

Investigation of Multi-Walled Carbon Nanotubes as Electrochemical Electrodes

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Abstract

Individual multi-walled carbon nanotubes were investigated for their usefulness as nanoscale electrochemical electrodes. The nanotubes were mounted on metal-coated atomic force microscopy tips, and the assembly was insulated with Parylene polymer. Approximately 200nm of the nanotube tip was exposed by use of a laser so the entire probe could be immersed in an electrolytic solution with only the nanotube tip left as the electroactive area. The nanotube electrodes were investigated through use of cyclic voltammetry in a solution of 1.0 mM potassium ferricyanide($\text{K}_3\text{Fe}(\text{CN})_6^{3-}$) in a supporting electrolyte of 0.10 M potassium chloride(KCl). It is shown that nanotubes are electrochemically active.

1. Introduction

Nanometer-sized electrodes have become an important tool in studying electrochemistry. Some of these uses include studying the structure of solid/liquid interfaces within nanodomains [1], detecting single molecules [2], and in bioelectrochemistry, probing neurochemical microenvironments, such as

monitoring neural transmitter release [3,4]. Although nanometer-sized electrodes are desirable for electrochemical probing with nanoscale spatial resolution, results from these systems are rare, mainly because of the lack of simple and reproducible methods of creating single electrodes that have very small electroactive areas. Producing such small electroactive areas requires efficient coating techniques, of which there are only a few methods [5].

The purpose of this experiment is to explore multi-walled carbon nanotubes as individual nanoscale electrochemical probes. Cyclic voltammetry measurements were taken with a carbon nanotube as the working electrode to investigate the electrochemical activity of such nanoscale probes.

2. Method

2.1 Voltammetry

Cyclic voltammetry is a common and useful electrochemical procedure used to test the properties of electrodes or solutions. Cyclic voltammetry uses a potentiostat to apply a linearly ramped potential to the working electrode versus a standard reference electrode (an Ag/AgCl pseudoreference in this case). To avoid redox reactions at the reference electrode (which can modify the potential from the desired ramp voltage) the reference electrode must be very high impedance. This is accomplished by an op amp buffer circuit, which takes the reference electrode potential as an input and supplies the necessary current via a counter electrode connected to the op amp output (i.e. current flows between the counter and working electrodes, the latter at virtual ground). The potentiostat provides the cyclic ramp voltage and monitors the working electrode current.

In an electrolytic solution, there are positive and negative ions evenly dispersed throughout. When a voltage is applied between two electrodes, ions respond to the potential by migrating to the electrodes. These charges surround the oppositely charged electrode in a diffuse layer so that little of the potential penetrates the bulk of the electrolyte outside of this diffuse layer. This layer of charge around an electrode is called the Debye layer.

The voltage between the working and reference electrodes in a one-peak, cyclic voltammetry experiment is ramped at a constant rate to a peak value, and then decreased at the same rate to the initial value. This is shown in Fig. 1a. As this voltage is increased, more ions are pulled to the surface of the electrode and if the potential at the electrode exceeds that at which redox can occur electrons are transferred. This transfer constitutes the current through the working electrode (beyond the transient current due to capacitive charging) and is the reason for the sharp increase in current seen in Fig. 1b with increasing voltage. As the bulk of the electroactive ions in the Debye layer are used up, a maximum in this current is reached, shown as the peak in Fig. 1b. Once peaked, the current falls to a steady-state limiting current, which is defined by the rate of diffusion of electroactive ions into the Debye layer surrounding the electrode. As the voltage is then ramped back down to its initial value, the same process can be observed if the electrochemical reaction is reversible.

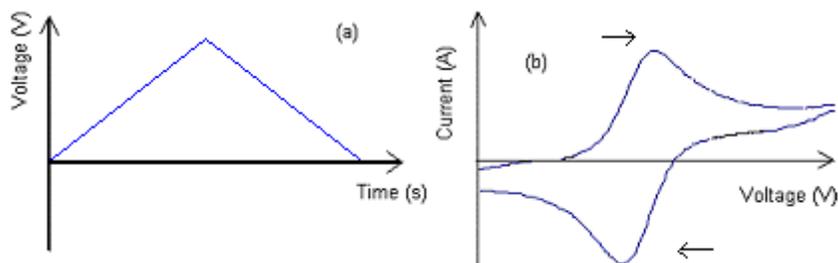


FIGURE 1. (a) Voltage vs. Time in a cyclic voltammetry measurement.

(b) A typical cyclic voltammogram. The top curve represents increasing voltage.

The bottom curve represents decreasing voltage.

2.2 Solution

Often in cyclic voltammetry it is advantageous to use a supporting electrolyte in the electrolytic solution. The supporting electrolyte does not react at the electrodes and is therefore an inert ion in the solution. The supporting electrolyte is added in excess, usually at least a hundredfold greater than the active electrolyte [6]. This excess of charge causes the Debye layer to be more compact. This more compact layer sharpens the peak in the voltammogram, since the Debye layer is more rapidly swept of electroactive species.

In the absence of a supporting electrolyte, there is a deviation from the expected currents. This deviation is far greater for small electrodes, particularly those of nanometer size [5]. Therefore, a 1.0 mM potassium ferricyanide ($\text{K}_3\text{Fe}(\text{CN})_6^{3-}$) solution was used as the aqueous electrolyte with 0.1 M potassium chloride (KCl) as the supporting electrolyte.

2.3 Electrodes

A platinum (Pt) wire was used as the counter electrode, and a silver/silver chloride (Ag/AgCl) wire was used as the pseudo-reference electrode. A multi-walled carbon nanotube was employed as the working electrode. All three electrodes are connected to the potentiostat and immersed in solution. This setup requires that the working electrode be entirely insulated except for the end of the nanotube (~200nm).

The process in creating the probe used as the working electrode requires that a nanotube be attached to a conductive support, and that the entire probe be insulated except for the end of the nanotube. The nanotube was mounted on a palladium (Pd) metal coated atomic force microscopy (AFM) tip. The nanotube was then attached to the tip ensuring that the nanotube and tip were in good electrical contact. The entire structure was then coated with a conformal layer of Parylene, an insulating polymer. The polymer was then evaporated from the nanotube by use of a laser. The only electroactive area left exposed was the tip of the nanotube [7].

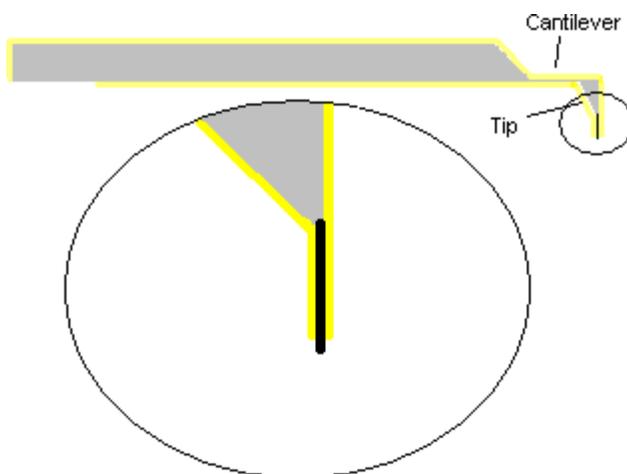


FIGURE 2. Parylene coated, laser exposed carbon nanotube mounted on an AFM probe coated with palladium and parylene. (Pd is shown as gray, parylene is yellow, and the carbon nanotube is black.)

3. Results

Cyclic voltammetric measurements at 50 mV/s were taken with a probe with an exposed nanotube as illustrated in Fig. 2. The capacitive current increased with increasing voltage to about 0.8V. If the voltage is greater than 0.8 V or less than -0.5 V, water begins to dissociate into oxygen gas and H⁺ ions. This is not the reaction of interest, hence potentials were kept within this window.

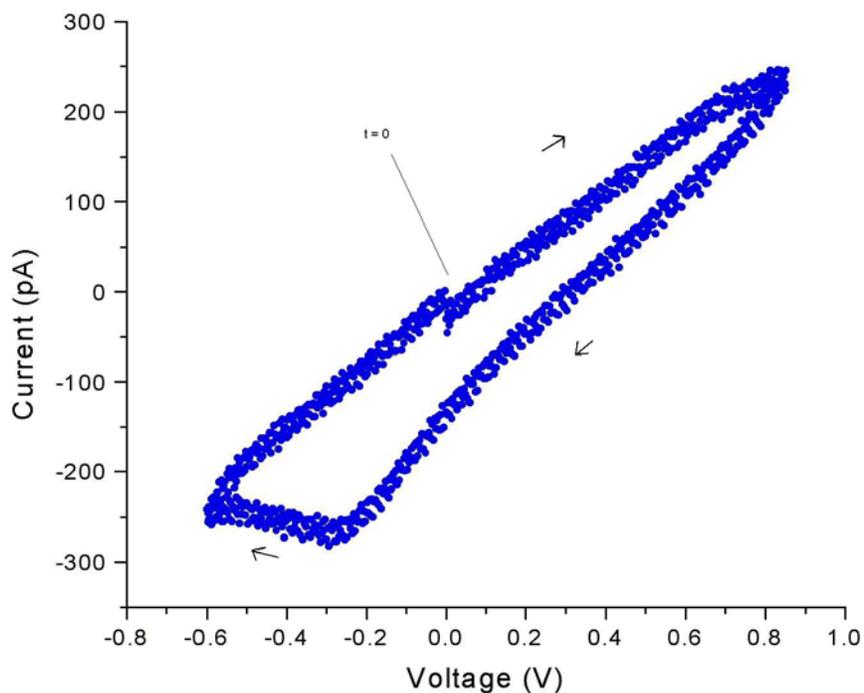


FIGURE 3. Cyclic voltammetric measurement at 50 mV/s in potassium ferricyanide and supporting electrolyte potassium chloride with a carbon nanotube as working electrode.

4. Conclusion

As is seen in Fig. 3, using a nanotube working electrode we observe a reduction peak at $\sim -0.3\text{V}$ with respect to the Ag/AgCl pseudo-reference electrode. These early results indicate that an individual multi-walled carbon nanotube having a nanoscale portion of its length exposed to the electrolyte may serve as the working electrode for

electrochemical measurements. Further work is certainly needed to understand the absence of the oxidative reaction and to quantify the utility of such probes.

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References

- [1] J.D. Norton, H.S. White, and S.W. Feldberg, *J. Phys. Chem.* **94**, 6772 (1990).
- [2] F.-R.F. Fan, J. Kwak, and A.J. Bard, *J. Am. Chem. Soc.* **118**, 9669 (1996).
- [3] A. Kuras and N. Gutmaniene, *J. Neurosci. Methods* **96**, 143 (2000).
- [4] B.J. Venton, D.J. Michael, and R.M. Wightman, *J. Neurochem* **84**, 373 (2003).
- [5] S. Chen and A. Kucernak, *J. Phys. Chem. B* **106**, 9396 (2002).
- [6] G.D. Christian, *Analytical Chemistry* (John Wiley & Sons, New York, 1980), p. 346.
- [7] A. Patil, J. Sippel, G.W. Martin, and A.G. Rinzler, *Nano Letters* **2**, 303 (2004).