

Carbon Nanotube–Ionic Liquid Composite Sensors and Biosensors

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A new composite electrode has been fabricated using multiwall carbon nanotubes (MWCNT) and the ionic liquid *n*-octylpyridinium hexafluorophosphate (OPFP). This electrode shows very attractive electrochemical performances compared to other conventional electrodes using graphite and mineral oil, notably improved sensitivity and stability. One major advantage of this electrode compared to other electrodes using carbon nanotubes and other ionic liquids is its extremely low capacitance and background currents. A 10% (w/w) loading of MWCNT was selected as the optimal composition based on voltammetric results, as well as the stability of the background response in solution. The new composite electrode showed good activity toward hydrogen peroxide and NADH, with the possibility of fabricating a sensitive biosensor for glucose and alcohol using glucose oxidase and alcohol dehydrogenase, respectively, by simply incorporating the specific enzyme within the composite matrix. The marked electrode stability and antifouling features toward NADH oxidation was much higher for this composite compared to a bare glassy carbon electrode. While a loading of 2% MWCNT showed very poor electrochemical behavior, a large enhancement was observed upon gentle heating to 70 °C, which gave a response similar to the optimum composition of 10%. The ease of preparation, low background current, high sensitivity, stability, and small loading of nanotubes using this composite can create new novel avenues and applications for fabricating robust sensors and biosensors for many important species.

Carbon nanotubes (CNTs) are considered an important group of nanomaterials with attractive electronic, chemical, and mechanical properties.^{1,2} Their unique properties make them extremely attractive for fabricating chemical sensors, in general,

and electrochemical ones, in particular.³ CNTs have been shown to impart good responses and minimization of surface fouling in electrochemical devices. They have a good electrochemical behavior toward catecholamine neurotransmitters,⁴ cytochrome c,⁵ ascorbic acid,⁶ NADH,⁷ and hydrazine compounds.⁸ The ability of carbon nanotubes to facilitate the electron-transfer reactions of NADH and hydrogen peroxide suggests great promise for dehydrogenase and oxidase based amperometric biosensors. Another important class of materials is ionic liquids (ILs). Because of their high stability, high electrical conductivity, and very low vapor pressure, ILs hold a great promise for green chemistry applications in general and for electrochemical applications in particular.^{9–11} Room temperature ionic liquids (RTILs) can be defined as liquid electrolytes made entirely of ions which have melting points below 100 °C.¹² ILs are basically made of an asymmetric heterocyclic cation such as *N,N*-dialkyl substituted imidazolium ions, and a small anion like tetrafluoroborate (BF₄[−]), hexafluorophosphate (PF₆[−]), or bis(trifluoromethylsulfonyl)imide (NTf₂).¹⁰ Electrochemical sensors and biosensors prepared using ILs for analytical purposes have been reported in a number of studies^{13–18} for detection of different types of

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compounds such as ascorbic acid, uric acid, phenols, dopamine, hydrogen peroxide, and glucose.

The use of electrodes prepared from carbon nanotubes and ILs have been reported in a number of articles. One way is to modify the surface of a glassy carbon or graphite electrode with a dispersion of carbon nanotubes/IL or carbon nanotubes/IL/polymer in a suitable solvent.^{19–22} This type of modification was useful in improving the sensitivity of measurement and lowering the detection potential to minimize the effect of interferences for a number of analytes such as NADH, and chloramphenicol,^{19,20} for thermal stabilization of enzymes such as laccase,²¹ and for direct protein electrochemistry.²² Another way of fabricating carbon nanotubes/IL electrodes is by layer-by-layer self-assembly taking advantage of the electrostatic adsorption between carbon nanotubes, ILs, and proteins such as cytochrome c.²³ Preparation of carbon nanotubes/IL pastes and composites by direct mixing of the nanotubes with a suitable IL (either solid or liquid at room temperature) has been limited by the very high background currents which would limit monitoring the analytical faradaic current and hence limit the use of such useful combination. The large background currents are probably due to a combination of the large electroactive surface area imparted by using carbon nanotubes and the ordering of the cations and anions comprising the IL in response to a change in the applied potential at the electrode-electrolyte interface. One approach to overcome this problem is as proposed by Compton's group who showed that the increased capacitive charging currents can be reduced by the use of steady state linear sweep voltammetry at rotating disk electrodes.²⁴ The enhanced mass transport under hydrodynamic conditions improved the ratio of analytical-to-charging currents and hence improved the sensitivity of measurement by such electrodes. Recently, Wang et al. have shown that it is possible to fabricate a graphite/IL paste biosensor with low background current via mixing the paste matrix with paraffin oil, "a non-conductive binder", which tends to decrease the background current and hence improve the sensor response.¹⁸ Several heme proteins were evaluated using this paste for the analysis of hydrogen peroxide including myoglobin, hemoglobin, and horseradish peroxidase. Another type of graphite/IL composite electrode which showed low background currents was demonstrated by the use of the IL "*n*-octyl-pyridinium hexafluorophosphate" that is solid at room temperature (melting point 65 °C).¹⁴ This new composite material showed very improved signal to background current for the detection of different analytes such as ascorbic acid and NADH. The reason behind this low background current using this IL is not fully understood and needs further investigation.

In the present paper we show that carbon nanotubes/IL composite electrodes with very low background currents can be fabricated using *n*-octyl-pyridinium hexafluorophosphate as the binder and the nanotubes as the conductive material. This new

composite has several advantages compared to the one prepared previously using graphite and other traditional CNT paste and composite electrodes, where it offers improved sensitivities toward a number of compounds, and at the same time lower detection potentials using very small amount of CNTs. The interaction between the nanotubes and the IL results in the formation of a robust composite electrode with no need for heating the electrode before measurement to lower the background current as previously shown.¹⁴ Other features of this composite material include but are not limited to the feasibility of bulk modification with biological recognition elements such as enzymes for selectivity enhancement. Finally it is also possible to use the unique nanotubes surface functionality for stable immobilization of enzymes and other bio-recognition elements based on the need for a specific application.

EXPERIMENTAL SECTION

Apparatus. Amperometric and cyclic voltammetric measurements were performed using a computer controlled μ -Autolab II potentiostat (Ecochemie, The Netherlands) with a three-electrode configuration. The working electrode, the reference electrode (a saturated calomel electrode, SCE, Radiometer, Copenhagen, Denmark), and the auxiliary counter electrode (a bright platinum wire) were inserted into the 20 mL glass cell (home made) through holes in its Teflon cover. A magnetic stirrer provided the convective transport during the amperometric measurement. Cyclic voltammetry experiments were carried out under quiescent conditions. SEM images were obtained with the JEOL JSM840F unit with a field emission gun as electron source and an acceleration voltage of 5 KV.

Chemicals and Reagents. Water was purified either by double distillation or by using an Elix UV-10 system. All analytical solutions were prepared from double-distilled water. All other solvents were used as supplied (analytical or HPLC grade) without prior purification. Potassium dihydrogen phosphate, dipotassium hydrogen phosphate, potassium ferricyanide, ascorbic acid, hydrogen peroxide, 1-butyl-3-methyl-imidazolium hexafluorophosphate (BMIFP), mineral oil, Teflon powder, and synthetic graphite powder consisting of irregularly shaped microparticles 2–20 μ m in diameter were purchased from Aldrich. Glucose oxidase (GOx) (EC 1.1.3.4, type X-S, *Aspergillus niger*, 234,900 U/g), β -D-(+) glucose (97%), and NADH were obtained from Sigma (Dorset, England). Multiwall carbon nanotubes (MWCNT) (ID 30 ± 10 nm, 5–20 μ m long, 95% pure) were obtained from NanoLab (Brighton, MA). The IL *n*-Octyl-pyridinium-hexafluorophosphate was kindly prepared by the Chemistry Research Laboratory at Oxford University and by the Chemistry Department at the American University of Sharjah. The procedure of synthesis is explained below. Melting points were recorded on a Gallenkamp hot stage apparatus and are uncorrected.

The IL 1-*n*-octylpyridinium hexafluorophosphate was prepared according to a modified version of the procedure described by Safavi et al.¹⁴

In brief, pyridine (0.89 mL, 11.0 mmol, 1.0 equiv) was added to neat 1-iodooctane (2.00 mL, 11.0 mmol, 1.0 equiv) and the resulting mixture was stirred at room temperature for 72 h. Acetonitrile (0.5 mL) was then added to the residue, and the resulting solution was washed with diethylether (Et₂O) (3 $\times$ 5 mL). The Et₂O washings were discarded, and the product was dried in

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vacuo at room temperature to give 1-*n*-octylpyridinium iodide as clear yellow viscous oil (3.50 g, quant) which was used without further purification.

To a stirred solution of 1-*n*-octylpyridinium iodide (1.00 g, 3.10 mmol, 1.0 equiv) in H₂O (1.5 mL) at room temperature was added a solution of ammonium hexafluorophosphate (0.51 g, 3.10 mmol, 1.0 equiv) in H₂O (1.5 mL) dropwise. After stirring at room temperature for 2 h, the resulting white precipitate was isolated by filtration and washed with H₂O (3 × 5 mL) followed by Et₂O (2 × 5 mL) and dried in vacuo at room temperature for 24 h to give 1-*n*-octylpyridinium hexafluorophosphate (OPFP) as a white powder (0.91 g, 87%) with a melting point $T_m = 64\text{--}65\text{ }^{\circ}\text{C}$ ($T_m = 65\text{ }^{\circ}\text{C}$).¹⁴

Electrode Fabrication. The required amount of IL was mixed using pestle and mortar with the needed amount of MWCNTs for 10 min. The specific loading percentage was expressed as weight percentage. Although this IL is a solid powder at room temperature, it has a sticky nature, so it tends to interact strongly with the MWCNT and forms a very mechanically stable solid composite upon mixing. The surface of the composite can be polished very well and shows features similar to solid surfaces. The glucose biosensor was fabricated using 1 mg of glucose oxidase for every 100 mg of the composite material. The composite was prepared first and then the enzyme was added, and the paste was mixed for another 10 min. Exactly 9.4 mm³ of the resulting paste was then packed firmly into the electrode cavity (2 mm diameter and 3 mm depth) of a glass sleeve. Electrical contact was established via a copper wire. The paste surface was smoothed on a weighing dish and rinsed carefully with double distilled water prior to each measurement.

Procedure. Measurements were carried out in a phosphate buffer (0.05 M, pH 7.5) supporting electrolyte medium for amperometric and cyclic voltammetry measurements. Amperometric detection was made under forced convection by stirring the solution using a magnetic stirrer, whereas quiescent conditions were used for cyclic voltammetry experiments. In the former the desired working potential was applied, and transient currents were allowed to decay to a steady-state value. All measurements were performed at room temperature.

RESULTS AND DISCUSSION

To investigate the properties of this new composite electrode made of MWCNTs and OPFP and to select the optimum composition for subsequent work, it is important to study the electrochemical properties of different electrodes made of different MWCNTs loadings. Figure 1, compares the effect of different MWCNTs loadings on the cyclic voltammetric responses for 5 mM potassium ferricyanide solution (Figure 1A) and 0.1 M potassium chloride blank solution (Figure 1B). Using a 40% loading, the electrode had a very large background current as can be seen in Figure 1Ba. This large background current limited the resolution of the analytical faradaic current toward potassium ferricyanide and resulted in small anodic and cathodic currents as shown in Figure 1Aa. By decreasing the loading of the MWCNTs, the background currents decreased and the corresponding analytical faradaic currents increased as shown in Figures 1A and 1B down to 10% loading. Going below 10%, the background currents decreased further, and the same was true for the analytical signals. We can also notice that the decrease in

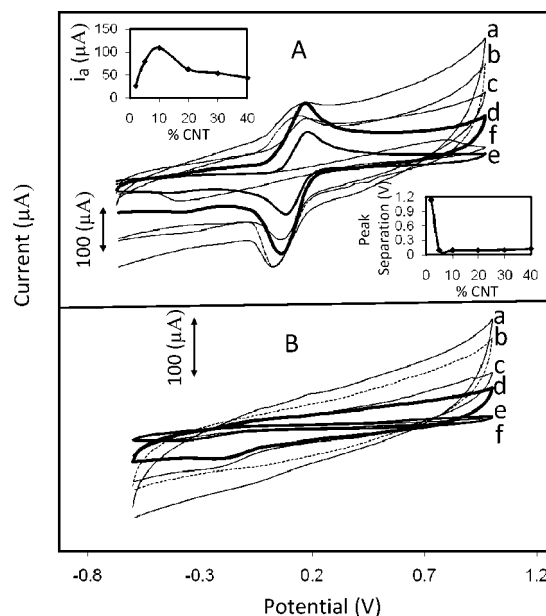


Figure 1. Cyclic voltammograms for 5 mM potassium ferricyanide (A) and 0.1 M KCl blank solution (B) using MWCNT/OPFP composite with different ratios: 40/60 (a), 30/70 (b), 20/80 (c), 10/90 (d), 5/95 (e), and 2/98 (f) respectively. Supporting electrolyte, 0.1 M potassium chloride, and scan rate 100 mV/s.

currents for compositions less than 10% resulted in much distorted voltammograms as clearly seen for the 2% composition in Figure 1Af. In addition, composites with 20% MWCNTs and higher were unstable in solution and resulted in a continuous increase in background current with repetitive cycling. This might tentatively be attributed to the low mechanical stability of the composite when it contains proportionally more nanotubes compared to the binder. The increase in background currents with increased loadings of MWCNTs can be attributed to the increase in surface area of the composite and to the increase in the double-layer capacitance and charge build-up at the double-layer interface. By decreasing the loading of the MWCNTs and having more of the OPFP IL, better filling between the nanotubes was reached and hence higher mechanical stability and lower background currents can be achieved. Further optimization of the loading was based on the comparison of anodic currents and peaks separation in response to 5 mM additions of potassium ferricyanide as shown in the insets of Figure 1A. As shown in the upper left inset, 10% MWCNT loading gave the highest anodic current in comparison to other loadings. At the same time, the lowest peak separation was obtained with loadings of 5, 10, and 20% MWCNTs. Loadings greater than 20% showed smaller increase in peak separation, while loadings less than 5% showed a dramatic increase in peak separation. On the basis of the above optimization, the 10% MWCNT loading was selected for subsequent work.

To exemplify the unique features and properties of this composite and to further show that the unique performance of this composite is not only due to the nanotubes but to the mixture of the nanotubes and the OPFP IL, it was necessary to compare the performance of this electrode with other electrodes having the same loading of MWCNTs but with other binders. To have a reasonable judgment, another IL “BMIFP” that is liquid at room temperature, a non-conductive solid binder “Teflon”, and a non-conductive liquid binder “mineral oil” were chosen for this

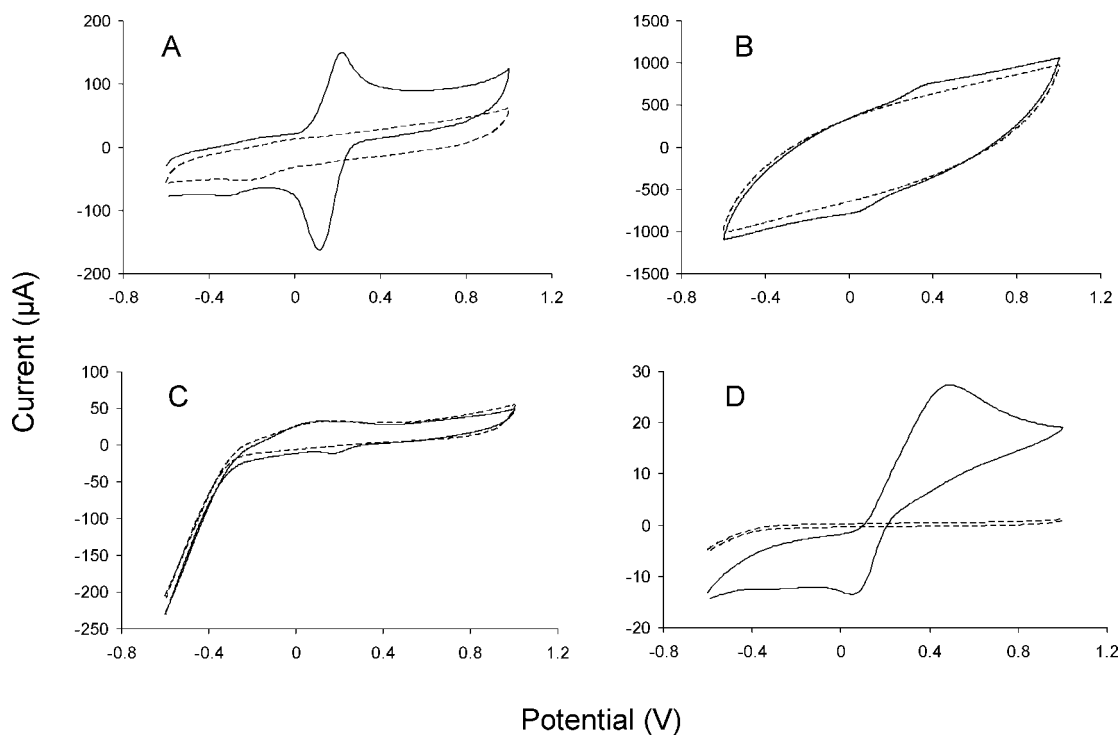


Figure 2. Cyclic voltammograms for 5 mM potassium ferricyanide using 10% MWCNT and 90% of different binders; OPFP IL (A), BMIFP IL (B), Teflon (C), and Mineral oil (D). Other conditions as in Figure 1.

comparison which is shown in Figure 2 using 5 mM of potassium ferricyanide.

The new composite is superior over the BMIFP based electrode in terms of having a much lower background response and better signal-to-background ratio as shown in Figures 2A and 2B. The exact reason behind this large background current for the BMIFP based composite compared to that for the OPFP based one is not fully understood. However, the difference in physical states (liquid to solid) might imply an increase in ion mobility which would explain the higher charging currents. Another possibility is the difference in chemical structure where the BMIFP IL is more hydrophilic relative to the OPFP which would increase the charging currents because of the increase in double layer capacitance as a result of stronger interaction with ions in solution and water molecules. Musameh et al. have lately shown that the BMIFP IL can be successfully used with graphite to make an IL based paste electrode with attractive performance.²⁵ However, even when graphite replaced CNTs in that paste, the paste was still showing high background currents presumably because of the BMIFP IL. Comparing Figure 2A with Figure 2C involving the use of Teflon powder as a binder, we can see clearly the advantage of this composite over Teflon binder where there is no signal at all indicating the very poor conductivity of the Teflon based composite even in the presence of 10% MWCNTs. Wang et al. have shown the unique features of the CNT/Teflon composite electrodes, but with loadings higher than 50%, which is not the case here.^{26,25} Finally, comparing our composite with a traditional paste using mineral oil and MWCNTs (Figure 2D), the new composite electrode has about a 10-fold improvement in signal compared to the mineral oil based electrode. This reflects

permeation of the MWCNTs by partial covering with mineral oil. This would lead to the partial insulation of the CNTs by the non-conductive mineral oil binder.

In addition, there was a smaller peak to peak separation (100 mV for MWCNT/OPFP vs 450 mV for the MWCNT/Moil) and anodic-to-cathodic currents ratio closer to unity (0.98 for MWCNT/OPFP vs 2.1 for the MWCNT/Moil).

Additional investigation of the MWCNT/OPFP composite electrode was carried out using other electroactive probes comprising different compounds such as ascorbic acid, NADH, and hydrogen peroxide in addition to potassium ferricyanide as shown in Figure 3 (solid bold line). Two conventional electrodes were used to compare with the new composite using the above probes, the first was a MWCNT/Moil paste and the other was a Graphite/OPFP each with 10% carbon loading as shown in Figure 3 (dashed line) and (solid regular line), respectively. Using potassium ferricyanide (Figure 3A) a comparison with the mineral oil based paste was already discussed in Figure 2. Using 10% graphite and 90% OPFP, the electrode was not responsive to potassium ferricyanide over the whole potential range. The same was observed for the 10% graphite with all other probes as shown in Figures 3A to 3D indicating that a composite made of only 10% graphite is actually non-conductive though it has 90% of the conductive OPFP IL. This observation reflects the superior performance of carbon nanotubes over graphite as a conductive material. In the case of ascorbic acid (Figure 3B), a lowering of overvoltage and signal amplification is observed at the MWCNT/OPFP electrode compared to the conventional mineral oil based electrode. The anodic peak potential for ascorbic acid is around 0.00 mV and the anodic current is about 190 μ A at the MWCNT/OPFP electrode, compared to 480 mV and 61 μ A at the mineral oil paste electrode. Similar behavior was also observed for NADH

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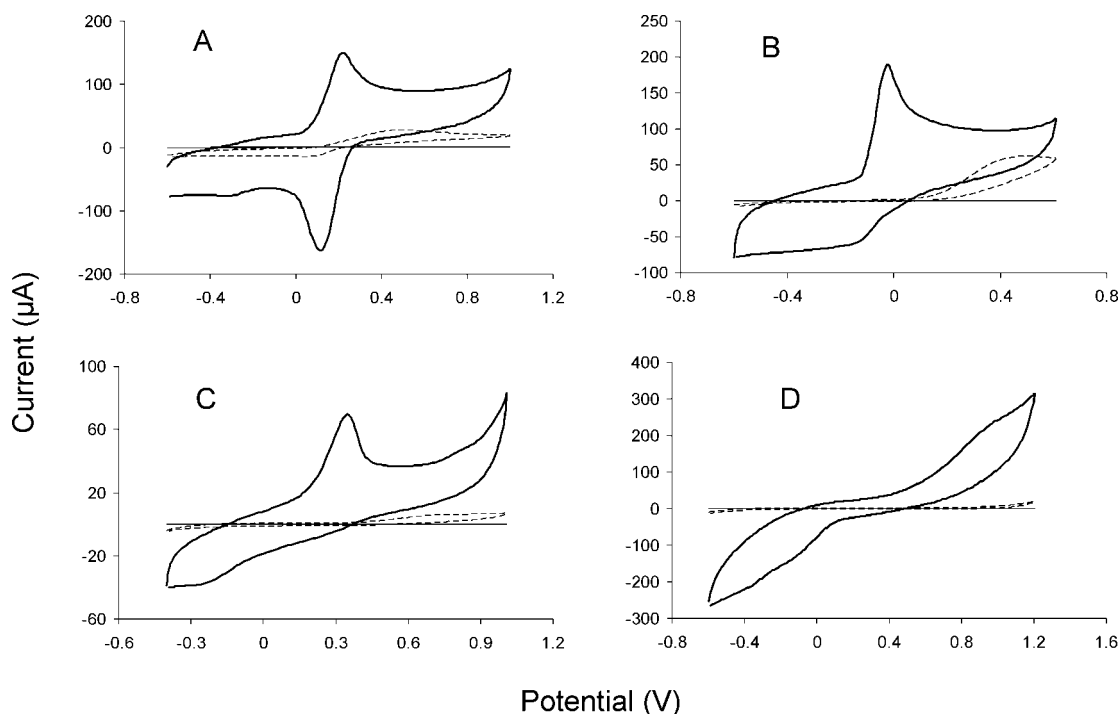


Figure 3. Cyclic voltammograms using MWCNT/OPFP (solid bold line), MWCNT/Mineral oil (dashed line), and Graphite/OPFP (solid regular line) for 5 mM Potassium Ferricyanide (A), Ascorbic acid (B), NADH (C), and Hydrogen peroxide (D). Supporting electrolyte for (A) is 0.1 M potassium chloride, and for (B), (C), and (D) is 0.05 M phosphate buffer, pH 7.4. Scan rate 100 mV/s. Carbon loading 10%.

(Figure 3C) with anodic peak potential around 350 mV and an anodic current around 70 μA at the MWCNT/OPFP electrode, compared to 850 mV and 6.0 μA at the mineral oil conventional electrode. Finally, using hydrogen peroxide (Figure 3D), the redox activity is only observed at potentials above 800 mV using the conventional mineral oil paste electrode. The overvoltage for the oxidation process is greatly lowered at the MWCNT/OPFP electrode surface, with oxidation starting around 350 mV. The oxidation for the MWCNT/OPFP electrode is about 20 times larger than that for the mineral oil counterpart. This improved lowering of overvoltages and signal amplification at the MWCNT/OPFP composite using several probes reflects the effective unpassivated MWCNT areas presented to solution compared to other electrodes. This indicates that combining the CNTs even at small loadings with the OPFP IL would not impart the catalytic properties of neither the CNTs nor the OPFP IL which is not the case with other binders such as the mineral oil or other carbons such as the graphite. SEM microscopy was employed to gain insights into the nature of the new MWCNT/OPFP composite.

To investigate the nature of the new MWCNT/OPFP composite, SEM images were taken for this new composite (see Figure 4 panel A) along with three different composites and pastes namely, MWCNT/BMIFP, MWCNT/Moil, and Graphite/OPFP electrode surfaces (Figure 4 panels B, C, and D, respectively). It can be seen that the electrodes prepared using a liquid binder (panels B and C) have clearly different morphology compared to the ones prepared using solid binder (OPFP) (panels A and D). The MWCNT/OPFP and Graphite/OPFP surfaces are characterized with uniform and homogeneous surfaces with multilayer surface distribution appearing in the graphite based surface reflecting the arrangement of graphene sheets in graphite. This layer distribution was not shown in the MWCNT/OPFP surface indicating better and stronger interaction between the nanotubes

and the OPFP IL. When the solid binder was replaced with a liquid binder, more irregular distribution of microsized carbon particles were observed within the paste matrix. The degree of homogeneity was better when BMIFP IL binder was used compared to the mineral oil indicating a better interaction between the nanotubes and the ILs regardless of their physical state.

To optimize the measurement conditions under amperometry for different probes using this new composite material, hydrodynamic voltammograms (HDV) for 5 mM hydrogen peroxide (Figure 5A) and 5 mM NADH (Figure 5B) at various composites namely, MWCNT/OPFP (curve a), MWCNT/Moil (curve b), and graphite/OPFP (curve c) composite electrodes with 10% carbon loading were investigated. It is clear that no redox activity is observed for either analyte at the MWCNT/Moil and graphite/OPFP electrodes using potentials lower than 0.8 (Figure 5A) and 0.4 V (Figure 5B). A small gradual increase of the response is observed at higher potentials only at the MWCNT/Moil electrode while no response is recorded for the graphite/OPFP electrode in the potential window from -0.4 V to 1.0 V. On the other hand, the MWCNT/OPFP electrode responds favorably to both analytes over the entire -0.10 to 1.00 V potential range. Appreciable oxidation and reduction currents, starting around $+0.20$ V, are thus observed for hydrogen peroxide. Similarly, the anodic signal of NADH increases rapidly between -0.10 and 0.4 V and levels off at higher potentials. Oxidation of NADH at the MWCNT/OPFP surface starts at low potential as -0.10 V and increases rapidly to 0.40 V and then slowly to 0.5 V where it levels off thereafter. The HDV for NADH at the MWCNT/OPFP surface displays two waves, the first one with a half-wave potential around -0.05 V, and a limiting current plateau starting around 0.0 V, and another wave with a half-wave potential around 0.30 V and a limiting current plateau starting around 0.50 V. The substantial

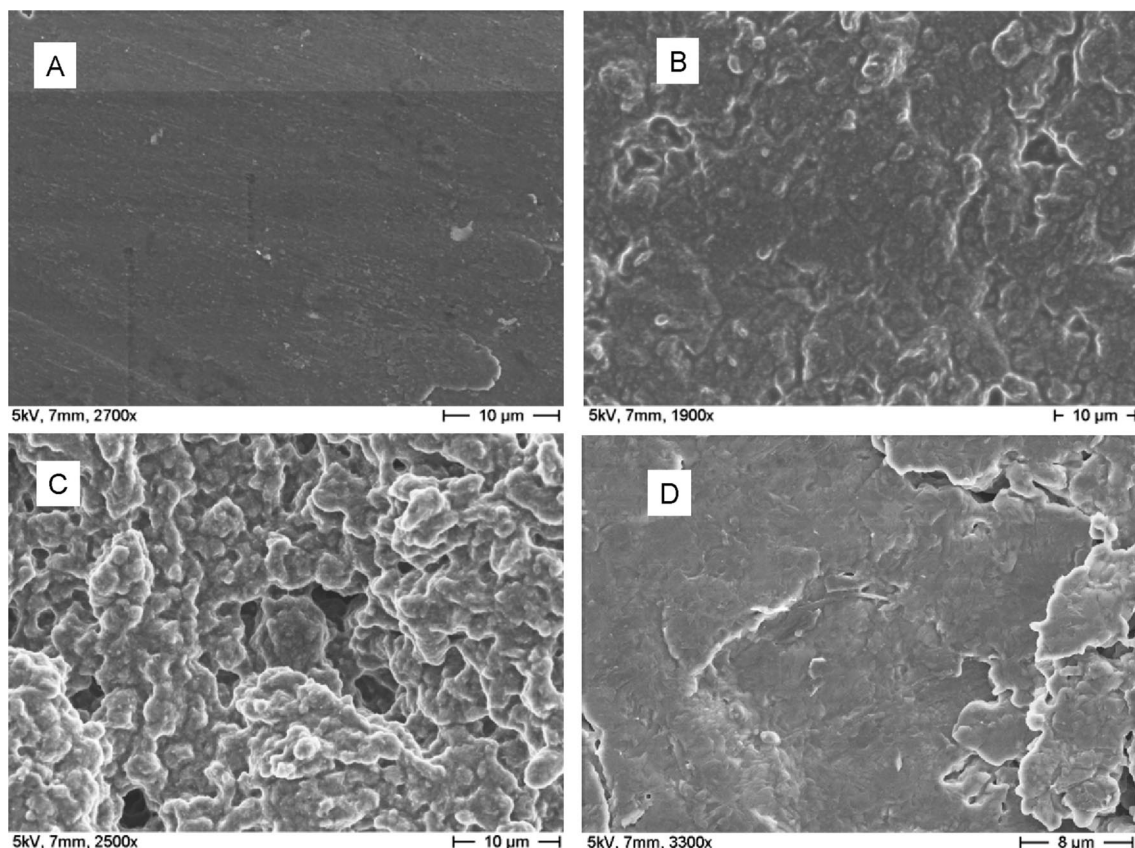


Figure 4. SEM images of the surfaces of the MWCNT/OPFP (A), MWCNT/BMIFP (B), MWCNT/Mineral oil (C), and Graphite/OPFP (D) electrodes. Accelerating voltage, 5 kV; carbon/binder composition ratio, 10:90 wt %.

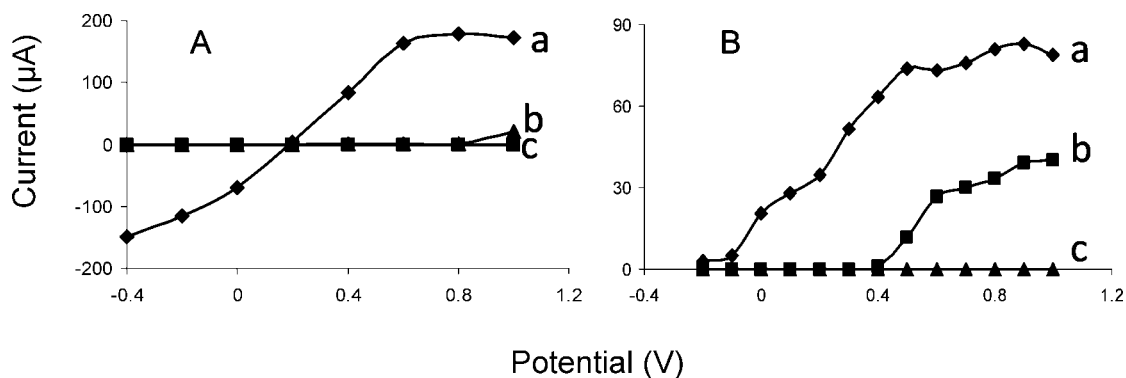


Figure 5. Hydrodynamic voltammograms for 5 mM hydrogen peroxide (A) and 5 mM NADH (B) using the MWCNT/OPFP (a), the MWCNT/Mineral oil (b), and the Graphite/OPFP (c) electrodes. Supporting electrolyte, phosphate buffer (0.05 M, pH 7.4); carbon loading 10%; stirring rate, ~400 rpm.

lowering of the detection potential observed for both analytes at the MWCNT/OPFP-based composite is coupled to significantly larger current signals. Overall, the data of Figure 5 indicate that the association of only 10% MWCNT with the OPFP binder can offer an improved surface which is not possible in the case of graphite.

The enhanced response at the MWCNT/OPFP surface offers the possibility for low-potential amperometric measurements of hydrogen peroxide and NADH. Figure 6 compares the amperometric responses at the MWCNT/OPFP (a), MWCNT/MoIl (b), and graphite/OPFP (c) electrodes recorded against successive additions of 0.2 mM hydrogen peroxide at +0.50 V (Figure 6A) and 1.0 mM NADH at +0.3 V (Figure

6B). In agreement with the voltammetric data, the MWCNT/MoIl and graphite/OPFP electrodes are not responsive to these concentration changes using this low-detection potential. In contrast, the MWCNT/OPFP electrode responds very rapidly to the changes in the level of hydrogen peroxide and NADH, producing steady-state signals within 4–6 s.

The ability of this composite toward sensitive and low-potential measurements of hydrogen peroxide and NADH along with minimal surface fouling makes the MWCNT/OPFP extremely attractive for amperometric biosensing in connection with oxidase or dehydrogenase enzymes. The new MWCNT/OPFP-based composite easily allows convenient and controlled incorporation of the desired enzyme (and its cofactor or

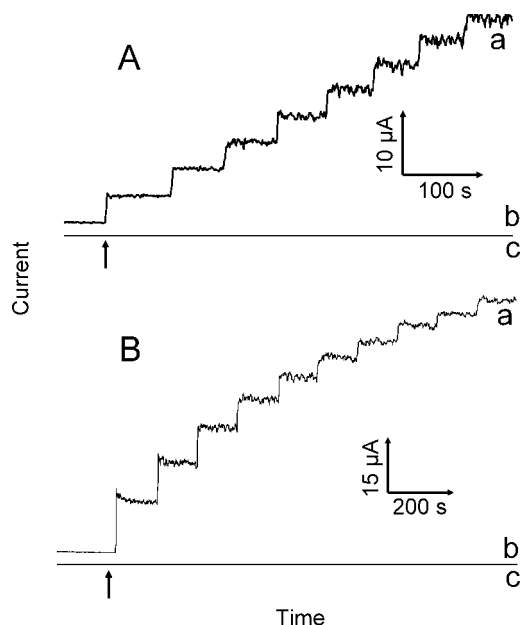


Figure 6. Current–time recordings obtained at the MWCNT/OPFP (a), the MWCNT/Mineral oil (b), and the Graphite/OPFP (c) composite electrodes upon increasing the concentration of hydrogen peroxide (A) and NADH (B) in steps of 0.2 and 1.0 mM, respectively. Operating potentials, +0.5 and 0.3 V, respectively; other conditions, as in Figure 5.

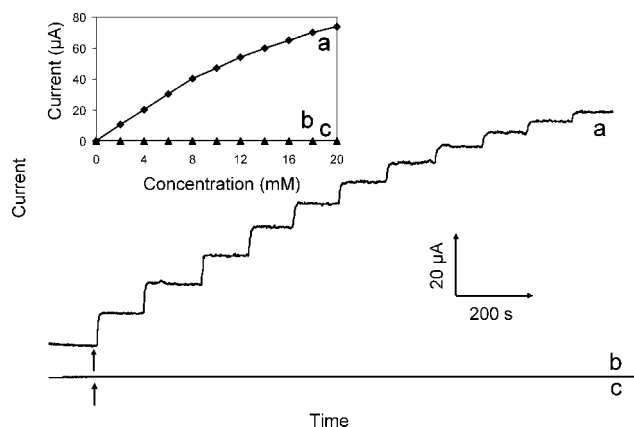


Figure 7. Current–time recordings for successive 2 mM additions of glucose at the MWCNT/OPFP (a), the MWCNT/Mineral oil (b), and the Graphite/OPFP (c) composite electrodes measured at +0.9 V. Electrode composition, 10:90:1 wt % carbon/binder/GOx. Other conditions, as in Figure 5.

mediator), in a manner analogous to other bulk-modified bioelectrodes.^{26–29} With this composite, it is possible to incorporate glucose oxidase by simple addition and mixing with the composite matrix to generate an efficient glucose biosensor as shown and described below in Figure 7, which compares the amperometric response to successive additions of 2 mM glucose at the MWCNT/OPFP/GOx (a), MWCNT/Moil/GOx (b), and the graphite/OPFP/GOx (c) electrodes with 10% carbon loading using an operating potential of +0.9 V, along with the resulting calibration plot (inset). As evident from the

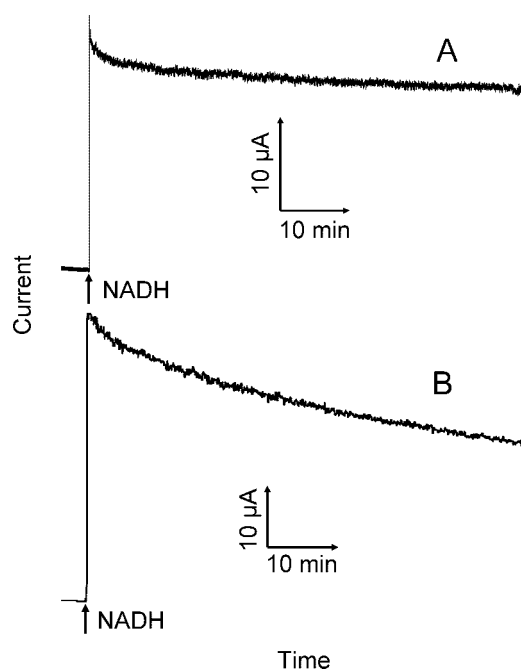


Figure 8. Stability of the response to 5 mM NADH using the MWCNT/OPFP (A) and bare glassy carbon (B) electrodes. Operating potentials, +0.30 V and +0.5 V, respectively. Other conditions, as in Figure 5.

hydrodynamic data (Figure 5), the graphite/OPFP/GOx was not showing any response toward the addition of glucose. On the other hand the MWCNT/Moil/GOx showed a very small response to glucose (3.0 nA/mM), but this was completely negligible when compared to the MWCNT/OPFP/GOx (5.0 $\mu\text{A}/\text{mM}$) as shown in Figure 7. The MWCNT/OPFP/GOx bioelectrode offers substantially larger signals reflecting the electrocatalytic activity of the MWCNT/OPFP composite (a vs b and c). Even when the graphite loading was increased to the optimal loading of 50%, the MWCNT/OPFP/GOx bioelectrode was showing higher signals (data not shown). The +0.9 V operation is coupled to good linearity up to 8 mM glucose, with a slight curvature at higher levels. To minimize the effect of interferences such as ascorbic and uric acid, the biosensor was tested at a low potential of +0.3 V which shows good sensitivity toward glucose (2 $\mu\text{A}/\text{mM}$) with good linearity up to 6 mM (data not shown). In addition, coating the surface with a layer of 1% Nafion polymer extended the linear response to 12 mM and improved the biosensor's selectivity toward interferences such as ascorbic and uric acids (data not shown) while maintaining nearly similar sensitivity. The MWCNT/OPFP/GOx bioelectrode showed fairly reproducible response. For 10.0 subsequent measurements of glucose, the coefficient of variation did not exceed 4.0%.

Another attractive feature of the MWCNT/OPFP composite electrodes is their highly stable amperometric response and antifouling properties toward the oxidation of NADH. Figure 8 compares the amperometric response to 5 mM NADH, as recorded over a continuous 60 min period, at the MWCNT/OPFP (Figure 8A) and a bare glassy carbon (Figure 8B) electrodes held at +0.30 V and +0.50 V, respectively. The bare glassy carbon electrode displays a rapid decay of the signal (up to 50%) current depressions after 60 min indicating a poor surface antifouling

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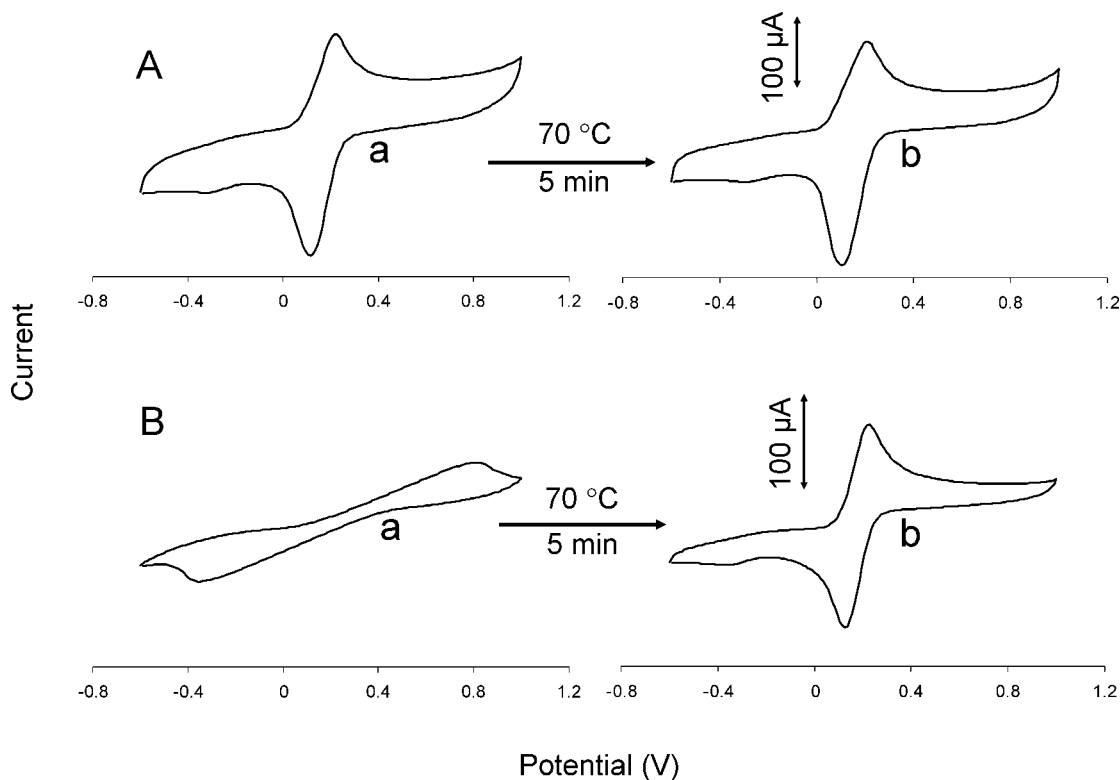


Figure 9. Cyclic voltammograms for 5 mM potassium ferricyanide before (a) and after (b) heating at 70 °C for 5 min at the 10/90 MWCNT/OPFP (A) and the 2/98 MWCNT/OPFP (B) composite electrodes. Scan rate 100 mV/s.

property. In contrast, the response of the MWCNT/OPFP electrode remains stable throughout the entire experiment, with only 15% current diminutions at 60 min. A similar loss of the response to the bare glassy carbon (of 50%) was observed in control experiments using MWCNT/Moile paste electrode (data not shown). The antifouling properties of this composite are attributed to both the carbon nanotubes and to the OPFP IL in agreement with the literature on carbon nanotubes⁷ and OPFP¹⁴ antifouling properties toward NADH oxidation.

To investigate the effect of heating on the performance of this composite in an analogous manner to what has been done using the graphite/OPFP composite,¹⁴ two MWCNT/OPFP composites were tested. The purpose of this experiment was to evaluate the need for this extra step to minimize the background current and hence improve the analytical response. As shown in Figure 9, 10% MWCNT (A) and 2% MWCNT (B) loadings were evaluated before and after heating for 5 min at 70 °C using 5 mM of potassium ferricyanide.

Surprisingly, the 10% loading was not affected by heating, and the responses before and after heating were nearly identical in contrast to the graphite/OPFP composite where heating was needed to get a better response. On the other hand, the 2% loading of the MWCNT, which had a very poor response before heating, showed an enhanced response similar to what was seen with the 10% loading. One possible reason for this could be the exposure of more carbon nanotubes to the surface upon heating and loss of partial passivation.

CONCLUSION

In this report, a new composite material made from mixing MWCNT with the IL OPFP was used to fabricate a highly sensitive, stable, and robust electrode which was used for sensing purposes of different probes such as ascorbic acid, ferricyanide, NADH, and hydrogen peroxide. In addition to that, the composite matrix was easily accessible for enzymes such as glucose oxidase which was applied for glucose determinations. The new composite material combines the unique and attractive electrocatalytic behavior of carbon nanotubes and the IL OPFP with very low background current and mechanically robust structure compared to many other forms of composites and pastes made from carbon nanotubes and other ILs. The ability of carbon nanotubes to show a good electrochemical performance of this composite even at such very low loadings as 2% is considered superior compared to other forms of carbon such as graphite. Through the incorporation of suitable functional groups on the nanotubes, this composite material can be further used for unlimited number of applications with outstanding performance.

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