

ELECTROCHEMISTRY OF CARBON NANOTUBE COMPOSITE ELECTRODES

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Introduction

Carbon nanotubes can be considered as molecular-scale wires with high mechanical strength and different electronic properties (metallic, semiconducting or semimetallic) depending mainly on the tube symmetry [1-4]. These properties have been utilized for the development of various electrochemical sensors for monitoring gases as NO₂ or NH₃ [5], the oxidation of biomolecules (dopamine, ascorbic acid, etc.) [6,7], the investigation of protein electrochemistry [8] and the electrocatalytic reduction of oxygen [9]. Most of the above sensors are mixtures of the nanotubes with inert organic binders (bromoform, Nujol or liquid paraffin) [7-9]. Other sensors schemes include the construction of electrodes based on single nanotubes attached to a Pt tip [10] or the use of whiskers of loosely packed multi-wall carbon nanotubes (MWNT) [11,12].

The sol-gel chemistry involves the fabrication of ceramic materials via the hydrolysis and condensation of suitable alkoxy silane precursors [13]. Sol-gel technology has been widely used for the development of chemical sensors and biosensors since it provides a relatively simple way to incorporate recognition species in a stable host environment [14,15]. Several sol-gels have been used in conjunction with carbon powder [16-18] or gold particles [19,20] for the construction of composite electrodes. The

applications of those electrodes include biosensing [18-20], chromatographic detection [21-23] and electrocatalysis [16,24].

In the present work new composite electrode materials were designed and characterized by combining carbon nanotubes and sol-gel technology. The multi-wall carbon nanotubes were dispersed into different types of sol-gel matrix for the construction of the electrode. The effect of the sol nature and the amount of the carbon nanotube on the electrochemical behavior of the composites electrodes is investigated.

Experimental

The MWNTs were prepared according to a previously reported procedure [25]. The electrodes were prepared according to the following procedure. Initially the silica sol was prepared by mixing 1.0 mL of the silane precursor, 1.5 mL of ethanol and 50 μ L of 12.1 M HCl. The sol was sonicated for 1 min after the mixing. Various amount of sol (25, 50 or 75 μ L) were added to 10 mg of the MWNTs and mixed thoroughly to ensure uniform composition. The mixture was packed tightly into the tip of a syringe and left to dry for 24 to 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

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weighting 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 of the electrodes was 0.0227 cm^2 .

Electrochemical experiments were performed using a PAR 273 potentiostat and model 270 software (EG&G Princeton Applied Research, Princeton, NJ). A silver/silver chloride reference electrode (in 3M NaCl) and a platinum counter electrode were used in all experiments. All measurements were made using 50 mM phosphate buffer (pH 7.4). Scanning electron microscopy (SEM) was performed using a Hitachi model S-3200N microscope (San Jose, CA).

Methyltrimethoxysilane (MTMOS), ethyltrimethoxysilane (ETMOS) and propyltrimethoxysilane (PTMOS) were purchased from United Chemical Technologies (Bristol, PA) and used as received. Potassium ferrocyanide was obtained from Mallinckrodt (St. Louis, MO). All other reagents used were of at least analytical grade. All solutions were prepared using deionized water (Milli-Q water purification system, Millipore, Bedford, MA).

Results and Discussion

Representative SEM pictures of the surface of the carbon nanotube (44% w/w MWNTs, 56% methyl-derived gel) sol-gel composite electrode are presented in Figure 1. Macroscopically, the surface of the electrodes was rather homogeneous having few micro-dimensional porous introduced during the sol drying process. Higher magnification reveals that the electrode's surface exhibited very porous morphology mainly due to the random orientation of the carbon nanotubes. The dimensions of these porous were in the sub-micro range.

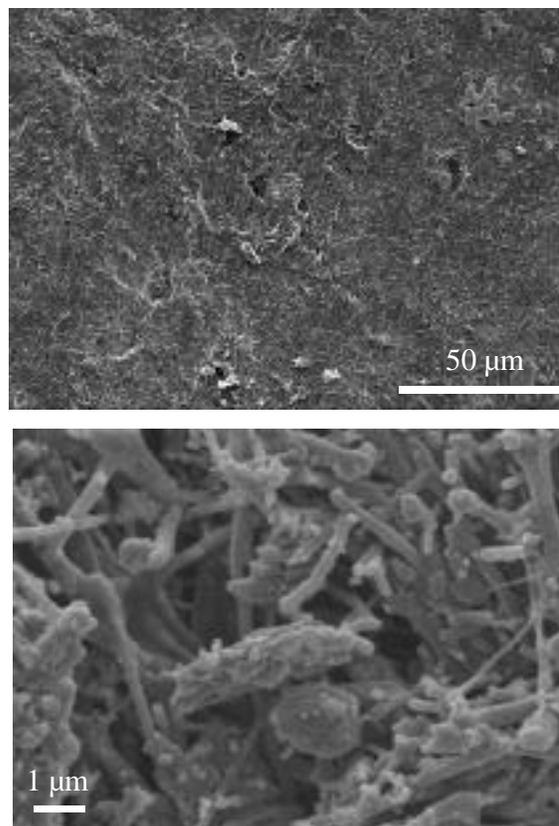


Figure 1. SEM pictures of the surface of the carbon nanotube sol-gel electrode.

The roughness of the surface indicates that the surface area of the electrodes will be larger than the macroscopic geometrical area. The electroactive surface of the electrodes was calculated using chronoamperometry. The recorded current for the oxidation of 10 mM $\text{K}_4\text{Fe}(\text{CN})_6$ was plotted as a function of the square root of the time and the area was calculated from the Cottrell equation:

$$A = \frac{i(t)^{1/2}}{n F C D^{1/2}}$$

where A is the surface area, i is the current, t is the time, n is the number of electrons, F is the Faraday constant, C is the concentration of $\text{K}_4\text{Fe}(\text{CN})_6$ and D is its diffusion coefficient.

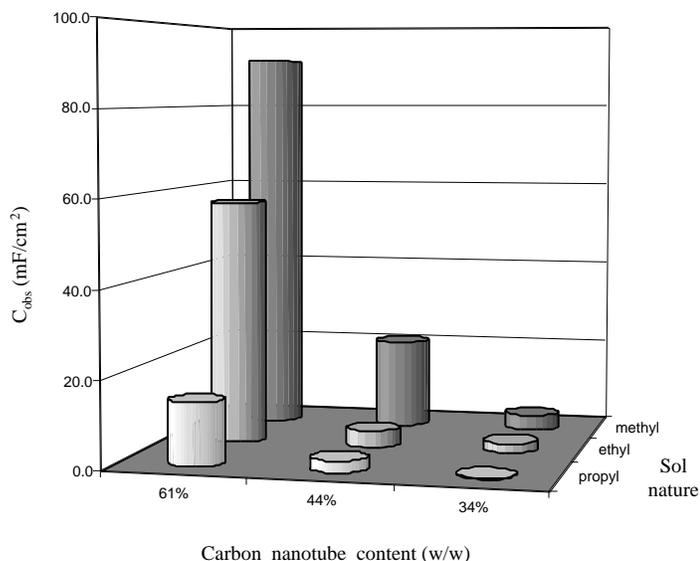


Figure 2. Dependence of the double-layer capacitance on the sol nature and the amount of the carbon nanotube.

The calculated surface area (varying between 0.035 and 0.058 cm²) was 1.5 to 2.5-fold higher than the geometrical area, varying with the nature and the amount of the gel. The effect of the gel nature and nanotube amount on the background current is presented in Figure 2. 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). Previous studies for sol-gel-derived ceramic-carbon composite electrodes have shown that by increasing the hydrophobicity of the electrode surface the double-layer capacitance was reduced [18]. This behavior was also observed in the case of the carbon nanotube based composite electrodes. The hydrophobicity of the surface can be increased either by reducing the amount of carbon nanotube or by using silane precursors with larger organic groups. In both approaches the double-layer capacitance was drastically reduced as it can be seen in Figure 2.

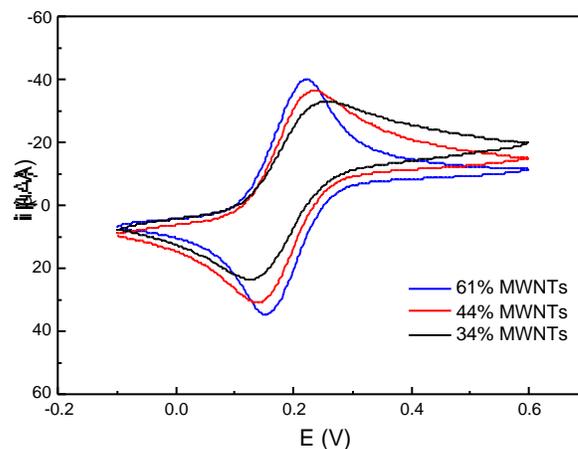


Figure 3. Cyclic voltammograms of 0.01 M ferrocyanide at different sol-gel based carbon nanotube electrodes. All electrodes contain propyl-derived silane and 61%, 44% or 34% (w/w) carbon nanotube. Scan rate: 50 mV/s, different scan rates.

The composition of the electrodes had also great influence in their electron transport properties. The influence of the electrode's carbon nanotube content on the ferrocyanide electrochemistry is demonstrated in Figure 3. The increased amount of the gel forms a barrier on the carbon nanotube surface that hinders the electron transfer. The highest value of observed standard heterogeneous electron transfer constant (k_{obs}°) was found to be 8.9×10^{-3} cm/s for the electrode constructed with the propyl-derived silane containing 61% w/w MWNT. A comparison with various types of different electrodes is presented in Table 1. The electron transfer process for carbon nanotube based sol-gel composite electrodes is faster than for carbon paste electrodes and comparable with the gold-based sol-gel composite electrodes. The favorable electron transfer can be attributed to the electronic properties of the carbon nanotubes.

TABLE 1. k_{obs}° (10^{-3} cm/s) for $\text{Fe}(\text{CN})_6^{-3/4}$ for Several Electrode Materials

Electrode Type	k_{obs}° (10^{-3} cm/s)
Sol-gel/Carbon Nanotubes	8.9
Carbon Paste	0.1 - 3.0*
Sol-gel/Au	10.7
Glassy Carbon	5 - 500**
Metallic (Pt, Au)	100 - 240

* depending on the nature of the oil used in the paste

** depending on the surface pretreatment

Conclusions

A new type of composite electrode based on the combination of carbon nanotubes and sol-gel technology has been reported. This approach combines the advantages of sol-gel based ceramic materials with the favorable electrochemistry of carbon nanotubes. The characteristics of the designed electrodes are controlled by altering the nature (in terms of methyl, ethyl or propyl-derived silane precursor) or the amount of the sol used. The composite electrodes exhibit well-defined electrochemical properties with superior characteristics compare to other carbon based composite electrodes.

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