Solubilization of Carbon Nanotubes by Nafion toward the Preparation of Amperometric Biosensors

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Since the discovery of carbon nanotubes (CNT),[1] there has been enormous interest in exploring and exploiting their unique properties.[2] One promising application of CNT is their use in chemical sensors and nanoscale electronic devices. Such potential applications would greatly benefit from the ability of carbon nanotubes to promote the electron-transfer reactions of important biomolecules, including cytochrome c,[3] NADH,[4] catecholamine neurotransmitters,[5] or ascorbic acid.[6] A major barrier for developing such CNT-based devices is the insolubility of CNT in all solvents.[7,8] The challenge of solubilizing CNT has been addressed through their covalent modification[8,9] or noncovalent functionalization.[7,10] In particular, "wrapping" of CNT in polymeric chains has shown useful for improving their solubility without impairing their physical properties.[11] Composite materials based on wrapping CNT with poly(*p*-phenylenevinylene)[7] or poly{(*m*-phenylenevinylene)-*co*-[2,5-dioctyloxy-(*p*-phenylene)-vinylene]}[10] have thus been reported. A similar use of polymeric materials that are commonly used in the preparation of biosensors is highly desired for fabricating CNT-based sensing and electronic devices. Here we report on the ability of the widely used perfluorosulfonated polymer Nafion to solubilize single-wall and multiwall CNT and on the dramatically enhanced redox activity of hydrogen peroxide at CNT/Nafion-coated electrodes in connection to the preparation of oxidase-based amperometric biosensors.

Because of their unique ion-exchange, discriminative, and biocompatibility properties, Nafion films have been used extensively for the modification of electrode surfaces and for the construction of amperometric biosensors.[12,13] Similar to other polymers used to wrap and solubilize CNT,[11] Nafion bears a polar side chain. We have found that CNT can be suspended in solutions of Nafion in phosphate buffer or alcohol. Such an ability of Nafion to solubilize CNT is clearly indicated by changes visible to the naked eye. For example, Figure 1 displays photographs of vials containing single-wall (A) and multiwall (B) CNT in the presence of Nafion (d−f) along with the corresponding control solutions (a−c). Increasing the Nafion content (from 0.1 to 5 wt %, d−f) results in dramatic enhancement of the solubility of both types of CNT. A homogeneous, well-distributed solution of the Nafion/CNT complex is observed in the 5% polymer solution. No such solubilization is observed using the corresponding ethanol or phosphate-buffer control solutions (a−c). The 0.5 wt % Nafion solution resulted in a homogeneous solution of the single-wall CNT, and an inhomogeneous one in the case of multiwall CNT (e). (While these photographs were taken 72 h after suspending the CNT, the 0.5 wt % Nafion/multiwall CNT solution appeared homogeneous over the first 36 h.) Figure 1C displays a TEM image of MWCNT dispersed in the 0.5 wt % Nafion solution. Well-separated CNT ropes (down to 20 nm diameter) are observed. In contrast, high-density large intertwined aggregates were observed in analogous TEM images
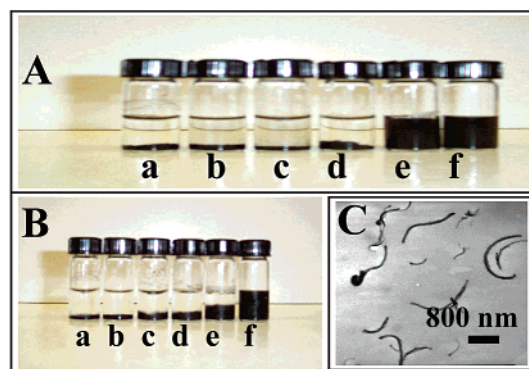

Figure 1. Photographs of vials containing 0.5 mg mL^{-1} of SWCNT (A) and MWCNT (B) in different solutions: phosphate buffer (0.05 M, pH 7.4) (a), 98% ethanol (b), 10% ethanol in phosphate buffer (c), 0.1% Nafion in phosphate buffer (d), 0.5% Nafion in phosphate buffer (e), and 5% Nafion in ethanol (f). Also shown (C) is a TEM image of a 0.5% Nafion solution containing 0.3 mg mL^{-1} of MWCNT.

for CNT dispersion in chloroform (not shown). UV/vis spectra for the pure polymer and for the polymer-MWCNT solutions exhibited a greatly increased absorption band around 230 nm, along with a larger absorption over the entire 200−800 nm range (not shown), in a manner analogous to the starch-induced solubilization of CNT.[14]

The Nafion-induced solubilization of CNT permits a variety of manipulations, including modification of electrode surfaces and preparation of biosensors. The CNT/Nafion association does not impair the electrocatalytic properties of CNT. Such behavior has been demonstrated for the redox processes of hydrogen peroxide that are of considerable interest to the operation of oxidase-based amperometric biosensors. There are no earlier reports on the electrocatalytic action of CNT toward hydrogen peroxide. The CNT/Nafion-coated electrode offers a marked decrease in the overvoltage for the hydrogen peroxide reaction to allow convenient low-potential amperometric detection. Figure 2 displays cyclic voltammograms for 5×10^{-3} M hydrogen peroxide as recorded at the bare (A) and CNT-modified (B) glassy carbon (GC) electrodes. The CNT-coated electrode exhibits significant oxidation and reduction currents starting around +0.20 V. In contrast, no redox activity is observed at the naked GC surface over most of the potential range. A similar lowering of the hydrogen-peroxide overvoltage was observed at other CNT-modified electrodes (not shown), indicating that the Nafion-CNT material retains the electrocatalytic properties of CNT. Also shown in Figure 2 (upper inset) is the amperometric response at 0.0 V of the bare (A) and CNT-coated (B) glassy-carbon electrodes to successive additions of hydrogen peroxide. While the modified electrode responds very rapidly and favorably to these changes in the peroxide concentration, no response is observed in analogous measurements at the ordinary GC electrode. The response of the modified electrode remained highly stable over a 2 h stirring

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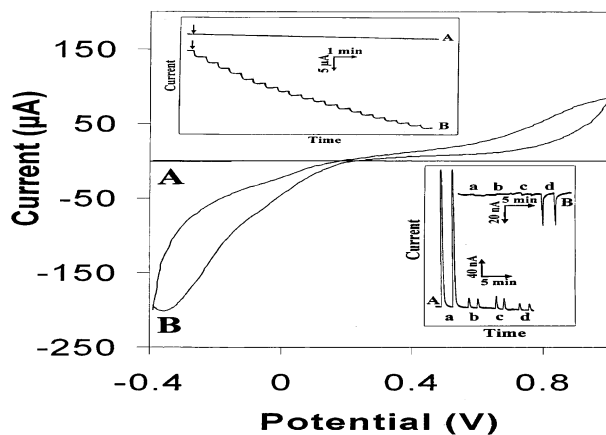‡ Pacific Northwest National Laboratory.

10.1021/ja028951v CCC: $25.00 © 2003 American Chemical Society

Figure 2. Cyclic voltammograms for 5×10^{-3} M hydrogen peroxide at unmodified (A), and MWCNT-modified (B) GC electrodes. Scan rate, 50 mV s^{-1}; electrolyte, phosphate buffer (0.05 M, pH 7.4). The voltammograms represent the first cycle on a freshly polished or modified surface. Also shown (upper inset) is the amperometric response for increasing hydrogen peroxide concentration in 1×10^{-3} M steps at unmodified (A) and MWCNT-coated (B) glassy carbon electrodes held at 0.0 V; (lower inset) flow-injection signals for 2×10^{-4} M acetaminophen (a), 2×10^{-4} M ascorbic acid (b), 2×10^{-4} M uric acid (c), and 1×10^{-2} M glucose (d), at the Nafion-coated GC electrode (A) at 0.8 V, and using the MWCNT-modified GC electrode (B) at -0.05 V. Flow rate, 1.25 mL min^{-1}.

period. Optimal performance was observed using a 0.5 wt % Nafion solution containing 2 mg mL^{-1} of CNT.

The use of Nafion as a solubilizing agent for CNT, along with the electrocatalytic detection of hydrogen peroxide, provide a useful avenue for preparing CNT-modified electrodes and offer great promise for oxidase-based amperometric biosensors. Such electrical biosensing is illustrated in Figure 2 (lower inset) in connection to flow-injection measurements of glucose. The accelerated electron-transfer reaction of hydrogen peroxide allows for glucose measurements at very low potentials where interfering reactions are minimized (B). While a well-defined glucose response is observed using a potential of -0.05 V (d), relevant physiological levels of acetaminophen, uric acid, and ascorbic acid result in negligible signals (a−c). No such discrimination is obtained at the Nafion-based biosensor (without the CNT) held at $+0.80$ V, where large oxidation peaks are observed for all potential interferences (A). Notice, in particular, the substantial acetaminophen contribution (a); even uric and ascorbic acids yield signals larger than that of glucose (b,c vs d), indicating that the permselective (charge-exclusion) properties of Nafion are not sufficient to fully eliminate anionic interferences. Yet, the coupling of such permselective properties with the electrocatalytic action of CNT allows for effective discrimination against both neutral and anionic redox constituents. Injections of glucose solutions of increasing concentrations $(2-20) \times 10^{-3}$ M resulted in well-defined peaks, proportional to the substrate concentration (not shown; potential, -0.05 V); no glucose response was observed for analogous measurements without the CNT modifier.

The distinct advantages of the CNT/Nafion coating were exploited also for dramatically improving the detection of catecholamine neurotransmitters in the presence of the common ascorbic acid interference. For example, the CNT/Nafion modified glassy-carbon electrode offered a greatly enhanced (electrocatalytic) dopamine response and discrimination against ascorbic acid, as compared to Nafion- and CNT-modified electrodes, respectively (not shown).

In conclusion, our findings indicate that the use of Nafion as a solubilizing agent for CNT provides a useful avenue for preparing CNT-based biosensors. The resulting biosensors greatly benefit from the coupling of the efficient electrocatalytic action of CNT toward hydrogen peroxide and NADH with the antifouling/discriminative properties of Nafion films. Additional experiments are needed for gaining further insights into the morphology of the CNT/Nafion structure.

Supporting Information Available: Related instrumentation and procedures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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JA028951V