Weak Backscattering in Deflected Doped Carbon Nanotubes

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Carbon nanotubes (CNTs) are highly sensitive towards dipole molecules, mechanical loads, interfacial contacts, chemical modifications and temperature fluctuations. Their applications are currently limited to electron-field-emission and gas-sensing devices. In fact, CNTs can also be used as strain-sensing elements; for example, variations in CNT resistance with bending strain have been characterized by deflecting nanotubes using an AFM tip. [1, 2] Tombler et al. discovered that, when deflected, nanotubes reach 14°, and their corresponding conductance reduces significantly as a result of temporary sp3 bonding. [3, 4] A similar phenomenon was observed by Paulson et al. Firstly, the CNT resistance increases considerably with tip-force application due to a tube movement with respect to the electrodes. Secondly, the tube resistance does not change with a small bending strain; it becomes immeasurable when the tube fractures. These examples, however, point to the fact that nanotube resistance increases with lattice distortions. We found that p-doped CNTs behave differently when subjected to bending. Constant bending of doped CNTs is accompanied by an indistinctive change of the tube resistance.

Experimental Section

Boron-doped multiwalled CNTs (BCNTs) were made by arc discharge between BN-containing graphite rods, as described previously. [5, 6] A tiny bundle of BCNTs was carefully extracted from protruding nanotube aggregates (Figure 1a) via a micromanipulator-controlled tungsten tip (Figure 1b). The bundles consisted of about 2–4 tubules. Each attached bundle was transferred and glued onto an Ag-paste-deposited electrode (Figures 1c and 1d). The bending strategy was carried out by moving a one-end-fixed BCNT bundle toward the opposite electrode; this allowed the in situ measurement of tube bending versus resistance between the electrodes. Figure 1e shows a high-resolution TEM image of a BCNT. The layer spacing along the c axis is 3.4 Å.

Figure 2 shows the variation of nanotube resistance with bending. The gap between the initially straight BCNTs and the opposite electrode is about 12 μm (tube bundle ca. 30 μm in length, panel a, Figure 2). The nanotube tip begins to bow in panel b (Figure 2), and the corresponding resistance fluctuates between 75 and 250 KΩ, mainly due to loose contact between tubes and electrodes. The resistance drops in panel c and becomes stabilized between panels c and e. A kinkinglike structure emerges in panel f (Figure 2), accompanied by a resistance promotion to about 75–100 KΩ. The nanotube tip retracts in panel g and completely detaches in panel h (Figure 2). The nanotube deflection as a function of gap reduction between electrodes is about 0.6 μm−1 for panel b and 2.5 μm−1 for panel d, that is, a 1-μm movement of the nanotube toward the opposite electrode produces 0.6° and 2.5° deflections, respectively. This phenomenon suggests that the nanotube bending was within elastic compliance before panel c (Figure 2), and a permanent deformation occurred approximately at panel d (Figure 2). This description is supported by a kinkinglike structure (panel f) and remaining bending morphology seen for the BCNT bundle (panel h, Figure 2). Stable conduction between panels c and e emerges as a result of the bending nanotubes acting as an axial load on the electrodes, thus forming a compact contact. Accordingly, the resistance recorded between panels c and e mainly arises from bowing BCNTs. The same bowing nanotube bundles were subsequently rebent by a similar manoeuvre. As a result, a drastic fluctuation of the tube–electrode resistance from panels b to g (Figure 3) was observed. This was due to the fact that the bowing bundle could no longer form a compact contact with the electrode because a permanent deformation, previously produced on the nanotubes (panel f, Figure 2), had reduced the axial load on the electrode. Interestingly, the detaching bundle (panel g, Figure 3) possesses a smaller deflection angle than that of the bundle in panel a (Figure 3), which is due to van der Waals and electrostatic attractions between the detaching nanotubes and the electrode. Consequently, the bent bundle is slightly stretched before its complete detachment from the electrode occurs. Previous works have evaluated the increase in tube resistance with bending strain to be at least 2–3 times greater than the pristine value. Herein, we only present a small change in tube resistance with bending (panels c and e, Figure 2). The resistance variation is of about 50 ± 2 KΩ.

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which corresponds to 4%. For an undoped CNT, the primary electrical conduction is carried out by surface $\pi$-electron carriers, and a strong backscattering of electrons occurs when the local mirror symmetry of axial C–C bonds is broken by lattice distortions (bending and twisting).\textsuperscript{[5]} Lattice distortions rehybridize the $\sigma$–$\pi$ orbitals and redistribute the charge polarization along the tube axis. As a result, the amplitude of electron hopping across surface $2P_z$ orbitals increases, and the effective vector potential along the tube axis discontinues. Recent calculations by Kane et al. described that the application of a constant bending to CNTs gives a relatively weak backscattering of the quantum particles compared with severe bends. This phenomenon is mainly due to the preservation of the local mirror C–C symmetry over bending, so the effective vector potential proceeds continuously along the tube axis, and the $\pi$-electron resonance at the tube surface remains undisturbed.\textsuperscript{[5]} A similar situation may account for the minor variation in the bent-tube resistance recorded between panels c and e (Figure 2). Firstly, lattice twist and buckles are both absent in our bent nanotubes because one end of the tube bundle is fixed by the Ag paste and the bending angle (60–80°, panels c and d) is lower than the tube-buckling regime (100°).\textsuperscript{[6]} Secondly, boron-mediated grown CNTs in arc processes preferentially form zigzag-edged lattices,\textsuperscript{[7]} and extra alignment of van Hove singularities with leads, due to an oscillation of local density of states (LDOS) at the bending region, mostly occurs in zigzag CNTs,\textsuperscript{[8]} which means that the zigzag nanotubes possess a higher probability of electron transmission between leads than do armchair CNTs. Thirdly, boron-doped CNTs have been previously verified as a genuine p-type system, and their primary conduction is no longer attributed to surface $\pi$ electrons but to hole carriers near the sp$^2$ valence-band edge (i.e. BC$^3$ state). It is apparent from electron paramagnetic resonance (EPR) data that the spin density for BCNTs is $6 \times 10^{15}$ spins g$^{-1}$, which is six times greater than the value obtained for undoped CNTs.\textsuperscript{[9]} The absence of tube buckling and twisting deformations in Figure 2 (panels c and e) suggests that the intact hybridized C–C bonds and the electron transmission through the BC$^3$ state near the valence edge remain undisturbed. The reduction of the total conduction due to a slight distortion at surface $2P_z$ orbitals over constant bending is therefore insignificant. This explains the observed minor change in tube resistance at a constant bending (panels c and e, Figure 2). Similar results were also observed in another experiment.
It is important to quantify the threshold of the tube axial load \( P_{\text{cri}} \) on the electrode which produces a compact contact and a stable conduction. Euler’s law is a common expression for evaluating the mechanical property of a supporting column or tube structure between beams, which is similar to Figure 2 and can be used to estimate the critical load of nanotube on electrodes before permanent deformation. The expression is written as follows [Eq. (1)]:

\[
P_{\text{cri}} = \frac{\pi^2 EI}{(KL)^2} \tag{1}
\]

where \( E \) is the elastic coefficient of the nanotubes; \( l = A \gamma^2 \) is the inertia moment of the bending bundle cross-section; \( A \) is the cross-section area of the CNTs; \( \gamma \) is the radius of gyration and \( L \) is the CNT length.

Equation (1) clearly indicates that the critical tube axial load acting on the electrodes before tube kinking (C–C bond breakage) is related to the intrinsic tube modulus, \( E \), the associated inertia moment, \( I \), and the tube length \( L \). Here, the bundle is longer than the gap between the electrodes, so that \( L \) must be modified by a “factor of effective length”, which is \( K = 0.5\ldots1 \). Equation (1) thus becomes [Eq. (2)]:

\[
P_{\text{cri}} = \frac{\pi^2 EI}{(KL)^2} \tag{2}
\]

Based on ref. [10] we consider \( E \) to be 0.9 TPa for nanotubes, \( l = 1.766 \times 10^{-18} \) cm \(^4\) (panel d, Figure 2) and \( K = 0.7 \), so that \( P_{\text{cri}} = 8.15 \times 10\ldots3 \) kg, which means that a compact contact can be achieved by applying a similar pressure at the tube–electrode junction. Equation (2) also implies that the threshold loading on the electrode is determined by the elastic modulus of the nanotube, that is, a larger tube modulus requires a greater \( P_{\text{cri}} \). Since the nanotube modulus is related to the tube-wall thickness, a straightforward analysis would be to determine the nanotube gyration radius \( \gamma \) as a function of the deflection angle. The estimated elastic deflection as a function of the nanotube gyration radius presented in Figure 2 (i.e. 0.6\(^\circ\) per \( \mu \)m) has reappeared in our repeated experiments and may be considered as a representative in justifying nanotube–electrode contact structures. It is noteworthy that the \( P_{\text{cri}} \) value obtained here for BCNTs is expected to be lower than that of pure CNTs because the strain energy of the B–C bond is lower by 0.03–0.05 eVatom\(^{-1}\). This gives a lower Young modulus for BCNTs (by ca. 0.08–0.1 TPa) compared to CNTs.\(^{[11]}\)

In summary, the constant bending of BCNTs gives a weak backscattering of the electron transmission because the primary conduction in p-doped nanotubes is switched to an “extra” energy level near the valence-band edge and the electron-hopping amplitude at bending 2p\(_z\) orbitals no longer plays a crucial role in the conduction mechanism. A compact contact between nanotubes and electrodes requires a critical loading of \( P_{\text{cri}} = 8.15 \times 10\ldots3 \) kg or a nanotube deflection versus gyration radius at 0.6\(^\circ\) per \( \mu \)m.

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