

Improving Single-Carbon Nanotube-Electrode Contacts using Molecular Electronics

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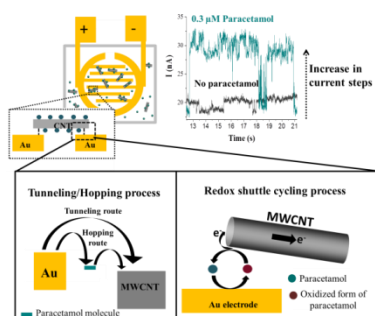
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We report the use of an electroactive species, acetaminophen, to modify the electrical connection between a CNT and an electrode. By applying a potential across two electrodes, some of the CNTs in solution occasionally contact the electrified interface and bridge between two electrodes. By observing a single CNT contact between two microbands of an interdigitated Au electrode in the presence and absence of acetaminophen, the role of the molecular species at the electronic junction is revealed. As compared with the pure CNT, the

current magnitude of the acetaminophen-modified CNTs significantly increases with the applied potentials, indicating that the molecule species improves the junction properties probably via redox shuttling.

TOC GRAPHICS



KEYWORDS Electrical contact, Carbon nanotube, Acetaminophen (Paracetamol)

Carbon nanotubes and their derivatives are commonly applied as both catalyst supports and catalysts in many electronic devices¹⁻². To achieve high performance electronics, researchers have focused intensive efforts into developing the chemical and physical properties of new materials but largely ignore the potentially fundamental problem of forming a high quality contact with the electrochemical substrate. When two materials are brought into contact, the junction causes a potential drop in the system resulting from a “contact resistance”³. Depending on the structure of the CNT and the operating temperature the nanomaterial can be either metallic or semiconducting⁴. It is a common assumption that the contact resistance at a CNT-metal junction is relatively small and follows an ideal Ohmic behavior. However, Lim, S.C. *et al.* showed that even for metallic type CNTs the Fermi level between metal and CNT does not perfectly align resulting in a gap between their energy

levels which is dependent on the metal type and their oxide barriers⁵. For semiconducting CNTs, the key factor is reportedly the band alignment of electronic energy level at their interfaces resulting from the difference in their material work functions. This phenomenon is known as a Schottky barrier⁶.

To understand the junction properties of metal/CNT interfaces, previous work has developed the “nano-impact” methodology as a route to measuring the resistance across individual CNT-electrode contacts⁷. In these experiments a single CNT in the solution phase may form a bridge across two adjacent gold electrode contacts (as shown in a schematic in Figure 1). When a nanotube diffuses to an electrode array and transiently sticks to the surface with an applied voltage difference across the two gold electrodes, the magnitude of current increases upon arrival of a CNT. This yields a measure of the resistance across the CNT bridge. The total resistance (R_{tot}) across the bridge can be viewed as being composed of three contributing terms, the internal resistance of individual particle (R_{int}) and two contact resistance ($2R_c$) between the gap of particle and electrode. From previous experiments an average bridging resistance of $1.1 \pm 0.1 \times 10^8 \Omega$ was measured for individual CNT. The magnitude of this resistance is significantly higher than the expected internal resistance of individual CNTs which ranges from 7.8 to 117 $\mu\Omega\cdot\text{m}$ (values reported relate to a CNT of 5 μm in length and 100 nm in diameter)⁸, indicating that it is not reasonable to assume that the potential drop from the electrode to the CNT is negligible.

Herein, the contact resistance between MWCNTs and Au electrodes are studied via the “nano-impact” technique⁷, first demonstrating the applicability of technique for smaller multi-walled carbon nanotubes. In this work bamboo-like CNTs with an average diameter of 30 nm and length in the range of 5-20 μm are utilized. Second, this work demonstrates how the presence of a redox active moiety in trace concentrations (0.1-0.4 μM) can alter the behaviour of the CNT/Au contact.

For nano-impact experiments, the IDE-Au electrode was immersed in a 0.05M phosphate buffer solution (PBS, pH 7.5) containing 2.4×10^{-13} M MWCNTs. No surfactant is added in the solution. A potential difference (0.10 – 1.0 V) was applied between the two interdigitated bands and the current recorded as function of time. Examples of the current-time responses recorded at the different applied potentials of 0.20, 0.40, and 0.60V are shown in Figures 1A, B, and C, respectively. The presence of MWCNTs in solution leads to the observation of steps in the current transients. These steps are attributed to the arrival of a single MWCNT at the electrode interface and where it bridging across two adjacent electrode contacts. The magnitude of the step was measured relative to the background signal. At low potentials (< 0.10 V), the bridging of an MWCNT only results in a small current step which is difficult to differentiate from the background. However, at potentials above 0.20 V (Figure 1A), current steps are clearly observed with a *near* linear increase in the step size after the applied potential difference. From the measurement of more than 100 collisions at each potential with the varying impact durations (from 150 ms to 350 ms), the average step current at different applied potentials is plotted against the applied potential (see Figure 1D). The slope from linear fitting I-V curve represents the average total resistance of a single MWCNT contacting between two bands of gold with a mean value of $2.6 \pm 0.1 \times 10^8 \Omega$. Deviations from linearity in figure 1D may reflect the non-constant density of electronic states near the Fermi level of the MWCNTs⁹. In comparison with our previous report⁷, even though the sizes and morphology of MWCNTs, and type of supporting electrolyte are different, the contact resistance in both works is of a similar magnitude, 10-30 G Ω . This observation again evidences that the contact resistance dominates the electrical response and that in this limit the response is largely independent of the intrinsic properties of the CNT.

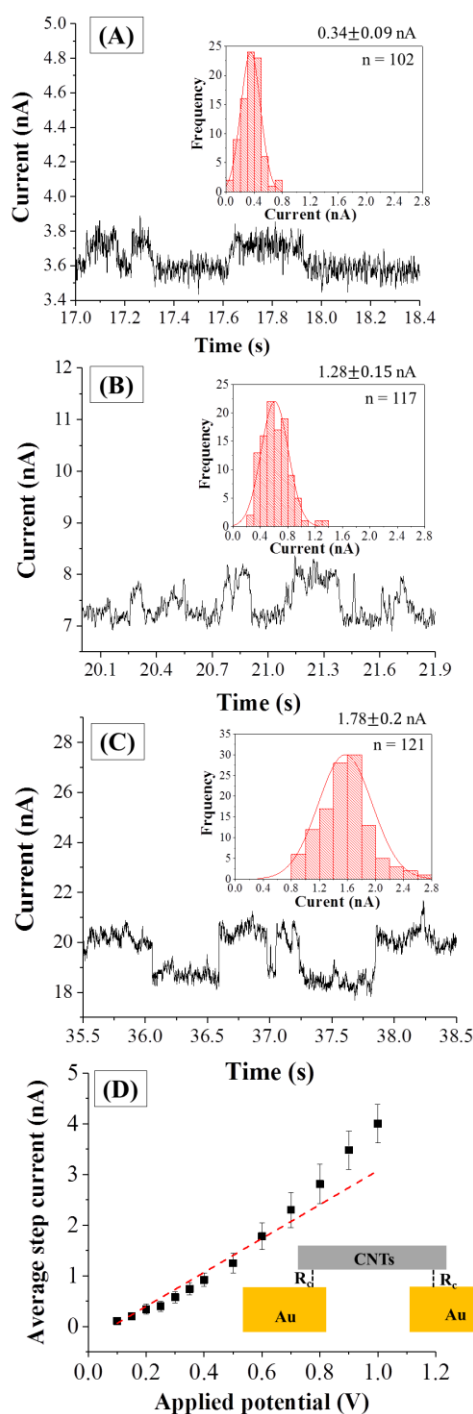


Figure 1. (A) Chronoamperometric profiles of IDE-Au in 2.4×10^{-13} M MWCNTs in 0.05 M PBS (pH 7.5) at different applied potentials (A) 0.2 V, (B) 0.4 V, and (C) 0.6 V, and (D) Average step current of MWCNTs (2.4×10^{-13} M) at different potential across two bands of IDE-Au. Dashed red line is the linear fitting curve. All inset images show the distribution of current steps.

Having evidenced the ability to detect and quantify the nanotube-electrode contact the work next moves to consider how the presence of adsorbed species may modulate and control the properties of the electrical contact. To this end, the MWCNTs were modified with acetaminophen (“paracetamol”). Cyclic voltammetry was then used to evidence the occurrence of the adsorption to the CNT surface further allowing the influence of the supporting electrode, accumulation time of paracetamol adsorption and paracetamol concentrations to be probed. In these experiments, the paracetamol modified MWCNTs were drop cast onto the surface of a carbon electrode and voltammetry run on the immobilised layer. More information is provided in the SI section 2. Figure 2 shows the voltammetric response of a MWCNTs modified BPPG electrode after immersion for one hour into solutions containing various paracetamol concentrations before being transferred to blank PBS for voltammetric analysis. The electrochemical redox response shows a clear quasi-reversible surface bound wave with an anodic oxidation peak at ca. 0.42 V (vs. SCE) and a cathodic reduction peak at ca. 0.24 V (vs. SCE). This electrochemical process corresponds to the oxidation of paracetamol generating two electrons, two protons and an oxidized form of N-acetyl-p-quinoneimine (NAPQI)¹⁰⁻¹² (see in the schematic in Figure 2) . As the concentration of paracetamol in the initial adsorption solution increases the anodic peak area increases (see Figure S6) . The surface coverage of the adsorbed paracetamol molecules at equilibrium can be expressed using a Langmuir isotherm as described elsewhere¹³. The equation is displayed in eq.(1) in the SI (section 4.1). The plot of $\frac{1}{\theta}$ against $\frac{1}{[C]}$ (see in Figure S6) shows a good linear relationship ($R^2 \approx 0.995$) with an intercept (y-axis) of 1.07 ± 0.1 , where θ is the fractional surface coverage of the adsorbed paracetamol molecules and $[C]$ represents the paracetamol concentration. The value of the adsorption equilibrium constant (K) can be determined from the slope of the straight line which is equal to ca. $0.022 \mu\text{M}^{-1}$.

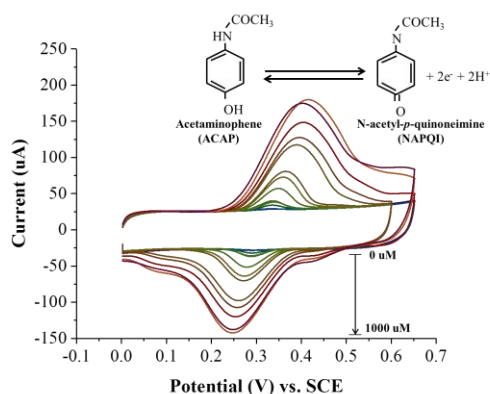


Figure 2. Cyclic voltammograms of MWCNT/BPPG electrode after immersed in 0.5, 1, 2, 5, 10, 15, 20, 25, 50, 75, 100, 200, 300, 400, 500, and 1000 μM Paracetamol (60 min) tested in 0.05 M PBS pH 7.5 at a scan rate of 100 mVs^{-1}

Having evidenced the adsorption of paracetamol on to the MWCNTs, the nano-impact of paracetamol-modified MWCNTs was next studied. The potential difference (0.1-1.0 V) was applied between the two microbands of IDE-Au immersed in the suspensions of $2.4 \times 10^{-13} \text{ M}$ MWCNTs containing different amounts of paracetamol in PBS (pH 7.5). The concentrations of paracetamol employed were 0.10, 0.20, 0.30, and 0.40 μM , corresponding to the paracetamol coverages (Γ) on MWCNTs of 1.7×10^{-13} , 3.5×10^{-13} , 5.2×10^{-13} , $6.9 \times 10^{-13} \text{ mol/cm}^2$, respectively (see in The SI section 4.2). The current signal was recorded as a function of time and representative resulting chronoamperograms are shown in Figure 3A.

As with the nano-impact currents of bare MWCNTs in the absence of paracetamol, the impact features of paracetamol-modified MWCNTs (Figure 3A) show current ‘steps,’ with an impact duration in the range of 150 ms to 390 ms. During the measurements, more than 80 collision events were observed and analyzed at each potential. The average values of current steps are plotted as a function of applied potential, as shown in Figure 3B. At potentials below ca. 0.20 V, the step currents of the paracetamol-modified MWCNTs are similar to that of the bare MWCNTs. However, at higher potentials ($E > 0.30 \text{ V}$) the step

currents of the paracetamol-modified MWCNTs become significantly larger than observed for the bare MWCNTs. The magnitude of the step currents increase further with increasing concentration of paracetamol in solution and hence with the increasing coverage of paracetamol on the MWCNTs. At a fixed concentration of paracetamol, the step currents increase non-linearly with the applied potentials. Note that the free paracetamol present in the solution is due to the desorption behaviour of the material.

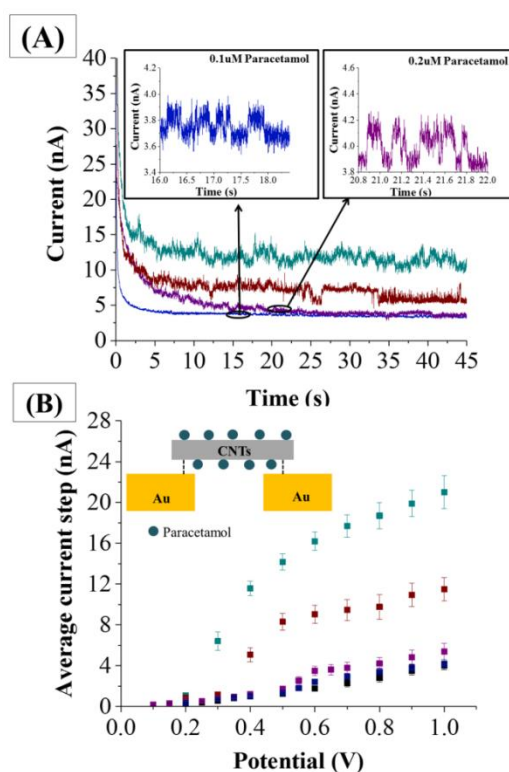


Figure 3. (A) Chronoamperometric profiles of IDE-Au at 0.2V in suspension of MWCNTs (2.4×10^{-13} M) containing different paracetamol concentrations (0.1 μM (navy), 0.2 μM (purple), 0.3 μM (red), and 0.4 μM (green)) in 0.05 M PBS (pH 7.5), Zoom in profiles at 0.1 μM, and 0.2 μM paracetamol, and (B) Average step current of different concentrations of paracetamol at various applied potentials.

The higher step currents of the paracetamol-modified MWCNTs as compared to the bare MWCNTs indicate a decrease in the resistance across the gold/CNT contact. As will be

discussed further below, this may arise either due to the paracetamol modifying the properties of the contact or may result from a Faradaic electron transfer process. First, in the absence of paracetamol the step currents relate to electrons tunneling between the MWCNT and Au electrode. As an electron has to tunnel through a small gap between the two materials, the rate of electron tunneling also depends on the nature of the medium contained in the gap¹⁴. Consequently, the presence of paracetamol, may serve to locally alter the intermolecular force between the solvent-solvent interaction, enhancing the rate of the electron tunneling across the gap between MWCNT and Au. Moreover, depending on the position of the paracetamol molecular energy level, its presence in the junction may enable an electron hopping mechanism across the void. Alternately the paracetamol may act as a redox shuttle cycling between the electrode and MWCNT. The presence of a significant contact resistance between the Au electrode and the CNT necessarily implies a potential drop across this junction. Since the potential drop is large enough the Au and CNT may act as a generator/collector system¹⁵⁻¹⁶ (see schematic presentation in graphical abstract). The current-potential plot shown in Figure 3B further supports this mechanistic interpretation as the step currents of paracetamol-modified MWCNTs only become larger after a threshold potential has been passed. Plausibly both paracetamol in solution and the paracetamol adsorbed on the surface of MWCNT can contribute to this mechanism. The adsorption of the molecules on the MWCNTs likely pre-concentrates paracetamol in the proximity of the contact between the MWCNT and the Au electrode.

In summary, by measuring the current signal across the bridge of single paracetamol modified MWCNT contact between the two microbands of the IDE-Au, the current response of paracetamol modified on MWCNT is significant higher than the bare MWCNT, indicating that the electronic properties of the single MWCNT-Au contact are improved by modifying

MWCNT with paracetamol. The adsorbed paracetamol molecules contribute to promoting the electron transfer processes between the junction of two materials.

ASSOCIATED CONTENT

Supporting Information.

The supporting information consists of four sections, experiment, paracetamol adsorption kinetic study, supporting figures, and calculation. The supporting figures include the IDE-Au electrode image, the optical microscope images of the CNTs, comparison of the cyclic voltammogram of MWCNTs modified different carbon-based electrodes (i.e., GCE, EPPG, and BPPG) adsorbed with paracetamol in PBS (pH 7.5), cyclic voltammogram of MWCNTs/BPPG modified in various paracetamol concentrations, and the study of paracetamol desorption via cyclic voltammetry.

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Notes

The authors declare no competing financial interest.

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