 amperometric detector (Metrohm, Herisau, Switzerland), connected to a $X$-$t$ recorder (L250E, Linseis, Selb, Germany). The electrochemical cell was assembled with a conventional three-electrode system: Carbon Nanotube Paste working electrode (3-mm diameter), an Ag/AgCl/KCl (3 M) reference electrode and a Pt counter electrode. Cyclic voltammetry (CV) and chronoamperometry experiments were performed using an Autolab electrochemical system (Eco Chemie, Utrecht, The Netherlands) equipped with PGSTAT-12 and GPES software (Eco Chemie, Utrecht, The Netherlands).

**Reagents**

Single Wall Carbon Nanotubes (CNT) Carbolex (purity 50–70%) and graphite particles (powder 1–2 $\mu$m) were purchased from Aldrich (Steinheim, Germany). Mineral oil was obtained from Fluka (Buchs, Switzerland). All chemicals from commercial source were of analytical...
grade. All solutions were prepared with 0.05 M phosphate buffer +0.1 M KCl, pH 7.4. Standard solutions were daily prepared in same buffer. For pH effect studies borate buffer (0.05 M + KCl 0.1 M, pH 9.0 and pH 10) was also used.

Glucose Oxidase (GOx) (EC 1.1.3.4, type VII from *Aspergillus Niger*, 185 units/mg), was Purchased from Sigma (St. Luis, MO).

**Preparation of CNT Modified With PB**

The PB was chemically synthesized in the presence of nanotube powder starting from its precursors K$_3$Fe(CN)$_6$ and FeCl$_3$ as follows: the nanotube powder (1 g) was suspended in 10 mL of a solution of K$_3$Fe(CN)$_6$ 0.10 M in 10 mM HCl. Next 10 mL of a 0.10 M solution of FeCl$_3$ in 10 mM HCl were added and the resulting mixture was stirred for 10 min. The nanotube powder (with adsorbed PB) was then collected by filtration and washed with 10 mM HCl until the washing solution became colorless and then dried in oven at 100°C for 1.5 h. The powder modified with Prussian Blue (referred as PBNT) was stored dark in a desiccator at room temperature. For graphite modification the same procedure was adopted.

**CNT Paste Electrodes Preparation**

The nanotube paste mixture was prepared mixing nanotube powder and mineral oil at a fixed ratio of 60/40 w/w respectively. The paste was carefully hand-mixed in a mortar and then packed into a cavity (3-mm diameter; 2-mm depth) at the end of a Teflon tube. Electrical contact was provided by a copper wire connected to the paste in the inner hole of the tube. The paste was kept at room temperature in a desiccator until used. Carbon Nanotube Paste electrodes modified with Prussian Blue (referred as PBNTPEs) were prepared by hand-mixing mineral oil (40%) and a mixture of PBNT/NT (60%). Prussian Blue graphite paste electrodes (referred as PBgraphitePEs) have been obtained by mixing PB modified graphite (66%) and mineral oil (34%).

**Preparation of PBNTP Glucose Biosensor**

Biosensors were prepared by hand mixing 60 mg of PBNT/NT/ enzyme mixture with 40 mg of mineral oil and then mixed continuously
until a homogeneous paste was obtained. The PBNT/NT/enzyme mixture had the following weight composition: 22.5% PB-NT, 72.5% NT and 5% glucose oxidase. An aliquot of the final paste filled the tip of the electrode; the remaining was kept in an aluminium foil at 4°C until reused.

**H₂O₂ and Enzymatic Substrate Measurements**

Measurements of H₂O₂ and enzymatic substrate were performed using amperometric batch analysis in a stirred phosphate buffer solution (20 mL) with an applied potential of 0.0 V vs. Ag/AgCl. When a stable baseline was reached, the analyte was added and the response recorded.

**RESULTS AND DISCUSSION**

**Characterization of PB Modified Carbon Nanotubes Paste Electrodes**

In a previous article [12] that deals with the use of Single Walled Carbon Nanotubes for the assembling of Carbon Nanotube Paste electrodes, it was already demonstrated that the best paste composition was 60/40 Nanotubes/mineral oil w/w. The physical properties [23] of Carbon nanotubes (CNTs) and their unique morphology are much different in respect of graphite powder and a complete study of their electrochemical behavior upon PB modification is not yet present in literature.

The CNTs here used are reported to have cylindrical geometry with a pore diameter of 1–2 nm and a length of microns. The surface area of CNTs calculated experimentally using BET method is 300 m²/g [13,14] while for graphite powder was ca. 10 m²/g [25]. CNTs were modified with Prussian Blue using the same procedure already optimized in previous articles [20,22] dealing with graphite and glassy carbon, which has brought to high electrochemical activity and good stability of the Prussian Blue layer. In Fig. 1 is shown the cyclic voltammetry obtained with the PBNTE prepared with 60% of PB modified carbon nanotube and 40% of mineral oil, which clearly shows the cathodic and anodic current peak due to the reduction and oxidation of Prussian Blue at the electrode surface.

Table 1a summarizes some of the electrochemical parameters obtained from cyclic voltammetry with PBNTEs and with PBgraphite.
Figure 1. Cyclic voltammetry of PBNTPE. Paste composition: 40% mineral oil, 60% PBNT. Phosphate buffer 0.05 M + KCl 0.1 M, pH 7.4. Scan rate 5 mV/s. Potential range −0.2; +0.5 V vs. Ag/AgCl.

Table 1a. Comparison between PBNTPEs and PBgraphitePEs. Cyclic voltammetry parameters, phosphate buffer 0.05 M + KCl 0.1 M, pH 7.4. Scan rate (i.e., υ = 50 mV/s, potential range −0.2; +0.5 V vs. Ag/AgCl. See text for details on paste composition. Underscript: a = anodic, c = cathodic.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>PBNTPEs</th>
<th>PBgraphitePEs</th>
</tr>
</thead>
<tbody>
<tr>
<td>I_a (nA)</td>
<td>272</td>
<td>61</td>
</tr>
<tr>
<td>I_c (nA)</td>
<td>265</td>
<td>58</td>
</tr>
<tr>
<td>ΔE_p (mV)</td>
<td>228</td>
<td>124</td>
</tr>
<tr>
<td>Q_a/A (mC/cm²)</td>
<td>21.7</td>
<td>1.3</td>
</tr>
<tr>
<td>Q_c/A (mC/cm²)</td>
<td>20.8</td>
<td>1.4</td>
</tr>
<tr>
<td>E_f (mV)</td>
<td>170</td>
<td>185</td>
</tr>
<tr>
<td>I_p/I_p_a</td>
<td>0.97</td>
<td>0.95</td>
</tr>
<tr>
<td>∂(log I_p)/∂(log υ)_a</td>
<td>0.65</td>
<td>0.56</td>
</tr>
<tr>
<td>∂(log I_p)/∂(log υ)_c</td>
<td>0.47</td>
<td>0.49</td>
</tr>
</tbody>
</table>

PEs. Relative amount of mineral oil and graphite is as previously reported.[22]

According to the equation: 
\[ Q = nF AT \]
where Q is the anodic or cathodic charge, n = 4, F is Faraday’s constant and A is the effective area of the electrode, which is assumed to be equivalent to its geometric area (0.07 cm²), the charge density of the electrode (Q/A) is directly proportional to the total amount of PB on the electrode surface (Γ).

Values of charge density (Q/A) for PBNTPE are about 22 mC/cm² while for PBgraphite paste the value found was ca. 1.3 mC/cm². This is
probably due to the fact that CNT possess a very high surface area and a large amount of PB can be easily adsorbed. This seems also to be confirmed by the values of peak currents of PBNTPE which are ca. 4–5 times higher than those of PBgraphite PE.

The dependence of the potential scan rate on the peak reduction current has been then evaluated. The log(Ip) vs. log(\( \nu \)) plot, in a range between 2 and 200 mV/s, gives slopes of 0.65 and 0.47 for the anodic and cathodic peak respectively demonstrating a diffusion controlled process as in the case of an adsorbed mediator. The \( \Delta E_p \) on the PBNTPEs is 228 mV, ca. 100 mV higher than that obtained with PBgraphitePE, demonstrating a slower electrode transfer kinetic in part due to the much higher amount of PB.

The formal potential of PBNTPEs is almost the same of that obtained with PB graphitePEs. For this reason the same applied potential (0.0 V) already chosen\[22\] for PBgraphitePEs has been selected for further amperometric experiments.

In Table 1b are summarized the analytical parameters obtained for amperometric measurements of hydrogen peroxide using PBNTPEs and PBgraphitePEs. For PB graphite paste electrodes sensitivity towards hydrogen peroxide was found to be 428 mA/M cm\(^2\) while for PBNTPEs is about 218 mA/M cm\(^2\). This seems to be in contrast with what observed in CV experiments where PB amount was ca. 4–5 times higher for PBNTPEs.

This difference could be in part due to the larger presence of non conductive material (i.e., mineral oil and the PB itself) at the PBNTPEs but also to a slow electrode kinetics of nanotube particles. This is also confirmed by the high current noise observed (i.e., 50 nA) that makes the

<table>
<thead>
<tr>
<th>Parameters</th>
<th>PBNTPEs</th>
<th>PBgraphitePEs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear range (M)</td>
<td>10(^{-5})–5 \times 10(^{-3})</td>
<td>5 \times 10(^{-7})–5 \times 10(^{-3})</td>
</tr>
<tr>
<td>LOD (M)</td>
<td>1.0 \times 10(^{-5})</td>
<td>5 \times 10(^{-7})</td>
</tr>
<tr>
<td>Noise (nA)</td>
<td>50</td>
<td>5</td>
</tr>
<tr>
<td>Sensitivity (mA/M cm(^2))</td>
<td>218</td>
<td>428</td>
</tr>
<tr>
<td>Response time (s)</td>
<td>5</td>
<td>15</td>
</tr>
<tr>
<td>Time to stabilize the baseline current (min)</td>
<td>80</td>
<td>150</td>
</tr>
</tbody>
</table>
detection limit of PBNTPEs towards hydrogen peroxide much higher than that obtained with PB graphite paste electrode. Taking into account the results obtained with the PB modified glassy carbon paste electrodes,\cite{20} we decreased the total amount of PB in the paste by mixing PBNT with unmodified NT before adding mineral oil. In fact, in the case of glassy carbon paste electrodes, by doing this, a better electrochemical behavior both in voltammetric and amperometric experiments has in fact been observed due to the improved electrode kinetic.

The effect of the paste composition on the electrochemical behavior of PBNTPEs was then evaluated studying the cyclic voltammetric parameters and the amperometric responses to H$_2$O$_2$. Considering these results, the best paste composition has been selected and used for further experiments. Paste was always made keeping the mineral oil percentage at 40% and 60% for the PBNT/NT mixture. The compositions of the PBNT/NT mixture tested were as follows: 75/25, 50/50, 25/75, 10/90, 2/98, w/w. In Table 2 are reported the cyclic voltammetric parameters obtained in phosphate buffer solution with all the mixtures prepared. Anodic and cathodic peak currents are, as it was expected, proportional to PB loading and increase with the increasing of the relative amount of PBNT. Same behavior is observed for the charge density of the electrode (Q). Amperometric parameters evaluated using Carbon Nanotube paste electrodes obtained with a mixture of PBNT/NT are summarized in Table 3. No improvement in sensitivity has been achieved in respect of that obtained using only PBNT, but the presence of non modified nanotube powder brings a faster electrode kinetics with a decrease of the noise current and of the detection limit. For this reason a paste obtained with a

Table 2. Cyclic voltammetry parameters upon paste composition. Paste was obtained mixing 40% of mineral oil and 60% of a mixture of PBNT/NT. Phosphate buffer 0.05 M + KCl 0.1 M, pH 7.4. Scan rate 50 mV/s, range –0.2; +0.5 V vs. Ag/AgCl.

<table>
<thead>
<tr>
<th>% PBNT/NT</th>
<th>$I_a$ (nA)</th>
<th>$I_c$ (nA)</th>
<th>$\Delta E_p$ (mV)</th>
<th>$Q_a/A$ (mC/cm$^2$)</th>
<th>$E_{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>272</td>
<td>265</td>
<td>228</td>
<td>21.7</td>
<td>170</td>
</tr>
<tr>
<td>75</td>
<td>230</td>
<td>199</td>
<td>203</td>
<td>17.5</td>
<td>168</td>
</tr>
<tr>
<td>50</td>
<td>135</td>
<td>122</td>
<td>179</td>
<td>10.8</td>
<td>167</td>
</tr>
<tr>
<td>25</td>
<td>73</td>
<td>68</td>
<td>119</td>
<td>5.4</td>
<td>170</td>
</tr>
<tr>
<td>10</td>
<td>18</td>
<td>18</td>
<td>102</td>
<td>1.4</td>
<td>172</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>10</td>
<td>125</td>
<td>0.8</td>
<td>177</td>
</tr>
</tbody>
</table>
Table 3. Amperometric parameters upon paste composition. Paste was obtained mixing 40% of mineral oil and 60% of a mixture of PBNT/NT, batch measurements in 20 mL phosphate buffer 0.05 M + KCl 0.1 M, pH 7.4. Applied potential 0.0 V vs. Ag/AgCl.

<table>
<thead>
<tr>
<th>% PBNT/NT</th>
<th>I (H₂O₂ 10⁻⁵ M) (nA)</th>
<th>I (H₂O₂ 10⁻⁴ M) (nA)</th>
<th>Noise (nA)</th>
<th>LOD (M)</th>
<th>Sensitivity (mA/M cm²)</th>
<th>Time to stabilize the baseline current (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>90</td>
<td>1500</td>
<td>50</td>
<td>1.0 × 10⁻⁵</td>
<td>214</td>
<td>80</td>
</tr>
<tr>
<td>75</td>
<td>60</td>
<td>700</td>
<td>20</td>
<td>8.5 × 10⁻⁶</td>
<td>100</td>
<td>65</td>
</tr>
<tr>
<td>50</td>
<td>45</td>
<td>525</td>
<td>20</td>
<td>1.1 × 10⁻⁵</td>
<td>75</td>
<td>70</td>
</tr>
<tr>
<td>25</td>
<td>37</td>
<td>408</td>
<td>10</td>
<td>7.4 × 10⁻⁶</td>
<td>58</td>
<td>40</td>
</tr>
<tr>
<td>10</td>
<td>16</td>
<td>172</td>
<td>5</td>
<td>9.0 × 10⁻⁶</td>
<td>24</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>66</td>
<td>2</td>
<td>9.2 × 10⁻⁶</td>
<td>9.4</td>
<td>20</td>
</tr>
</tbody>
</table>
A mixture of PBNT/NT 25/75 w/w was selected and used for further experiments. Table 4 summarizes the analytical characteristics of this PBNTPE towards H$_2$O$_2$ reduction: i.e., detection limit (reported as two times the background noise), linearity range, sensitivity variations (related to the slope variation of calibration curves continuously carried out for 8 h), and reproducibility (reported as the RSD of the current values due to the H$_2$O$_2$ reduction by 4 different sensors obtained from the same paste matrix). Response time, expressed as the time needed to reach 90% of the steady state current, and the time necessary to obtain a stable baseline current, are also reported, while in Fig. 2 are shown some original amperometric recordings.

Comparison with the amperometric parameters of PB modified graphite paste electrodes shows how the use of PB modified carbon nanotubes does not bring any important improvement on the sensitivity towards hydrogen peroxide. Moreover a higher detection limit was observed using PB modified nanotube. This is greatly due to the much higher noise current obtained in the case of PBNTPEs, probably caused by a slow electrode kinetic of Nanotube particles. This property of Single Walled CNTs (SWCNT) has been already observed by some research groups and an article by Avouris$^{[26]}$ clarified the reason for such behavior. In this article, the strong background impedance of the SWNTs is attributed to the fact that the current synthetic schemes for SWNTs generate mixtures of metallic (m) and semiconducting (s) nanotubes, where the latter is responsible for a leakage in conductance that negatively affects the electrode kinetic. The slow electrode kinetics of the PBNTPEs due to the large amount of mineral oil and to the presence of semiconductor SWNT seems to represent the major drawback of this material to assemble PB based amperometric sensors.

### Stability of PBNTPEs

Stability of the PB deposited is one of the most important parameters needed to evaluate the possible use of these sensors in biosensors assembling. We have already demonstrated with other materials (i.e., glassy carbon$^{[20]}$ and graphite$^{[22]}$) that the PB modification procedure here adopted has brought a good stability of PB in a broad pH range.

PBNTPEs were then studied at basic pHs in order to evaluate any possible improvement of the pH stability. Sensors were left in a batch system with the applied potential (0.0 V), and amperometric
Table 4. Amperometric parameters, batch measurements in 20 mL phosphate buffer 0.05 M + KCl 0.1 M, pH 7.4. Applied potential 0.0 V vs. Ag/AgCl PBNTPEs paste composition: 40% mineral oil, 60% PBNT/NT mixture (25%PBNT-75% NT). PBGraphitePEs paste composition: 34% mineral oil, 66% PBgraphite.

<table>
<thead>
<tr>
<th>H₂O₂ probe</th>
<th>LOD (M)</th>
<th>Linear range (M)</th>
<th>Sensitivity (mA/M cm²)</th>
<th>RSD%</th>
<th>Response time (s)</th>
<th>Time to stabilize the baseline current (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBNTPEs</td>
<td>7.4 × 10⁻⁶</td>
<td>10⁻⁵−5 × 10⁻³</td>
<td>58</td>
<td>17</td>
<td>5</td>
<td>40</td>
</tr>
<tr>
<td>PBGraphitePEs</td>
<td>5 × 10⁻⁷</td>
<td>5 × 10⁻⁷−5 × 10⁻³</td>
<td>428</td>
<td>14</td>
<td>15</td>
<td>150</td>
</tr>
</tbody>
</table>
measurements of fixed concentration of hydrogen peroxide (10^{-4} \text{M}) were performed every two hours. During the night sensors were kept under stirring, with the applied potential, in a 5 \times 10^{-4} \text{M} hydrogen peroxide solution and every morning the solution was renewed. pH’s values tested were 8, 9, and 10. At pH 8 (not shown) after 3 days of continuous work no decrease of the initial signal was observed. At pH 9 the same behavior was observed and no inactivation was detected after a total of 52 h (Fig. 3a). Same strong stability of the PB deposited was found by using cyclic voltammetry. 250 continuous cycles were performed at the same pH values (i.e., 8 and 9) and a very little decrease on the peak currents of the last scan was observed in both cases. At pH 10 a decrease of the initial signal for H_2O_2 of 25\% was detected after three days of continuous work. This is in our knowledge the best operative stability of any PB modified material at basic pH. In Fig. 3a and 3b a direct comparison with PBgraphitePEs is presented which clearly shows the better operative stability of nanotubes based PB paste electrodes.

One of the most attractive properties of carbon nanotubes is their robustness that makes them similar to a diamond material. Single walled nanotubes are constituted of hollow cylindrically wound graphene sheets...
Figure 3. Stability studies of PBNTPEs. Continuous amperometric measurements of hydrogen peroxide. (a) Borate buffer 0.05 M + KCl 0.1 M, pH 9. (b) Borate buffer 0.05 M + KCl 0.1 M, pH 10. ■ PBNTPEs: paste composition: 40% mineral oil, 60% PBNT/NT mixture (25% PBNT-75% NT).  ■ PBGraphitePEs: paste composition: 66% mineral oil, 34% PBGraphite.

PBNTPEs: paste composition: 40% mineral oil, 60% PBNT/NT mixture (25% PBNT-75% NT).
that tend to assemble in ropes of nanotubes.\textsuperscript{[30]} Probably, during PB modification, intercalation of PB crystals, that according to Keggin and Miles\textsuperscript{[29]} has a basic cubic structure of the dimension equal to 10.2 Å, occurs in the inner space of the cylinders or in the space between nanotubes bundles. Carbon nanotubes are reported to be well resistant towards oxidant compounds and so no fragmentation of the structure should occur during stability studies at high H\textsubscript{2}O\textsubscript{2} concentration. This means that the PB intercalated in the pores between CNT remains protected during the whole experiment. In the case of graphite instead, during PB modification the PB crystals intercalate the graphite sheets, but a desegregation of the original structure could generate after prolonged exposure to high concentration of hydrogen peroxide, reducing the protective action to PB crystals and decreasing the stability of the PB modified sensor at basic pHs values.

**Oxidase Application**

Glucose Oxidase enzyme was loaded in the PBNTP mixture by a mean of 5%, to assemble a glucose biosensor. Analytical performances of this probe are summarized in Table 5. LOD (S/N = 2) was estimated to be \(7 \times 10^{-5}\) M, the linear range was up to \(10^{-2}\) M and the sensitivity was 3.3 mA/M cm\(^2\). A comparison with what as obtained using graphite as electrodic material shows the better behavior of the PB nanotube

| Table 5. Amperometric parameters towards glucose. Amperometric parameters, batch measurements in 20mL phosphate buffer 0.05 M + KCl 0.1 M, pH 6.0. Applied potential 0.0 V vs. Ag/AgCl, PBNTPs +5% glucose oxidase, PBgraphitePEs +5% glucose oxidase (see text for details). |
|---------------------------------|---------------------------------|
| Linear range (M)                 | \(10^{-4.5} \times 10^{-2}\)        |
| LOD (M)                          | \(7 \times 10^{-5}\)              |
| Sensitivity (mA/M cm\(^2\))      | 3.3                               |
| Response time (s)                | 5                                 |
| RSD\%                           | 18                                |
| Time to stabilize the baseline current (min) | 45                                 |
| Linear range (M)                 | \(10^{-4.2} \times 10^{-2}\)        |
| LOD (M)                          | \(10^{-4}\)                          |
| Sensitivity (mA/M cm\(^2\))      | 2.3                               |
| Response time (s)                | 15                                |
| RSD\%                           | 14                                |
| Time to stabilize the baseline current (min) | 150                                 |
glucose biosensors. This is probably due to the high biocompatibility of carbon nanotubes, already observed in other articles,\textsuperscript{[24,31]} which causes a retention of the enzyme activity overcoming the effect of the high noise current.

CONCLUSIONS

The present investigation describes for the first time the modification with PB of single walled carbon nanotubes and the assembling of paste electrodes. Voltammetric and amperometric parameters have been fully characterized and compared with those obtained with PB graphite. The PBNTPES resulted in low electrode kinetics that did not improve the analytical performance of the sensors towards hydrogen peroxide detection. At 0.0 V they exhibited in fact detection limits higher than that observed with graphite as electrode materials. Sensitivity was found to be in the same range of PB graphite paste electrodes.

PB nanotube electrodes showed a poorer electrochemical behavior and a lower sensitivity even in respect of what obtained with paste electrodes studied in a previous work using PB modified Glassy Carbon particles as electrode material.\textsuperscript{[20]} By now, in our opinion, glassy carbon particles have resulted to be, if compared with graphite and carbon nanotube, the best electrode material for assembling of PB based paste sensors.

Despite this, PBNTPES proved to possess a better stability at basic pH's. We have proposed a physical explanation for this behavior based on the peculiar structure of SWNT and on their unique resistance. This characteristic makes this electrodic material an attractive tool for the assembling of stable and robust sensors.

By loading on the paste mixture 5% of glucose oxidase, a glucose biosensor was also assembled and its analytical parameters evaluated. The possible use of different enzymes is at present in progress in our laboratory to verify the biocompatibility of carbon nanotubes for the assembling of enzyme based biosensors.

ACKNOWLEDGMENT

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