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Carbon Nanotube Sol–Gel Composite Materials

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ABSTRACT

This paper describes a new class of composite materials designed by combining multiwall carbon nanotubes (MWNTs) and sol–gels. These materials provide new capabilities for the development of electrochemical devices by taking advantage of the favorable electrochemical characteristics of MWNTs. Further, variations in the silane precursors used and in the carbon nanotube content of the composites results in materials with a range of capacitance, electron-transfer rates, and potential to control selectivity.

Carbon nanotubes have attracted much attention during the past decade[1] due to their unique mechanical, chemical, and electrical properties.[2,3] Of particular interest is the use of carbon nanotube-based materials for the development of electromechanical actuators,[4] supercapacitors,[5−8] batteries,[9] and electrochemical sensors.[10−15] Most efforts in this area deal with carbon nanotube papers, aligned nanotube whiskers and single nanotube arrangements. Chemical derivatization of carbon nanotubes has been challenging[16−18] and, consequently, has not been used to adjust the electrochemistry of such materials. To broaden the applicability of carbon nanotubes, an approach for controlling their electrochemical properties is reported herein using carbon nanotube sol−gel composites.

Sol−gel technology involves the fabrication of materials through the hydrolysis and condensation of suitable alkoxysilane precursors.[19,20] Composite materials based on sol−gels have been employed in electrochemical sensing devices.[21,22] The driving force for these efforts is that sol−gel chemistry provides a relatively simple way to incorporate recognition species in a stable host environment. The composite materials reported in the literature have been based mainly on the incorporation of carbon powder[23−25] or gold[26,27] particles into the sol−gel.

An advantage of sol−gel chemistry is the ability to use different silane precursors to modify the properties of the gel in a controlled fashion. In our studies, three different silane precursors were used for the preparation of the composites: methyltrimethoxysilane (MTMOS), ethyltrimethoxysilane (ETMOS), and propyltrimethoxysilane (PTMOS). The sols were prepared by mixing 1.0 mL of the silane precursor, 1.5 mL of ethanol, and 50 μL of 12.1 M HCl. The sol was sonicated for 1 min after the mixing. Various amounts of sol (25, 50, or 75 μL) were added to 10 mg of the multiwall carbon nanotubes[28] and mixed thoroughly to ensure uniform composition. The mixture was packed tightly into the tip of a 1 cm^3 Tuberculin plastic syringe body and left to dry for 24−48 h (depending on the amount of the sol). Electrical contact was achieved through the back surface of the composite material with a stainless steel wire. The electrodes were polished using weighing paper to yield a smooth surface. Depending on the amount of sol added (25, 50, or 75 μL), the final composite contained 61%, 44%, or 34% (w/w) carbon nanotube, respectively. The geometrical surface area was 0.0227 cm^2. All electrochemical measurements were made using 50 mM phosphate buffer (pH 7.4), a silver/silver chloride reference electrode (in 3M NaCl), and a platinum counter electrode. A representative SEM picture of the surface of the carbon nanotube (44% w/w MWNT) sol−gel (MTMOS-derived) composite is presented in Figure 1. It can be seen that the material exhibits porous structure with clearly visible nanotube fibers, implying that the electroactive surface area of the electrodes will be larger than the macroscopic geometrical area. The slopes of the Cottrell plots obtained from chronoamperometric data (using $K_4Fe(CN)_6$) were used to calculate the surface area. The calculated surface area (varying between 0.035 and 0.058 cm^2) was 1.5−2.5-fold higher than the geometrical area, varying with the nature and the amount of the gel. It should be mentioned that the calculation of the surface area with the Cottrell equation is based on one-dimensional diffusion.

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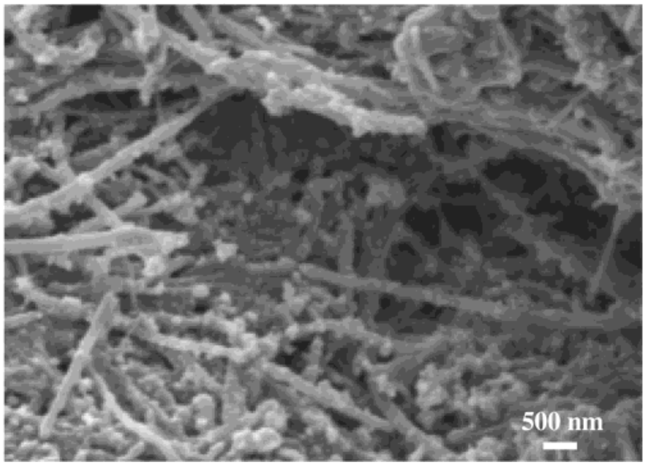

Figure 1. Typical SEM image of the surface of sol−gel (MTMOS-derived) carbon nanotube composite (44% w/w carbon nanotube). The bar corresponds to 500 nm.

Table 1. Dependence of Electrochemical Properties on Composition

silane precursor	% w/w MWNTs	C_{obs} mF/cm^2	ΔE_p,[a] mV	i_{ox},[a] μA
MTMOS	61	91.6	74	55.2
MTMOS	44	57.4	105	61.5
MTMOS	34	14.5	136	4.05
ETMOS	61	21.0	66	54.0
ETMOS	44	3.85	77	28.5
ETMOS	34	2.67	119	18.4
PTMOS	61	3.67	58	33.6
PTMOS	44	2.17	84	17.2
PTMOS	34	0.26	106	20.0

[a] Calculated at 10 mV/s scan rate. The solution was 10 mM $K_4Fe(CN)_6$. i_{ox} is the current of the oxidation peak.

Thus, the presence of nanotubes having vertical placement with respect to the surface geometry (for example, in the lower left corner of Figure 1), would not contribute to the calculated surface area regardless of their electrochemical activity.

The voltammetric behavior of the different composites prepared was studied using cyclic voltammetry over the potential range −1.0 to +1.5 V (vs Ag/AgCl). The composites, regardless of composition, exhibited a relatively wide working potential window (from +1.0 to −0.4 V), characteristic of carbon-based electrodes.[29] The nature of the gel and the carbon nanotube content influence the observed background current. Thus, the effect of the gel nature and nanotube amount on the background current was further examined.

The double-layer capacitance (proportional to the background current) of the electrodes was calculated from the charging current (at +300 mV) at different scan rates (10−100 mV/s).[26,30] The results are presented in Table 1. The charging current was linearly increased with increasing scan rate up to 50 mV/s, while at higher scan rates the measured capacitance was decreased. This behavior has been observed previously for carbon nanotube based electrodes,[8] as well as for other carbon type electrodes,[31] and it has been attributed to the presence of "slow" and "fast" charging mechanisms. Reducing the carbon nanotube content of the composite from 61% to 34% w/w caused a dramatic reduction in the observed double-layer capacitance, regardless of the nature of the gel in terms of methyl-, ethyl-, or propyl-derived silane precursor. Additionally, the capacitance is further reduced when larger organic groups are incorporated into the gel network. Overall, the double-layer capacitance of the electrodes decreases when a higher percentage of sol gel with larger organic groups is used. This behavior can be attributed to the increased hydrophobicity of the electrode surface, and it is in accordance with previous studies for sol−gel-derived carbon powder composite electrodes.[23] Consequently, increasing the amount of the gel yields a smaller fraction of exposed carbon nanotubes on the electrode surface, resulting in lower background currents. The wide range of capacitance attainable by these composites is advantageous because it enables the selection of optimal material compositions given a desired application. For example, higher capacitance is required in the development of energy storage devices, whereas electrochemical sensors require lower capacitance materials.

The electron-transfer properties of the materials were evaluated by performing cyclic voltammetry with the model redox couple $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$. The symmetrical shape of the peaks obtained and the linear dependence of the current to the square root of the scan rate indicate linear diffusion conditions. The separation of the peaks (ΔE_p) for the 61% (w/w) carbon nanotube and PTMOS silane composite was 58 ± 2 mV at scan rates of 5 and 10 mV/s, revealing fast electron transfer. Similar results were recently reported using MWNT microbundle electrodes.[15] The observed fast electron-transfer kinetics has been attributed to the high local density of electronic states.

As can be seen in Table 1, the electron transfer properties of the composite electrodes were greatly influenced by the composition. Decreasing the amount of the carbon nanotubes resulted in a drastic increase of the peak separation, regardless of the nature (propyl-, ethyl-, or methylsilane) of the gel. Thus, it can be inferred that when the amount of the gel is increased, a barrier is formed on the carbon nanotube surface that hinders the electron transfer. The ΔE_p values for the composites prepared using the PTMOS precursor were significantly smaller than the ΔE_p for the corresponding composites based on the MTMOS precursor. This effect of the gel nature was rather surprising. Similar studies for carbon paste electrodes demonstrated that the use of heavier hydrocarbons as part of the paste resulted in a decrease of the k°_{obs} over 1 order of magnitude, which was attributed to the stronger adsorption of the liquid on the carbon and the decreasing active area.[32] In the present study, the influence of the nature of the gel was noticeably smaller. The smaller extent and the reverse order of the effect indicate that the influence of the gel nature may arise primarily from the porosity of the matrix, and to a lesser degree from its hydrophobicity.

The composition of the material can also be used to tune the observed electrochemistry of electroactive species. In

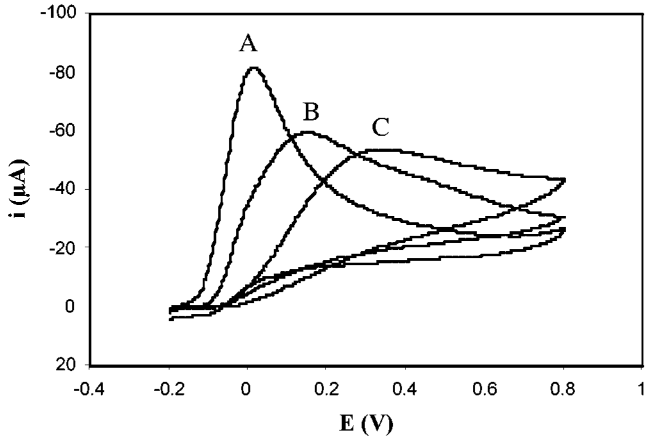

Figure 2. Cyclic voltammograms of 10 mM ascorbic acid with three different composites based on PTMOS with (A) 61%, (B) 44%, and (C) 34% (w/w) carbon nanotube. Scan rate: 50 mV/s.

Figure 2 the oxidation of ascorbic acid is presented. The oxidation peak is shifted to more positive potentials (from +15 to +150 and +330 mV for the propyl-derived gel) as the gel content of the electrode is increased from 39% to 56% and 66%, respectively. This can be attributed to the presence of negatively charged silanol groups[23] in the gel that can partially reject the ascorbate ions and modify the selectivity of the composite.

In summary, we have demonstrated that carbon nanotube sol−gel composite materials provide new capabilities for the development of electrochemical devices. These composites integrate the advantages of sol−gels with the favorable electrochemistry of carbon nanotubes. The ability to control the electrochemical characteristics (capacitance, electron-transfer rates, and selectivity) by varying the silane precursors and the carbon nanotube content has been demonstrated. An additional advantage of sol−gel materials is their aptitude to incorporate biomolecules. Work in this direction employing the carbon nanotube sol−gel composites is currently underway in our laboratory.

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Supporting Information Available: Cyclic voltammogram of ferrocyanide at different scan rates. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Iijima, S. *Nature* **1991**, *354*, 56.
(2) Dresselhaus, M. S.; Dresselhaus, G.; Eklund, P. C. *Science of Fullerenes and Carbon Nanotubes*, Academic Press: San Diego, CA, 1996.
(3) Ajayan, P. M. *Chem. Rev.* **1999**, *99*, 1787.
(4) Baughman, R. H.; Cui, C.; Zakhidov, A. A.; Iqbal, Z.; Barisci, J. N.; Spinks, G. M.; Wallace, G. G.; Mazzoldi, A.; De Rossi, D.; Rinzler, A. G.; Jaschinski, O.; Roth, S.; Kertesz, M. *Science* **1999**, *248*, 1340.
(5) Niu, C.; Sichel, E. K.; Moy, D.; Tennent, H. *Appl. Phys. Lett*. **1997**, *70*, 1480.
(6) Liu, C. Y.; Bard, A. J.; Wudl, F.; Weitz, I.; Heath, J. R. *Electrochem. Solid State Lett.* **1999**, *2*, 577.
(7) Frackowiak, E.; Metenier, K.; Bertagna, V.; Beguin, F. *Appl. Phys. Lett.* **2000**, *77*, 2421.
(8) Barisci, J. N.; Wallace, G. G.; Baughman, R. H. *J. Electroanal. Chem.* **2000**, *488*, 92.
(9) Frackowiak, E.; Gautier, S.; Gaucher, H.; Bonnamy, S.; Beguin, F. *Carbon* **1999**, *37*, 61.
(10) Davis, J. J.; Coles, R. J.; Hill, H. A. O. *J. Electroanal. Chem.* **1997**, *440*, 279.
(11) Campell, J. K.; Sun, L.; Crooks, R. M. *J. Am. Chem. Soc*. **1999**, *121*, 3779.
(12) Downs, C.; Nugent, J.; Ajayan, P. M.; Duquette, D. J.; Santhanam, K. S. V. *Adv. Mater.* **1999**, *11*, 1028.
(13) Kong, J.; Franklin, N. R.; Zhou, C.; Chapline, M. G.; Peng, S.; Cho, K.; Dai, H. *Science* **2000**, *287*, 622.
(14) Gao, M.; Huang, S.; Dai, L.; Wallace, G.; Gao, R.; Wang, Z. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 3664.
(15) Nugent, J.; Santhanam, K. S. V.; Rubio, A.; Ajayan, P. M. *Nano Lett.* **2001**, *1*, 87.
(16) Mickelson, E. T.; Huffman, C. B.; Rinzler, A. G.; Smalley, R. E.; Hauge, R. H.; Margrave, J. L. *Chem. Phys. Lett.* **1998**, *298*, 188.
(17) Chen, J.; Hamon, M. A.; Hu, H.; Chen, Y.; Rao, A. M.; Eklund, P. C.; Haddon, R. C. *Science* **1998**, *282*, 95.
(18) Bahr, J. L.; Yang, J.; Kosynkin, D. V.; Bronikowski, M. J.; Smalley, R. E.; Tour, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 6536.
(19) Pierre, A. C. *Introduction to Sol−Gel Processing*; Kluwer Academic Publishers: Boston, MA, 1998.
(20) Avnir, D.; Braun, S. *Biochemical Aspects of Sol−Gel Science and Technology*; Kluwer Academic Publishers: Hingham, MA, 1996.
(21) Lev, O.; Tsionsky, M.; Rabinovich, L.; Glezer, V.; Sampath, S.; Pankratov, I.; Gun, J. *Anal. Chem.* **1995**, *67*, 22A.
(22) Collinson, M. M.; Howells, A. R. *Anal. Chem.* **2000**, *72*, 702A.
(23) Tsionsky, M.; Gun, G.; Glezer, V.; Lev, O. *Anal. Chem.* **1994**, *66*, 1747.
(24) Ha, S. Y.; Kim, S. *J. Electroanal. Chem.* **1999**, *468*, 131.
(25) Wang, P.; Wang, X.; Yuan, Y.; Zhu, G. *J. Non-Cryst. Solids* **2000**, *277*, 22.
(26) Wang, J.; Pamidi, P. V. A. *Anal. Chem.* **1997**, *69*, 4490.
(27) Bharathi, S.; Lev, O. *Anal. Commun.* **1998**, *35*, 29.
(28) The MWNTs were prepared according to a previously reported procedure: Andrews, R.; Jacques, D.; Rao, A. M.; Derbyshire, F.; Qian, D.; Fan, X.; Dickey, E. C.; Chen, J. *Chem. Phys. Lett.* **1999**, *303*, 467. The MWNTs were grown on quartz, forming thick mats of well-aligned nanotubes that were harvested by brushing the surfaces. The average length of the nanotubes was 50 μm, while the density was 1.8−2.0 g/mL.
(29) Kinosita, K. *Carbon. Electrochemical and Physicochemical Properties*; John Wiley: New York, 1988.
(30) Urbaniczky, C.; Lundström, K. *J. Electroanal. Chem.* **1984**, *176*, 169.
(31) Oren, Y.; Soffer, A. *J. Electroanal. Chem.* **1985**, *186*, 63.
(32) Rice, M. E.; Galus, Z.; Adams, R. N. *J. Electroanal. Chem.* **1983**, *143*, 89.

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