Electrochemical Functionalization of CVD-grown Carbon Nanotubes

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We have grown multiwalled carbon nanotubes by chemical vapor deposition onto conductive surfaces such as nickel-plated metal wires. These nanotube-covered wires allow electrical connection through the nanotubes and can serve as the working electrode for voltammetric methods such as cyclic voltammetry. We have found that interfacial electron transfer occurs primarily through the ends of the nanotubes and not through the sidewalls. The CNT electrodes exhibit very high capacitance, presumable through double layer charging along the sidewalls where electrons find a high barrier for charge transfer. The work reported here is focused on creating defects in the nanotube sidewalls through electrochemical means and thus changing the electrochemical performance. We have observed greatly increased redox currents for the treated nanotubes.

The behavior of the CNT electrodes with the ferri/ferrocyanide redox couple is shown in Figure 1 in comparison with a bare gold wire electrode. The large increase in the electrode capacitance is attributed to the large sidewall area relative to the tube ends where ferricyanide redox is thought to occur.

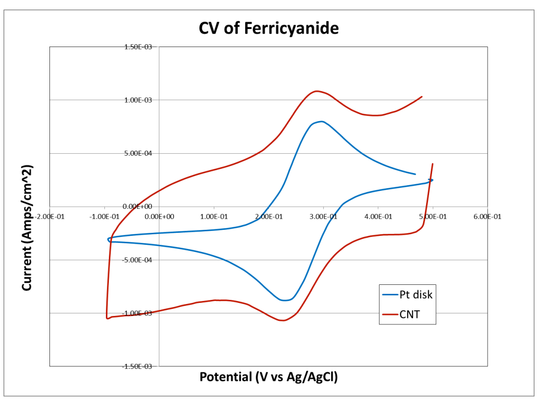

Figure 1: Comparison of platinum with the carbon nanotube electrode.

On cycling the electrode between 0.8 and -0.1 volts (relative to Ag/AgCl) in $K_3Fe(CN)_6$ and KNO_3 , some CNT electrodes develop additional redox couples with greatly enhanced current, see Figure 2. The large current indicates a greatly increased electrode area over the ferricyanide couple and also a higher redox potential. The identity of this new redox couple has not yet been established. However on removing the electrode from the

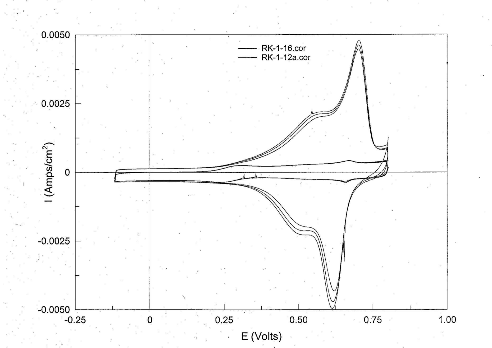

Figure 2: New cathodic and anodic peaks on cuycling the CNT electrode in ferricyanide solution.

ferricyanide solution to a KNO_3 solution, the new redox couples remained while the ferricyanide couple was eliminated. This leads us to believe the nanotube sidewall has been functionalized with a reducible species.

The Raman spectra of the functionalized nanotube shows a new peak at approximately 2700 cm^{-1}, in addition to the D- and G- bands. This leads us to believe that we have attached a reversible redox couple to the sidewalls of the carbon nanotube.

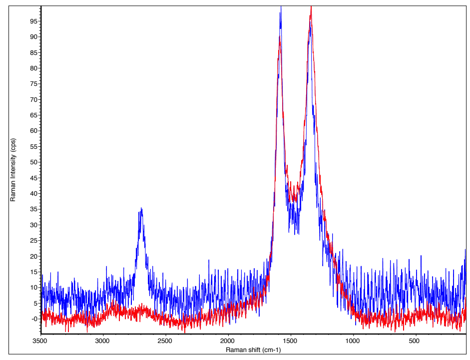

Figure 3: Raman spectra of the functionalized and unfunctionalized nanotubes showing the additional band at 2700 cm^{-1}.