

Quantifying Single Carbon Nanotube-Electrode Contact via the Nanoimpact Method

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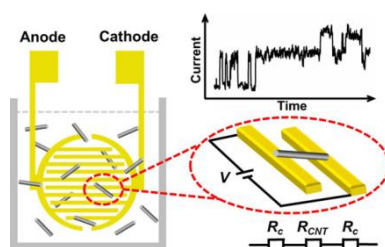
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ABSTRACT

A new methodology is developed to enable the measurement of the resistance across individual carbon nanotube-electrode contacts. Carbon nanotubes (CNTs) are suspended in the solution phase and occasionally contact the electrified interface, some of which bridge a micron sized gap between two microbands of an interdigitated gold electrode. A potential difference is applied between the contacts and the magnitude of the current increase after the arrival of the CNT gives a measure of the resistance associated with the single CNT-gold contact. These experiments reveal the presence of a high contact resistance ($\sim 50 \text{ M}\Omega$) which significantly dominates the charge transfer process. Further measurements on ensembles of CNTs made using a dilute layer of CNTs affixed to the interdigitated electrode surface and measured in the absence of solvent showed responses consistent with the same high value of contact resistance.

TOC GRAPHICS



The development of energy transformation technologies is, in part, built on the production of new and advanced catalytic materials.¹⁻³ These materials often seek to lower the overpotential associated with a redox reaction, prime examples being the reduction of oxygen or the oxidation of organic fuel stocks.⁴⁻⁷ Carbon nanotubes feature extensively in this work both as catalyst supports and as catalysts in themselves, either chemically modified or not.^{6, 8} At early stages of development the synthesized material of interest (i.e. CNTs) is often added as a layer on to a supporting electrode, the resulting electrochemical response of the modified electrode is recorded and used to evidence the ‘activity’ of the catalyst. SI section 1 provides an illustrative overview of some of the numerous reports in the literature based on the use of CNTs as electrode materials and as the bridge between two electrodes. Importantly, it is commonly implicitly assumed that an ohmic contact with a relatively small resistance between the supporting electrode and the material of study is made. This issue of electrical connectivity becomes yet more complex when multilayer formations of the catalyst are considered.

Recent work focusing on the electrochemical response of *individual* carbon nanotubes (CNTs) has demonstrated how the connectivity of the material to the electrode surface influences the electrochemical response.⁹⁻¹⁰ Specifically the behavior of individual CNTs has been shown to be highly sensitive to the nature and quality of the contact with the electrode. Although removal of the solvent via drying the contact has been found to experimentally improve the systems response, an apparently large contact resistance is still observed (see SI section 2). However, direct information regarding the connectivity of a carbon nanotube to an electrode surface is not readily obtainable using conventional electrochemical techniques. The present work seeks to answer the question of the magnitude of the resistance between a single CNT and electrode, and then extends the study to consider ensembles of CNTs which are shown to have a similar high

contact resistance to the single tube measurements. To enable single tube measurements, a method called nano-impact is applied based on using multi-walled carbon nanotubes (MWCNTs) to bridge a micron sized gap between two electrodes. Previous work using the nano-impact method relates to the measurement of electrical currents arising from an electrochemical reaction at the nanoparticle/solution interface. Conversely, in the present work, by contacting two electrodes with different potentials a current is induced to occur *across* the CNT. The magnitude of the current increase after the bridging of the CNT allows the associated resistance to be readily measured, revealing the presence of a high contact resistance of the single CNT-gold contact. The MWCNTs are semi-metallic and their inner conductivity sufficient that no significant potential drop occurs along the length of the nanotube. Conventional methods of measuring contact resistances as previously reported require complicated device fabrication and can only measure a single or a few CNTs in an experiment.¹¹⁻¹² In contrast, the present methodology enables a simple, statistical and non-destructive measurement of the contact resistance between the CNT and electrode, and is a novel application of the nano-impacts technique.

The CNTs used in this work were characterized with Transmission Electron Microscopy (TEM) and dark-field optical microscopy. In order to form a suspension of the carbon nanotubes in solution, sonication of the sample is conducted in a Fisherbrand ultrasonic bath S60 (230V 50/60Hz 150W). The influence of sonication upon the tube length is assessed using dark-field optical microscopy. As shown in Figure 1A, tube shaped nanostructures are observed in the TEM image and the diameter distribution of the tubes is displayed in the inset of Figure 1A. The analysis of typical TEM images gives the mean diameter of the CNTs to be 100 ± 29 nm (96 samples). The inset of Figure 1B shows a representative optical microscopy image of CNTs after

sonication for 10 min. Well dispersed individual CNTs were observed. The analysis of the images gives the length distribution of the CNTs (Figure 1B) and the mean length to be 7.1 ± 6.7 μm (412 samples). In the absence of sonication, although the tubes were found to be on average longer (13.3 ± 10.3 μm , 292 samples) they are highly agglomerated and unsuitable for use in the subsequent experiments (see SI section 4 for more details on the influence of sonication).

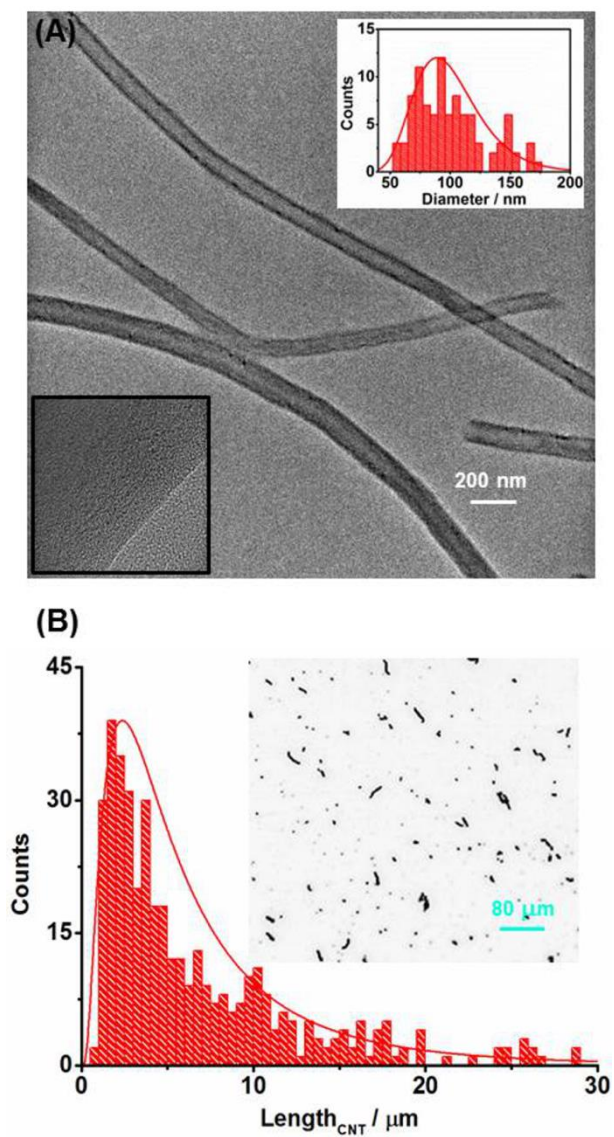


Figure 1. (A) Typical TEM image of the CNT. Upper inset is the diameter distribution of the CNT. Lower inset shows the amorphous outer edge and structured inner part of the CNT. (B) Length distribution of CNTs shown in dark-field optical microscopy images. The inset is a typical image of CNTs. The contrast of the image has been inverted for clarity.

As a first approximate route to determining the resistance between the electrode and carbon nanotube a suspension of carbon nanotubes (0.70 ng) in ethanol was drop cast on to a gold interdigitated band electrode array (IDE-Au). The array consists of 180 pairs of bands which are 5.0 mm in width and separated by 5.0 mm gaps. An illustration of the electrode, an optical microscope image and a picture of the whole electrode are shown in the Scheme S1, SI section 5. More detailed parameters and images of the electrodes can be found on the website of Micrux Technologies in Spain (ED-IDA3-Au). Upon evaporation of the solvent (drying under an N₂ atmosphere) the carbon nanotubes form a sub monolayer coverage (<0.1%) on the surface. A significant number of these tubes will contact both sets of arrays on the electrode surface. Hence, upon application of a potential difference between the two sets of electrodes an electrical current is passed, the magnitude of which is equal to the sum of the currents across all of the bridging contacts. The chronoamperometric response of the modified IDE-Au was measured using potential differences of 0.1, 0.3, 0.6, 0.9 V between the two sets of electrodes (SI section 6). The magnitude of the recorded current scales approximately linearly with the applied potential difference and in the absence of CNTs the current across the two electrodes is negligible. A plot of the average current measured against the applied potential was fitted and the resistance between the two arrays of microbands was determined to be $5.9 \times 10^4 \Omega$. From knowledge of the mass of CNTs dropcast onto the surface and that from optical microscopy 79 wt. % are determined to have lengths greater than 5 μm . Then the number of tubes on the surface able to

bridge the contact between the two interdigitated electrodes is predicted to be $\sim 4.4 \times 10^3$. On this basis the resistance per tube is predicted to be $2-3 \times 10^8 \Omega$ (see SI section 6). Although indicative of a large contact resistance between the carbon nanotubes and the electrode, the above interpretation is subject to a number of assumptions. Specifically the potential drop between the CNT-CNT contacts¹³ and the orientation of the tubes will be influential. Consequently, in order to gain a more accurate measurement of the resistance associated with the carbon nanotube a series of experiments on *individual* nanotubes were performed.

Bridging contacts associated with individual carbon nanotubes were investigated by submersion (vertically) of the interdigitated electrode array into a carbon nanotube containing solution (1.2×10^{-13} M, subject to 10 minutes sonication). The suspension contained no electrolyte. Due to Brownian motion the tubes collide randomly with the array. If a potential difference is held across the two interdigitated contacts and assuming an electrical contact is made between them, then an increase in current will be recorded corresponding to the presence and arrival of a carbon nanotube at the interface. The magnitude of the current gives a gives a direct measure of the resistance associated with the bridge between the two interdigitated electrodes. Experimentally, in the absence of CNTs the background signal is related to small parasitic current between the interdigitated arrays, which is slightly variable (Figure S4) and the average corresponds to a resistance of $\sim 0.5 \text{ G}\Omega$. In the presence of CNTs current features were observed. A typical chronoamperometric profile is shown in Figure 2A (blue line). Although no features are present on some chronoamperometric profiles, a number of scans exhibit continuous current steps, where the current switches between two (Figure 2A) or more (Figure S5) apparently discrete levels. These steps are ascribed as relating to the collision of individual CNTs with the IDE-Au. Some of the impacting CNTs lie on the surface of the IDE-Au, and for those with the length over $5 \mu\text{m}$

their landing may bridge the gap between neighboring bands and consequently switch 'on' the electric circuit (Figure 2B). The regular current steps in one or more consecutive scans were recognized to be one collision event and attributed to the physical motion of the landing CNTs during the contact. 79 collision events (at 0.1 V) of individual CNTs were recorded with chronoamperometry and the current steps were analyzed, giving a mean current of $5.5 \pm 0.3 \times 10^{-10}$ A. The distribution of the current steps is shown in the inset of Figure 2A.

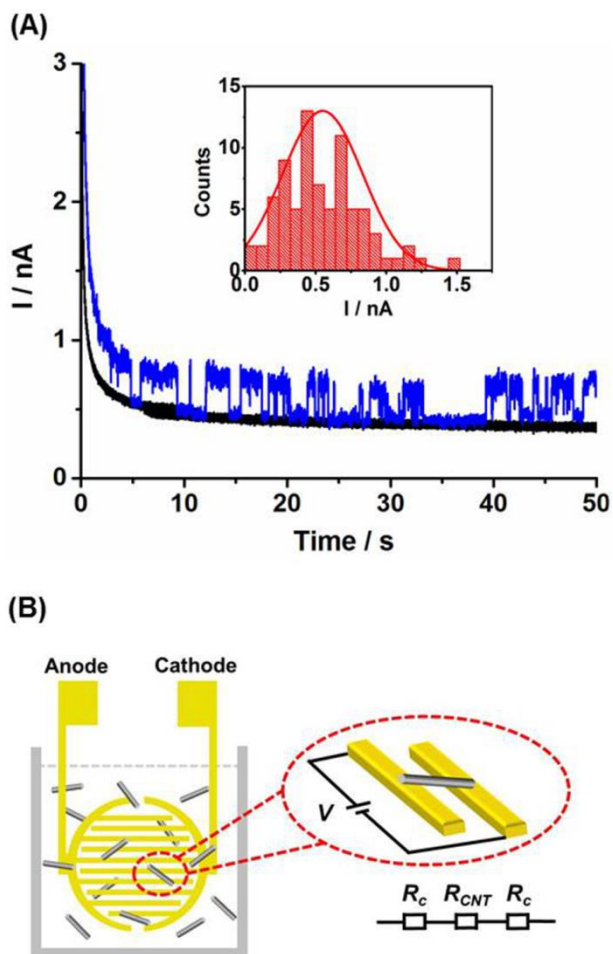


Figure 2. (A) Chronoamperometric profiles of IDE-Au in pure ethanol (black line) and a suspension of CNT (1.2×10^{-13} M) (blue line) at 0.1V. Inset: the distribution of current steps from 79 collision events. (B) Illustration of the nano-impact experiment of CNTs at IDE-Au.

In order to further evidence that the recorded current fluctuations are in fact associated with the carbon nanotubes, nano-impact experiments were also performed in the suspension of the CNTs with 120 min of sonication treatment. No current steps were detected (Figure S6) in the chronoamperometric profile. From the optical microscopy measurements after 120 min of sonication the CNTs have a mean length of $3.2 \pm 2.3 \mu\text{m}$ (Figure S2C). Consequently, after such a duration of sonication few of the tubes have the required length to bridge the inter-electrode gap. Since the concentration of the remaining CNTs longer than $5 \mu\text{m}$ is very low, the frequency of the collision events is decreased to undetectably low levels during the period of the measurement.

Quantitative evaluation of the electrical transport performance of single CNTs on the gold substrate was further carried out by investigating the current steps at four different potentials applied between the arrays of microbands. Figure 3A shows the representative chronoamperometric profiles of IDE-Au in a suspension of CNTs ($1.2 \times 10^{-13} \text{ M}$) at 0.1, 0.3, 0.6 and 0.9 V. It is found that the current steps increase with the increase of the applied potential. During the measurements, 79, 58, 60, 44 current steps were collected at 0.1, 0.3, 0.6 and 0.9 V respectively, and the plot of average current against potential shows good linearity (Figure 3B). Note that the current for each step was obtained by averaging the recorded current on the step. From the slope of the linear fitting the average total resistance of a single CNT bridging two gold substrates was realised with the nano-impact method and determined to be $1.1 \pm 0.1 \times 10^8 \Omega$. It should be recognized that the magnitude of the measured resistance is sensitive to the nature of the CNTs and the surface of the electrode.

Returning to the ensemble experiments where a layer of CNTs were dropcast so that when 0.7 ng of CNTs were affixed to the IDE-Au, the maximum number of the CNTs which are able to bridge the gaps of the IDE-Au can be estimated to be 4.4×10^3 (see SI section 6). Therefore, the expected resistance from a single CNT-gold contact in air is calculated as $2.6 \pm 0.4 \times 10^8 \Omega$ by directly multiplying 4.4×10^3 to the total measured resistance ($5.9 \pm 0.8 \times 10^4 \Omega$) of the dropcast CNTs. This value is comparable to that ($1.1 \pm 0.1 \times 10^8 \Omega$) obtained from the single CNT-gold contacts in ethanol via the nano-impact method. It is therefore indicated that, in terms of the electron transport performance, the property of the CNT-gold contacts in ethanol is similar to that in the dropcast CNTs which is *dry* and performed in the absence of a solution phase. The slightly higher value of single CNT-gold contact resistance estimated from the ensemble measurement than that directly obtained using the nano-impact method is attributed as relating to a possible overestimate of the number of CNT bridging contacts formed.

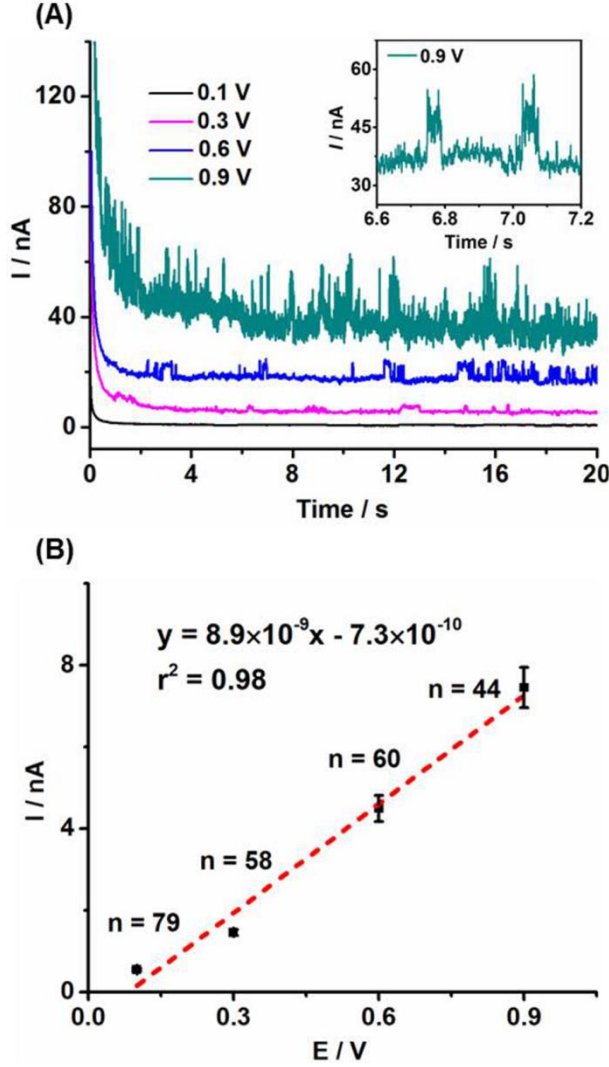


Figure 3. (A) Chronoamperometric profiles of IDE-Au in a suspension of CNT (1.2×10^{-13} M) at 0.1, 0.3, 0.6 and 0.9V. The Inset is a zoom in of the profile at 0.9V. (B) The average step current at 0.1, 0.3, 0.6 and 0.9V. Dashed red line is the linear fitting curve.

We next consider the origin of this ~ 100 M Ω bridging resistance. As schematically shown in Figure 2B, for a single CNT with two ends contacting the gold substrate, the total measured resistance (R_{tot}) consists of the internal resistance of the CNT (R_{CNT}) and two contact resistances ($2R_c$) between the CNT and gold substrate. It has been reported that R_c contains both an intrinsic (R_{int}) and extrinsic (R_{ext}) component.¹² R_{int} is the quantum resistance ($R_{\text{int}} = R_q = 3.25$ k Ω)

arising from interfacing with a quantum confined system,¹⁴ while the R_{ext} component results from the transport of carriers at the CNT-gold contact. The literature reported resistivity of individual CNTs ranging from $7.8 \mu\Omega\cdot\text{m}$ to $117 \mu\Omega\cdot\text{m}$,¹⁵ moreover, the R_{CNT} of a single CNT with $5 \mu\text{m}$ in length (the distance between the electrode arrays) and 100 nm in diameter can be estimated to be within the range of $0.8\text{-}15 \text{ k}\Omega$. This value for R_{CNT} is significantly less than the measured resistance ($1.1 \pm 0.1 \times 10^8 \Omega$) for an individual bridging contact. Moreover, the magnitude of the impact currents is found to be insensitive to the size of the gap between the two electrodes, see SI section 10. Hence, it is concluded that the major component of the measured resistance is associated with the contact between the gold and carbon materials. The magnitude of this measured contact resistance ($\sim 50 \text{ M}\Omega$) is significant and implies that, for many experimental cases, a practical limit in terms of the current per particle may exist. For an isolated particle with an associated current of only 1000 pA and a contact resistance of $50 \text{ M}\Omega$, a measurable (50 mV) drop in potential at the electrode/particle interface will exist. An important and yet unanswered question is how the morphology and architecture of large ensembles of tubes – with numerous electrode-CNT contacts – may influence the connectivity of the entire CNT catalyst network.

In conclusion, the present method allows the rapid measurement of the resistance across individual CNT-electrode contacts. The charge transfer process is shown to be significantly dominated by the presence of a high contact resistance ($\sim 50 \text{ M}\Omega$). This is consistent with ensemble measurements made in the absence of solvent where a dilute layer of CNTs were affixed to the electrode surface. When studying new nanomaterials electrochemically, either at the single particle or bulk (ensemble) scale, the desire is for the experimental rate determining

step to be the reaction at the catalyst/solution interface and not that of the contact between the electrode and nanomaterial. The magnitude of the above reported contact resistance suggests this may not always be the case.

ASSOCIATED CONTENT

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Notes

The authors declare no competing financial interests.

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Supporting Information

Overview of some of the numerous reports in the literature based on the use of CNTs as electrode materials and as the bridge between two electrodes, comparison of CVs of HOR for different CNT-electrode contacts, experimental section, characterization via the dark-field optical microscopy of the CNTs and the scheme illustration, optical microscopy and picture of the interdigitated gold electrode are shown in the Supporting Information. Also included is the

electrochemical data of the chronoamperometry for the IDE-Au dropcast with CNTs, the chronoamperometry of IDE-Au in ethanol without CNT, the chronoamperometry of IDE-Au showing two discrete current steps in the suspension of CNTs, the chronoamperometry of IDE-Au in the suspension of CNTs after 120 min of sonication and comparison of current steps distribution at the IDE-Au with different width of bands and gaps. The Supporting Information is available free of charge on the ACS Publications website.

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