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

**Francesco Ricci,^{1,*} Aziz Amine,² Danila Moscone,¹
and Giuseppe Paleschi¹**

¹Dipartimento Di Scienze e Tecnologie Chimiche,
Università di Roma Tor Vergata, Via della Ricerca
Scientifica, Rome, Italy

²Faculté Des Sciences et Techniques de
Mohammedia, Morocco

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 7.4×10^{-6} M. They also proved to possess a strong stability even at

*Correspondence: Francesco Ricci, Dipartimento Di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, Via della Ricerca Scientifica, 00133 Rome, Italy; E-mail: francesco.ricci@uniroma2.it.

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

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

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INTRODUCTION

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54 Carbon nanotube is a novel carbon material discovered by Iijima in
55 1991^[1] and it has been found to have excellent electrode performances.^[2]
56 Single walled carbon nanotubes constitute a new form of molecular
57 diameter metallic semiconducting wire. Their high conductance, tensile
58 strength, and chemical stability have attracted much attention^[3] and
59 interest for many applications.^[4-8] Single wall carbon nanotubes, reported
60 for the first time in 1993 were firstly studied and characterized as electrode
61 material by two research groups.^[9-11] The electrodes were obtained casting
62 a film of single wall carbon nanotubes on a glassy carbon electrode and
63 were found to have an electrochemical activity towards some biomolecules
64 such as dopamine, epinephrine, and ascorbic acid.

65 In a recent article by our research group an extended study of the
66 electrochemical properties of carbon nanotubes paste electrodes has been
67 presented.^[12] Paste electrodes were constructed mixing single walled
68 carbon nanotubes with mineral oil. Performances of carbon nanotube
69 paste were evaluated studying the parameters of cyclic voltammetry
70 towards several electroactive molecules. Due to their high surface
71 area,^[13,14] single walled carbon nanotubes required a higher amount of
72 mineral oil (40%) in respect of what observed with graphite (34%)^[22] and
73 glassy carbon (20%)^[20] in the assembling of paste electrodes. Moreover,
74 electrodes showed an enhanced electroactivity towards hydrogen per-
75 oxide, dopamine, NADH oxidation in respect of classic graphite based
76 paste electrodes.^[12] This behavior together with the compatibility with
77 biological tissues makes the nanotubes suitable for the development
78 of new chemical sensors and biosensors. Nowadays the largest number
79 of biosensors are based on the use of oxidase enzymes that catalyze the
80 oxidation of a substrate with the consequence reduction of O₂ to hydro-
81 gen peroxide. A rapid, interference free, and precise detection of H₂O₂
82 (whose concentration is proportional to the substrate concentration)
83 is then always required to give an accurate measure of the enzymatic
84 substrate which represents in much cases the analyte. For this reason

85 Prussian Blue, a selective catalyst of the H_2O_2 reduction, has been fully
86 investigated during last decade.^[15–18] The modification of an electrode
87 surface with a layer of PB makes in fact it possible to measure H_2O_2 at
88 low applied potential (around 0.0 V) and to greatly decrease any electro-
89 chemical interference, as demonstrated in a previous article.^[19]

90 In this work, we report for the first time the modification of single
91 walled carbon nanotube powder with Prussian Blue and the successive
92 assembling of composite electrode for H_2O_2 detection. The electro-
93 chemical behavior of these probes has been fully characterized by
94 cyclic voltammetry in terms of surface charge, peak currents, formal
95 potential, and ΔE_p . Amperometric experiments have been carried out
96 to evaluate the H_2O_2 response and analytical parameters such as
97 detection limit, linear range, RSD, and sensitivity have been evaluated.
98 A comparison with PB modified graphite electrodes is also presented.
99 This is in our knowledge the first article reporting the direct modification
100 of carbon nanotubes with an electrochemical mediator. An application
101 obtained by simply loading aliquots of oxidase enzyme in the paste
102 mixture is also presented.

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EXPERIMENTAL

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Apparatus

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Reagents

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Single Wall Carbon Nanotubes (CNT) Carbolex (purity 50–70%)
and graphite particles (powder 1–2 μm) were purchased from Aldrich
(Steinheim, Germany). Mineral oil was obtained from Fluka (Buchs,
Switzerland). All chemicals from commercial source were of analytical

127 grade. All solutions were prepared with 0.05 M phosphate buffer +0.1 M
128 KCl, pH 7.4. Standard solutions were daily prepared in same buffer. For
129 pH effect studies borate buffer (0.05 M + KCl 0.1 M, pH 9.0 and pH 10)
130 was also used.

131 Glucose Oxidase (GOx) (EC 1.1.3.4, type VII from *Aspergillus Niger*,
132 185 units/mg), was Purchased from Sigma (St. Luis, MO).

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Preparation of CNT Modified With PB

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CNT Paste Electrodes Preparation

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Preparation of PBNTP Glucose Biosensor

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Biosensors were prepared by hand mixing 60 mg of PBNT/NT/
enzyme mixture with 40 mg of mineral oil and then mixed continuously

Modified Nanotube Paste Electrodes

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169 until a homogeneous paste was obtained. The PBNT/NT/enzyme mixture
170 had the following weight composition: 22.5% PB-NT, 72.5% NT and 5%
171 glucose oxidase. An aliquot of the final paste filled the tip of the electrode;
172 the remaining was kept in an aluminium foil at 4°C until reused.

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H₂O₂ and Enzymatic Substrate Measurements

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RESULTS AND DISCUSSION

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

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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.

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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 PBNTPE 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.

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Table 1a summarizes some of the electrochemical parameters
obtained from cyclic voltammetry with PBNTPEs and with PBgraphite

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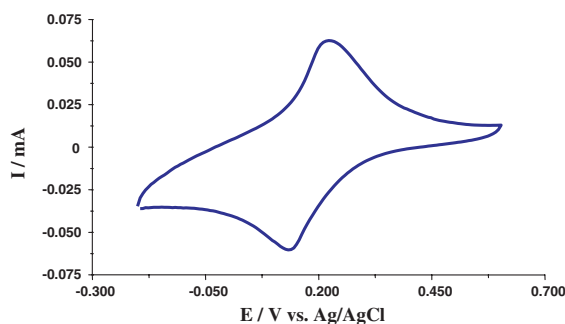


Figure 1. Cyclic voltammety of PBNTPE. Paste composition: 40% mineral oil, 60% PBNT. Phosphate buffer 0.05 M + KCl 0.1 M, pH 7.4. Scan rate 5 mV/s. Potential range -0.2 ; $+0.5$ V vs. Ag/AgCl.

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

Parameters	PBNTPEs	PBgraphitePEs
I_a (nA)	272	61
I_c (nA)	265	58
ΔE_p (mV)	228	124
Q_a/A (mC/cm ²)	21.7	1.3
Q_c/A (mC/cm ²)	20.8	1.4
E_f (mV)	170	185
I_{p_c}/I_{p_a}	0.97	0.95
$\partial(\log I_p)/\partial(\log \nu)_a$	0.65	0.56
$\partial(\log I_p)/\partial(\log \nu)_c$	0.47	0.49

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

According to the equation: $Q = nFA\Gamma$ 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 $\log(I_p)$ 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 ΔE_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 cm² while for PBNTPEs is about 218 mA/M cm². 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 1b. Comparison between PBNTPEs and PBgraphitePEs. 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.

Parameters	PBNTPEs	PBgraphitePEs
Linear range (M)	10^{-5} – 5×10^{-3}	5×10^{-7} – 5×10^{-3}
LOD (M)	1.0×10^{-5}	5×10^{-7}
Noise (nA)	50	5
Sensitivity (mA/M cm ²)	218	428
Response time (s)	5	15
Time to stabilize the baseline current (min)	80	150

295 detection limit of PBNTPEs towards hydrogen peroxide much higher
296 than that obtained with PB graphite paste electrode.

297 Taking into account the results obtained with the PB modified glassy
298 carbon paste electrodes,^[20] we decreased the total amount of PB in the
299 paste by mixing PBNT with unmodified NT before adding mineral oil. In
300 fact, in the case of glassy carbon paste electrodes, by doing this, a better
301 electrochemical behavior both in voltammetric and amperometric experi-
302 ments has in fact been observed due to the improved electrode kinetic.

303 The effect of the paste composition on the electrochemical behavior
304 of PBNTPEs was then evaluated studying the cyclic voltammetric param-
305 eters and the amperometric responses to H₂O₂. Considering these
306 results, the best paste composition has been selected and used for further
307 experiments. Paste was always made keeping the mineral oil percentage at
308 40% and 60% for the PBNT/NT mixture. The compositions of the
309 PBNT/NT mixture tested were as follows: 75/25, 50/50, 25/75, 10/90,
310 2/98, w/w. In Table 2 are reported the cyclic voltammetric parameters
311 obtained in phosphate buffer solution with all the mixtures prepared.
312 Anodic and cathodic peak currents are, as it was expected, proportional
313 to PB loading and increase with the increasing of the relative amount of
314 PBNT. Same behavior is observed for the charge density of the electrode
315 (Q). Amperometric parameters evaluated using Carbon Nanotube paste
316 electrodes obtained with a mixture of PBNT/NT are summarized in
317 Table 3. No improvement in sensitivity has been achieved in respect of
318 that obtained using only PBNT, but the presence of non modified nano-
319 tube powder brings a faster electrode kinetics with a decrease of the noise
320 current and of the detection limit. For this reason a paste obtained with a

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

328 % 329 PBNT/NT	I _a (nA)	I _c (nA)	ΔE _p (mV)	Q _a /A (mC/cm ²)	E _{1/2}
331 100	272	265	228	21.7	170
332 75	230	199	203	17.5	168
333 50	135	122	179	10.8	167
334 25	73	68	119	5.4	170
335 10	18	18	102	1.4	172
336 2	10	10	125	0.8	177

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.

% PBNT/NT	I (H ₂ O ₂ 10 ⁻⁵ M) (nA)	I (H ₂ O ₂ 10 ⁻⁴ M) (nA)	Noise (nA)	LOD (M)	Sensitivity (mA/M cm ²)	Time to stabilize the baseline current (min)
100	90	1500	50	1.0 × 10 ⁻⁵	214	80
75	60	700	20	8.5 × 10 ⁻⁶	100	65
50	45	525	20	1.1 × 10 ⁻⁵	75	70
25	37	408	10	7.4 × 10 ⁻⁶	58	40
10	16	172	5	9.0 × 10 ⁻⁶	24	40
2	6	66	2	9.2 × 10 ⁻⁶	9.4	20

337 mixture of PBNT/NT 25/75 w/w was selected and used for further
338 experiments. Table 4 summarizes the analytical characteristics of this
339 PBNTPE towards H₂O₂ reduction: i.e., detection limit (reported as two
340 times the background noise), linearity range, sensitivity variations
341 (related to the slope variation of calibration curves continuously carried
342 out for 8 h), and reproducibility (reported as the RSD of the current
343 values due to the H₂O₂ reduction by 4 different sensors obtained from
344 the same paste matrix). Response time, expressed as the time needed to
345 reach 90% of the steady state current, and the time necessary to obtain a
346 stable baseline current, are also reported, while in Fig. 2 are shown some
347 original amperometric recordings.

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

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Stability of PBNTPEs

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

376 PBNTPEs were then studied at basic pHs in order to evaluate
377 any possible improvement of the pH stability. Sensors were left in a
378 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.

H ₂ O ₂ probe	LOD (M)	Linear range (M)	Sensitivity (mA/M cm ²)	RSD%	Response time (s)	Time to stabilize the baseline current (min)
PBNTPEs	7.4×10^{-6}	10^{-5} – 5×10^{-3}	58	17	5	40
PBGraphitePEs	5×10^{-7}	5×10^{-7} – 5×10^{-3}	428	14	15	150

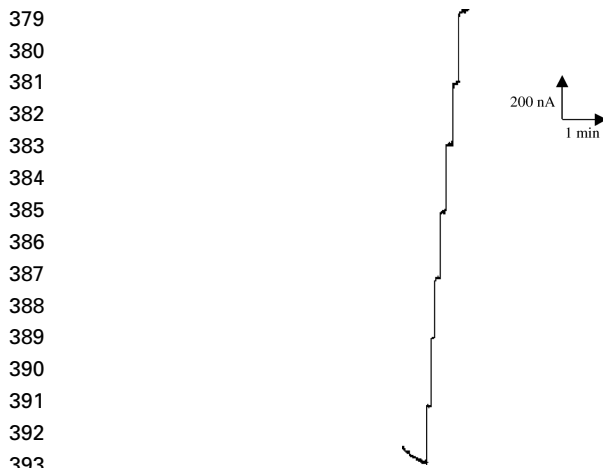


Figure 2. Amperometric responses towards hydrogen peroxide. Loadings of 10^{-4} M of hydrogen peroxide. Batch measurements in 20 mL phosphate buffer 0.05 M + KCl 0.1 M, pH 7.4. Applied potential 0.0 V vs. Ag/AgCl. PBNTPEs paste composition: 40% mineral oil, 60% PBNT/NT mixture (25% PBNT-75% NT).

measurements of fixed concentration of hydrogen peroxide (10^{-4} M) were performed every two hours. During the night sensors were kept under stirring, with the applied potential, in a 5×10^{-4} 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

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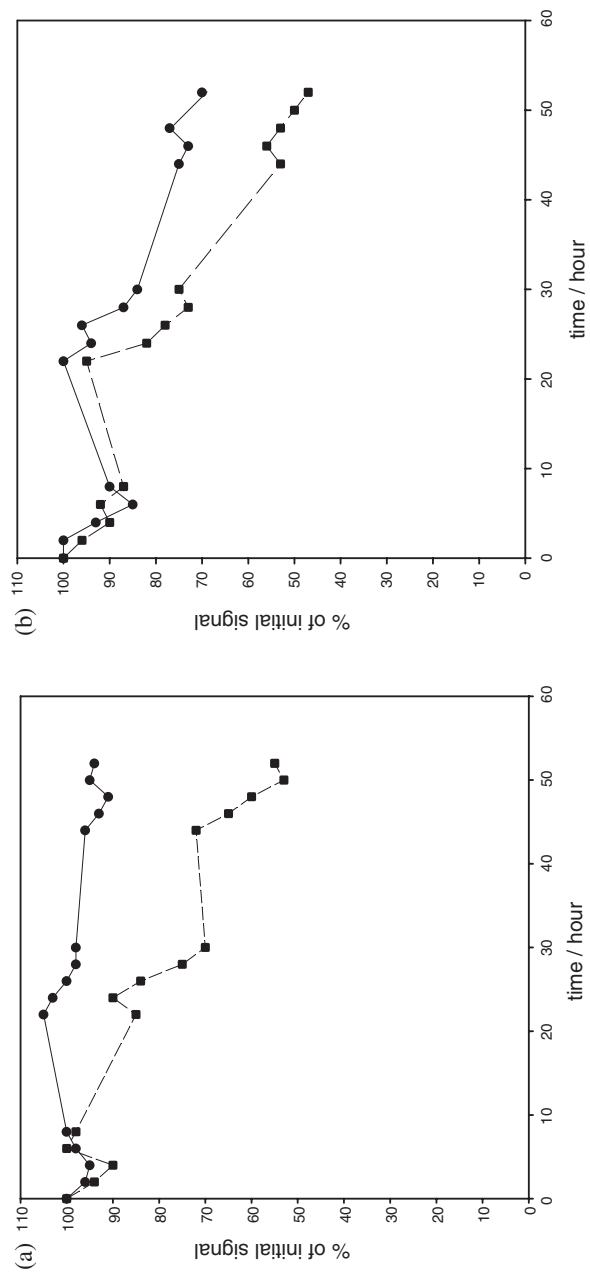


Figure 3. Stability studies of PBNTPEs. Continuous amperometric measurements of hydrogen peroxide. (a) Borate buffer 0.05 M + KCl 0.1 M, pH 9. (b) Borate buffer 0.05 M + KCl 0.1 M, pH 10. ● PBNTPEs: paste composition: 40% mineral oil, 60% PBNT/NT mixture (25%PBNT-75% NT). ■ PBGraphitePEs: paste composition: 66% mineral oil, 34% PBGraphite.

Table 5. Amperometric parameters towards glucose. Amperometric parameters, batch measurements in 20 mL phosphate buffer 0.05 M + KCl 0.1 M, pH 6.0. Applied potential 0.0 V vs. Ag/AgCl, PBNTPEs +5% glucose oxidase, PBgraphitePEs +5% glucose oxidase (see text for details).

	PB-NT glucose biosensor	PB-graphite glucose biosensor
Linear range (M)	10^{-4} – 5×10^{-2}	10^{-4} – 2×10^{-2}
LOD (M)	7×10^{-5}	10^{-4}
Sensitivity (mA/M cm ²)	3.3	2.3
Response time (s)	5	15
RSD%	18	14
Time to stabilize the baseline current (min)	45	150

that tend to assemble in ropes of nanotubes.^[30] Probably, during PB modification, intercalation of PB crystals, that according to Keggin and Miles^[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 H₂O₂ 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 PBNTPE 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 7×10^{-5} M, the linear range was up to 10^{-2} M and the sensitivity was 3.3 mA/M cm². A comparison with what as obtained using graphite as electrodic material shows the better behavior of the PB nanotube

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463 glucose biosensors. This is probably due to the high biocompatibility of
464 carbon nanotubes, already observed in other articles,^[24,31] which causes a
465 retention of the enzyme activity overcoming the effect of the high noise
466 current.

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CONCLUSIONS

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

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

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

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

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ACKNOWLEDGMENT

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