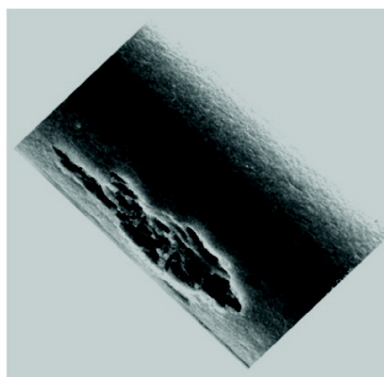
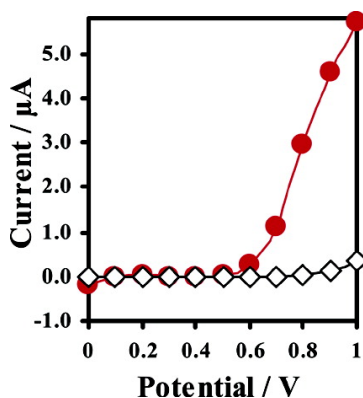


## Carbon Nanotube Fiber Microelectrodes

Joseph Wang, Randhir P. Deo, Philippe Poulin, and Maryse Mangey

*J. Am. Chem. Soc.*, **2003**, 125 (48), 14706-14707 • DOI: 10.1021/ja037737j • Publication Date (Web): 08 November 2003

Downloaded from <http://pubs.acs.org> on March 30, 2009



### More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 9 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



**ACS Publications**  
 High quality. High impact.

## Carbon Nanotube Fiber Microelectrodes

Joseph Wang,<sup>\*,†</sup> Randhir P. Deo,<sup>†</sup> Philippe Poulin,<sup>‡</sup> and Maryse Mangey<sup>‡</sup>

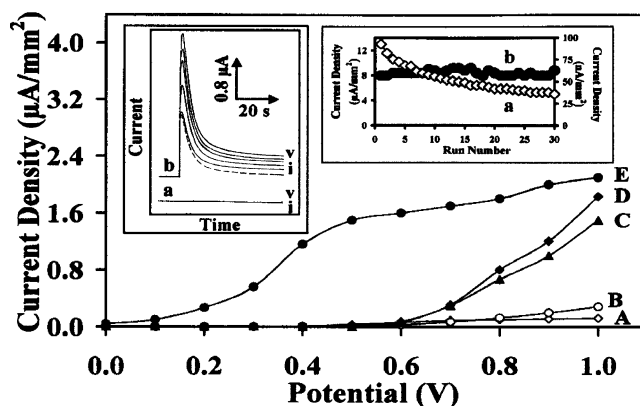
*Department of Chemistry and Biochemistry, New Mexico State University, Las Cruces, New Mexico 88003, and  
Centre de Recherche Paul Pascal/CNRS, Université Bordeaux I, Avenue Schweitzer, 33600 Pessac, France*

Received August 4, 2003; E-mail: joewang@nmsu.edu

Carbon nanotubes (CNT) have gained considerable attention in recent years because of their remarkable electronic and mechanical properties.<sup>1,2</sup> The unique features of CNT make them extremely attractive for a wide range of sensing applications.<sup>3,4</sup> The ability of CNT-modified electrodes to promote electron-transfer reactions and resistance to surface fouling has been documented in connection to important biomolecules.<sup>5–8</sup>

Here, we report on the preparation and favorable electrochemical behavior of CNT fiber microelectrodes. The growing interest in microelectrodes has led to a widespread use of carbon fibers for exploring microscopic domains and measurements of local concentration profiles.<sup>9,10</sup> CNT fibers, developed recently by Vigolo et al.,<sup>11</sup> are prepared by a simple particle-coagulation spinning (PCS) process, involving the injection of a homogeneous and relatively concentrated aqueous CNT suspension in a flowing coagulating bath.<sup>12</sup> This preparation process results in a novel form of CNT, consisting of an interconnected CNT/polymer-chain network, and possessing mechanical flexibility, high toughness, and high porosity, while retaining the attractive electrochemical behavior of CNT materials. By combining the advantages of CNT with those of fiber electrodes, the new material brings new capabilities to electrochemical devices and has many potential sensing applications. Such attractive capabilities are illustrated below in connection to electrocatalytic reactions of several important biomolecules (NADH, hydrogen peroxide, and dopamine), because of their broad significance for biosensing and in-vivo sensing, and in view of their enhanced electron-transfer activity on a large-sized CNT microelectrode.

CNT fibers were activated at 300 °C for 60 min and subsequently inserted into pulled glass capillaries and produced CNT fiber cylinder microelectrodes of 18 (SWCNT) and 34 (MWCNT)  $\mu\text{m}$  diameter and 5 mm length. The carbon fibers (7  $\mu\text{m}$  diam) used for comparison were prepared in the same way. Figure 1 shows hydrodynamic voltammograms (HDV) for NADH obtained at untreated and heat-treated carbon (A,D) and CNT (B,C,E) fiber microelectrodes. Both untreated fiber electrodes display minimal electrochemical reactivity over the entire range (A,B). At the treated carbon (D) and SWCNT (C) fiber electrodes, redox activity is observed only above +0.6 V, with a slow increase of the response thereafter. The treated MWCNT fiber electrode, in contrast, responds favorably to NADH over most of the potential range, with significant oxidation currents starting at +0.1 V and leveling off above +0.4 V (E). Such a profile reflects the marked acceleration of the NADH redox process and is in agreement with the HDV reported at MWCNT-based macroelectrodes.<sup>8</sup> While no apparent activation was observed by using a "milder" heat treatment (at 150 °C), we have observed minimal activation of the electron-transfer reactivity of the CNT fiber electrode upon electrochemical polarization (1 min at +1.5 V; not shown). This is in contrast to carbon



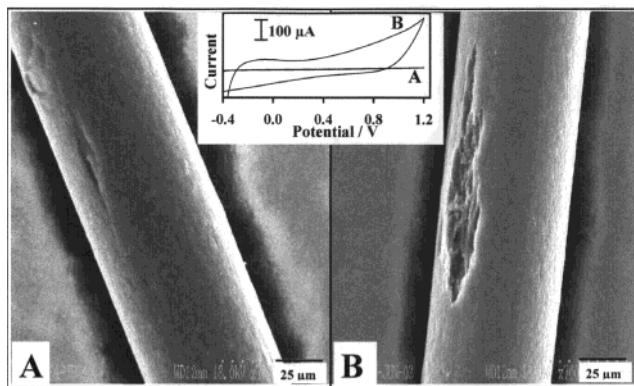
**Figure 1.** Hydrodynamic voltammograms (current density vs applied potential) for 1 mM NADH at carbon (A,D) and CNT (B,C,E) fiber microelectrodes (untreated (A,B) and heat treated (C,D,E) fibers). Left inset: chronoamperometric signals measured at +0.2 V of NADH from 1.0 (i) to 5.0 (v) mM at the carbon (a) and CNT (b) fiber microelectrodes. Dashed line indicates the blank solution. Right inset: the chronoamperometric response for repetitive measurements at +0.7 V of 3 mM NADH at the carbon (a, right axis) and CNT (b, left axis) fiber electrodes. Electrolyte, phosphate buffer (0.05 M, pH 7.4).

fiber electrodes where an anodic treatment has a profound effect upon the electron-transfer properties.<sup>13</sup> The CNT fiber displays good resistance to surface fouling common to NADH oxidation, thus imparting high stability onto NADH measurements. Figure 1 (right inset) compares the stability of the response for 30 repetitive chronoamperometric measurements of 3 mM NADH at the carbon (a) and CNT (b) fiber electrodes. The carbon fiber electrode displays a rapid loss of its activity (with up to 62% decrease of the response and a RSD of 29%). In contrast, a highly stable signal is observed over the entire operation upon using the CNT microelectrode (RSD = 4%). Such minimization of NADH passivation effects is in agreement with early observation at CNT macroelectrodes.<sup>8</sup> The electrocatalytic action of CNT fiber electrodes (34  $\mu\text{m}$ ) facilitates low-potential amperometric measurements of NADH (Figure 1, left inset). While the treated carbon fiber surface is not responsive to the changes in the level of NADH (a), the CNT microelectrode responds favorably using a detection potential of +0.2 V (b) over the entire concentration range.

Changes in the morphology of the CNT fiber upon the heat treatment, observed in scanning electron microscopy (SEM), shed useful insights into the heat-induced activation of CNT fiber microelectrodes. Figure 2 displays SEM images (obtained with 700 $\times$  magnification) of the untreated (A) and treated (B) MWCNT fiber microelectrodes. A quite uniform nonporous structure is observed for the untreated microelectrode, reflecting the aligned filament of the outer surface of CNT.<sup>14</sup> The heat treatment results in fracturing of the fiber skin, removal of some nonconducting polymeric material and amorphous carbon impurities, and exposure of the internal nanofelt porous conducting bundles (B). The surface

<sup>†</sup> New Mexico State University.

<sup>‡</sup> Université Bordeaux I.

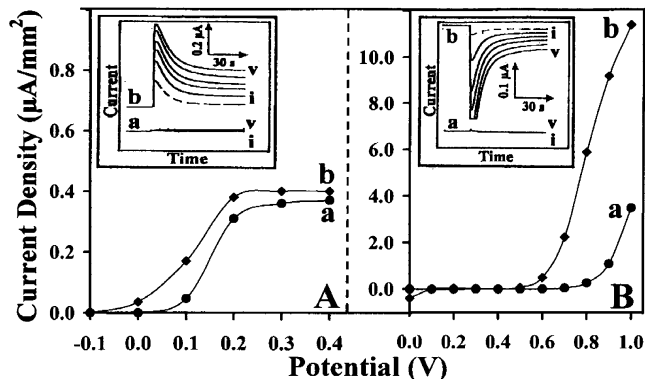


**Figure 2.** SEM images of untreated (A) and heat-treated (B, at 300 °C for 60 min) CNT fiber microelectrodes. Magnification, 700 $\times$ ; accelerating voltage, 18 kV. Also shown (inset) are the background cyclic voltammograms of the untreated (A) and treated (B) CNT fibers at 100 mV/s; electrolyte, phosphate buffer (0.05 M, pH 7.4).

(outside this pit) remains smooth, with no apparent increase in roughness. The increase in area (accrued from the increased porosity) is indicated from the dramatic increase of the cyclic-voltammetric background-current envelop (inset), which reflects the substantially higher double layer capacitance. Accordingly, the main reasons for the improved electrochemical properties are believed to be removal of nonconducting polymer residues that are blocking the access to the CNT electrocatalytic sites and exposure of ends of nanotubes with higher catalytic activity than walls. Similar enhanced electrochemical activity was suggested for thermal activation of SWCNT<sup>15</sup> and of carbon electrodes.<sup>16</sup> The thermal activation of the CNT fiber exhibited good reproducibility (RSD 8.7% for the measurements of 1 mM NADH at five different CNT fiber electrodes).

Carbon fiber microelectrodes have been widely used for monitoring catecholamine neurotransmitters and for designing glucose microensors.<sup>10</sup> As indicated from Figure 3, the new MWCNT fiber offers a substantial enhancement of the response for dopamine (A) and hydrogen peroxide (B), with lowering of their overvoltage by ca. 150 and 300 mV, respectively. The MWCNT microelectrode thus allows highly sensitive low-potential detection of both analytes (see insets). The dopamine and hydrogen-peroxide response (at +0.10 (A) and 0.0 (B) V) increases linearly with the concentration over the entire range (b). No response is observed for analogous measurements at the treated carbon fiber electrodes (a). The treated CNT microelectrodes retained their favorable electrochemical properties over several weeks.

In conclusion, CNT fiber electrodes have been shown to couple the attractive properties of CNT with the advantages of microelectrodes. Such a combination opens the door for using CNT in a wide range of sensing applications. The ability of carbon nanotubes to promote the electron-transfer reactions of NADH and hydrogen peroxide suggests great promise for dehydrogenase- and oxidase-based amperometric microensors. The devices reported here are robust and reusable as compared to single CNT fiber tips proposed for scanning-probe microscopy.<sup>17</sup> Further studies are desired for



**Figure 3.** Hydrodynamic voltammograms for 100  $\mu$ M dopamine (A) and 1 mM hydrogen peroxide (B) at treated carbon (a) and CNT (b) fiber microelectrodes. Also shown (insets) are the chronoamperometric signals for successive additions (*i-v*) of 50  $\mu$ M dopamine (at +0.1 V) and of 4 mM hydrogen peroxide (at +0.0 V) at the carbon (a) and CNT (b) fiber microelectrodes. Dashed line indicates blank solution. Other conditions are as in Figure 1D,E.

elucidating the structure–reactivity relation of the new CNT fiber electrode material and for understanding the relationship between the surface pretreatment and the electrode performance. Current efforts in our research groups are aimed at further shrinking the dimensions of the CNT fibers.

**Acknowledgment.** This work was supported by the National Science Foundation (Grant Number CHE 0209707).

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

## References

- (1) Rao, C. N.; Satishkumar, B. C.; Govindaraj, A.; Nath, M. *ChemPhysChem* **2001**, *2*, 79.
- (2) Baughman, R. H.; Zakhidov, A.; de Heer, W. A. *Science* **2002**, *297*, 787.
- (3) Sherigara, B. S.; Kutner, W.; D'Souza, F. *Electroanalysis* **2003**, *15*, 753.
- (4) Zhao, Q.; Gan, Z.; Zhuang, Q. *Electroanalysis* **2002**, *14*, 1609.
- (5) Wang, J.; Li, M.; Shi, Z.; Li, N.; Gu, Z. *Anal. Chem.* **2002**, *74*, 1993.
- (6) Yu, X.; Chattapadhyay, D.; Galeska, I.; Papdimitrakopoulos, F.; Rusling, J. F. *Electrochem. Commun.* **2003**, *5*, 408.
- (7) Gooding, J. J.; Wibowo, R.; Liu, J.; Yang, W.; Losic, D.; Orbons, S.; Mearns, F.; Shapter, J.; Hibbert, B. D. *J. Am. Chem. Soc.* **2003**, *125*, 9006.
- (8) Musameh, M.; Wang, J.; Merkoci, A.; Lin, Y. *Electrochem. Commun.* **2002**, *4*, 743.
- (9) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*, 2nd ed.; Wiley: New York, 2001.
- (10) Wang, J. *Analytical Electrochemistry*, 2nd ed.; Wiley: New York, 2000.
- (11) Vigolo, B.; Penicaud, A.; Coulon, C.; Sauder, C.; Pailler, R.; Journet, C.; Bernier, P.; Poulin, P. *Science* **2000**, *290*, 1331.
- (12) Poulin, P.; Vigolo, B.; Launois, P. *Carbon* **2002**, *40*, 1741.
- (13) (a) Brajter-Toth, A.; El-Nour, K.; Cavalheiro, E.; Bravo, R. *Anal. Chem.* **2000**, *72*, 1576. (b) Swain, G. M.; Kuwana, T. *Anal. Chem.* **1991**, *63*, 517.
- (14) Neimark, A.; Ruetsch, S.; Kornev, K.; Ravikovitch, P.; Poulin, P.; Badair, S.; Maugey, M. *Nano Lett.* **2003**, *3*, 413.
- (15) Guiseppi-Elie, A.; Lei, C.; Baughman, R. H. *Nanotechnology* **2002**, *13*, 559.
- (16) Hu, I.; Karweik, D.; Kuwana, T. *J. Electroanal. Chem.* **1985**, *188*, 59.
- (17) Campbell, J. K.; Sun, L.; Crooks, R. M. *J. Am. Chem. Soc.* **1999**, *121*, 3779.

JA037737J