Cyclic Voltammetry and Bulk Electronic Properties of Soluble Carbon Nanotubes

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The progress in the investigation of carbon nanotubes, NT, is growing on a nearly daily basis. NTs are now proposed for innumerable applications in a process that is accompanied by a constantly increasing understanding of many of their properties.[1] Difficult issues, such as their processibility in liquid phases, are being overcome.[2,3] In particular, the technique developed in our laboratories yields functionalized NT, *f*-NT, see Figure 1, with a solubility as high as 50 g L^{-1} [2] through the attachment of pyrrolidines to the external wall of NT. Two major issues with *f*-NT, thus far unsolved, are the nature of their bulk electronic properties and to what extent they retain those of pristine NT. Here we address these questions by a combination of electrochemical measurements and quantum chemical calculations.

Figure 2a shows the cyclic voltammetric (CV) curve in reduction obtained in a saturated *f*-NT solution of tetrahydrofuran, under highly aprotic conditions at a platinum disk electrode ($r = 62.5$ μm). The curve displays a continuum of diffusion-controlled cathodic current, with onset at ∼−0.5 V, which is attributed to the reduction of *f*-NTs (compare background current in red). The broad shoulder at −2.9 V corresponds to an irreversible reduction, likely due to the chemical degradation of multiply reduced *f*-NT. An analogous irreversible CV behavior was found under similar conditions with fulleropyrrolidine C$_{60}$ bisadducts.[4]

Figure 2b extends the CV curve with a smaller electrode ($r = 12.5$ μm). Oxidation beyond 1.8 V triggers electrode fouling and causes the trace crossing observed at 1.45 V, between the forward and backward positive scans, and the large decrease of cathodic current in the second scan toward negative potentials (blue line). This behavior is ascribed to the formation of a film, of possibly decomposed *f*-NT on the electrode, through which electron transfer is hindered. The passive layer is then effectively removed from the electrode surface by scanning the potential beyond ∼−1.8 V (Figure 2b, blue line). The steady-state curve of Figure 2b is stable on repetitive potential cycling over long time periods.

Figure 2c shows that the further reduction of the electrode dimensions ($r = 5$ μm) does not result in a current density increase. Since decreasing the electrode size greatly enhances the mass transport rate,[5] one must conclude that current has reached its kinetic limiting value in the conditions of Figure 2, b and c.[5]

Figure 2d, together with the comparison with Figure 2, b and c, proves that the presence of a self-assembled monolayer of dodecanethiol on a Gold electrode[6] does not modify the CV curve.
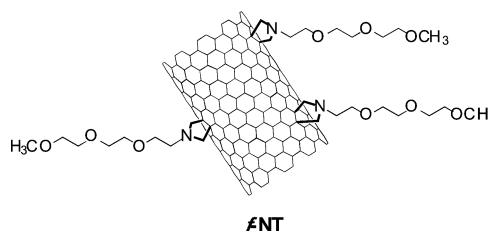

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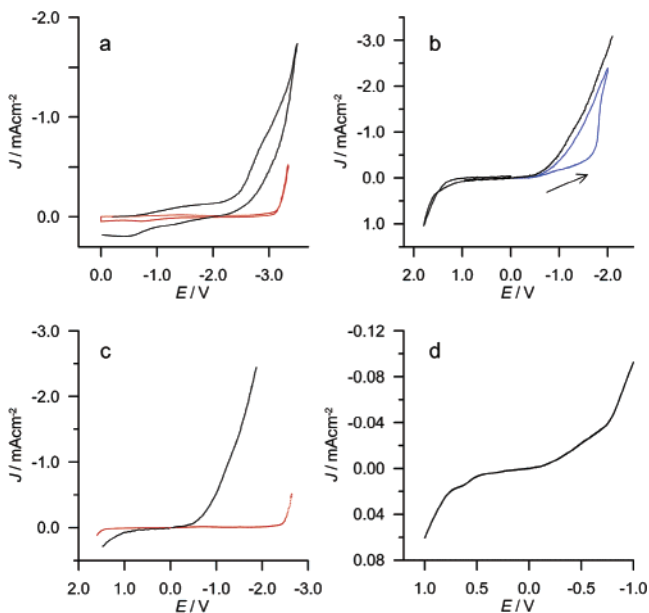**Figure 1.** Partial structure of functionalized NT (*f*-NT) used in this work.

Figure 2. CV curves of saturated f-NTs, 0.01 M tetrabutylammonium hexafluorophosphate, THF solution 1.67 mg mL^{-1}. $v = 0.5$ V/s, $T = 25$ °C: (a) working electrode is Pt disk ($r = 62.5$ μm); (b) working electrode is a Pt disk with $r = 12.5$ μm. In blue, the second scan toward negative potentials after the positive scan up to 1.8 V; (c) working electrode is a Pt disk with $r = 5$ μm; (d) working electrode is a gold electrode (area: 0.5 cm^2) derivatized with a dodecanethiol self-assembled monolayer. In (a) and (c) the red curve corresponds to the response of the blank supporting electrolyte solution. Potentials are measured vs silver quasi-reference electrode: cathodic (negative) currents correspond to reduction (transfer from the electrode to the NT), while anodic ones (i.e., positive) correspond to oxidation (transfer from the NT to the electrode).
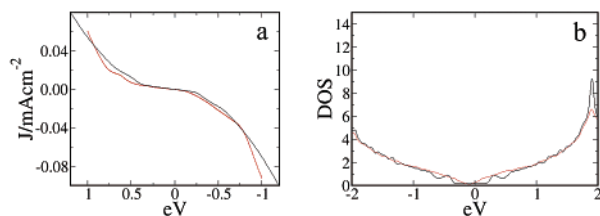
However, the presence of the organic monolayer slows down the purely electron transfer, which is therefore the sole responsibility for the signal (corrections for the effect of diffusion is carried out using standard convolution techniques[6]).

Figure 3. (a) Comparison of the experimental current (red line) of Figure 2d with the calculated current (black line) for pristine NT; (b) comparison of the averaged DOS for pristine (black line) and functionalized NT (red line). The DOS units are normalized to the states of C atom. The energy level in Figure 3a is measured with respect to the Ag quasi-reference electrode, that is ~-4.7 eV with respect to the energy of a free electron in a vacuum.

Several points are worth emphasizing: (i) The present electrochemical measurements differ at a fundamental level from those obtained by scanning tunneling microscopy[7] because they reflect average collective values rather than single f-NT properties. (ii) The nonzero slope where the CV behavior of f-NT switches from cathodic (electron transfer to empty states) to anodic (electron transfer from filled states) at ~-0.05 V is indicative of the presence of metallic behavior. In turn, this indicates that functionalization does not strongly modify the bulk or averaged electronic structure of the NT. Notice that, at least for another class of f-NT, the metallic tubes react preferentially and should therefore be the most affected.[8] (iii) The purely electronic current is related to the electronic density of states, which can be calculated quantum chemically and used for a comparison to understand the modifications introduced by functionalization.

Indeed, in the condition of the experiments, the current, i, can be calculated from the electronic density of states[6]

$$i(E_f) \propto \int_0^{E_f} (\text{Density of States})dE \qquad (1)$$

To calculate the density of states, DOS, we use a tight binding model, with periodic boundary conditions, that accurately reproduces high level quantum chemical results for carbon nanotubes[9] and consider the 39 NT with diameters between 8.82 and 12.20 Å that cover 75% of tubes contained in the HiPCO synthesized sample that is used here to prepare f-NT.[10] The complete list of the NT is given as Supporting Information together with their diameter, angle pitch, and unit cell size. Their relative weight in the overall DOS is taken from ref 10 and is also given in the SI.

Figure 3a compares experimental and calculated currents. The experiments are relative to f-NT, while the calculations are for pristine systems. The good agreement between the two currents appears as a further indication that functionalization does not strongly modify the bulk electronic properties of the tubes.

Addition patterns to NT are still the subject of major investigations.[8] Despite this uncertainty, we decided to calculate the density of states for random functionalization patterns. Compatibly[11] with the number of atoms in the NT unit cell, the effect of a pyrrolidine group every 80 carbon atoms was introduced. Notice that this is a slight excess with respect to the estimated percentage of functionalization which, in the case of the formation of pyrrolidines on the

NT surfaces, is one group in 100 carbon atoms of the NT.[2] For each NT of the 39 NT, the random functionalization was repeated until the average DOS converged. Figure 3b shows the weighted sum of the DOS of the f-NT, and compares it with the result for pristine NT. For the weights, see Supporting Information. The bulk DOS is not strongly affected by the chemical modification and shows the presence of filled, i.e., metallic states. While this is in agreement with the previous discussion, an important feature of the DOS of f-NT is the smoothing of the peaks that appear upon averaging of the pristine NT DOS at about ±0.5 eV. They are related to the van Hove singularities between which electronic transitions take place. Experimentally (see Figure 3 of ref 2a) this class of f-NT shows a rather flat near-infrared spectrum, which agrees with the calculated smearing of the DOS.

In conclusion, we have shown that electrochemistry and quantum chemical simulations can be used to investigate the bulk electronic properties of a class of f-NT. Functionalization obviously modifies the electronic state of pristine NT, for instance, the low lying electronic transitions.[2] However, the present work shows that (some) metal character is retained and that the overall electronic density of states is not strongly affected when the functionalization is carried out on the NT through the formation of pyrrolidine rings.

Supporting Information Available: Experimental and computational details plus the complete list of NT used in the calculation of the density of states together with some of their characteristics.

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(11) The number of atoms present in the unit cell may cause small variations in the percentage of functionalized bonds.

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