Chemically Doped Double-Walled Carbon Nanotubes: Cylindrical Molecular Capacitors

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A double-walled carbon nanotube is used to study the radial charge distribution on the positive inner electrode of a cylindrical molecular capacitor. The outer electrode is a shell of bromine anions. Resonant Raman scattering from phonons on each carbon shell reveals the radial charge distribution. A self-consistent tight-binding model confirms the observed molecular Faraday cage effect, i.e., most of the charge resides on the outer wall, even when this wall was originally semiconducting and the inner wall was metallic.

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Nanometer-scale capacitive charging effects are already familiar, e.g., the Coulomb blockade phenomenon in quantum dots. However, it is difficult to resolve the detailed radial charge distribution within a nanostructure. Using bromine-doped double-walled carbon nanotubes (DWNTs), we have resolved the radial charge distribution within the positive carbon electrode of a multilayered molecular capacitor. The walls of a DWNT are weakly coupled and so maintain distinct resolvable vibrational modes, even when they are in intimate electrical contact. The bromine acts as a “radial gate” with very different band filling effects on each shell and nano-scale electrostatics dominates over quantum confinement.

The high-frequency Raman-active vibrations of sp² carbon (e.g., solid C₆₀) are sensitive to chemical doping [1–3]. The C-C bond contracts (expands) for acceptor (donor) [1,2,4], as seen in electrochemically intercalated graphite-H₂SO₄ compounds via neutron diffraction [5]. Single-walled carbon nanotubes (SWNTs) can be doped either p or n type [6–8]. The DWNT is the latest well-ordered all-carbon structure to be found [9], following fullerene, multiwalled and single-walled carbon nanotubes (MWNT, SWNT) [10], nanohorns [11], and peapods [9,12,13]. The DWNTs studied here were made by a high temperature coalescence of C₆₀ peas within peapods (C₆₀@[n,m]) [9]. Our peapod sample has a filling factor close to 100%, as estimated from TEM observation [14] and x-ray diffraction (XRD) profiles [15], with a shell spacing (0.36 nm) close to that in graphite [9,16].

Resonant Raman scattering is a powerful probe of both SWNT and DWNT systems [9,16–18]. Previous reports indicate that bromine can either chemically dope SWNTs and MWNTs [4] or form a C-Br complex [19]. In this work, in situ Raman spectra of bundled SWNT and DWNT samples during vapor phase bromine doping were acquired through the walls of a glass ampoule connected to a separate liquid bromine source. Self-supporting DWNT or SWNT films were placed in an evacuated glass tube via a valve connected to a bulb of frozen bromine. Doping occurred as the bromine warmed slowly to room temperature. The SWNT comparison spectra came from the same starting material that was used to synthesize the DWNTs.

The Raman spectra in Fig. 1 show the low-frequency radial breathing modes (RBMs) [Fig. 1(a)] and the high-frequency tangential (T) modes [Fig. 1(b)] for pristine and bromine-doped DWNT samples, collected with a Bomem DA3+ spectrometer (1 cm⁻¹ resolution). Consistent with previous Raman results [16] and band structure calculations [20,21], the incident photon (1064 nm) can resonate with E₁₁ in the outer semiconducting tubes and E₁₁ in the inner semiconducting tubes simultaneously, where E₁₁ is the energy difference between filled and empty Van Hove singularities [2]. In the pristine DWNT sample, three low-frequency and three high-frequency RBMs are observed and assigned to the most dominant outer (d = 1.45, 1.33, and 1.26 nm) and inner shells (d = 0.75, 0.70, and 0.68 nm) using the expression ω_RBM(cm⁻¹) = 234/d(cm mm⁻¹) [16]. The proportionality constant (234 cm⁻¹nm) is an average over several literature values [16]. Small changes in ω_RBM due to sp³ hybridization in the inner shell would induce small deviations from this 1/d form, without affecting our main conclusions. Although the scattering from the RBMs of the outer tube is extinguished by bromine doping, the signal from the inner tube is essentially unaffected. Note that we do not see the 260 cm⁻¹ peak reported earlier in bromine saturation doped SWNT bundles [4]. In the present work, we took ~100 spectra, one every few minutes during an in situ experiment. As the RBMs begin to up-shift with bromine doping, the intensity drops quickly. The extinction of the outer tube radial breathing band may be due to the loss of Raman...
resonance via the depression of the Fermi level by the bromine, which depopulates the initial states of the $E_{22}$ transitions. A Lorentzian line shape analysis of the 1064 nm $T$-band spectra [Fig. 1(b)] also suggests that most of the charge is transferred from the bromine shell to the outer layer of the DWNT. For convenience, a single Lorentzian represents the three unresolved tangential modes in the strongly curved inner tube ($1581\,\text{cm}^{-1}$) and the outer tube ($1590\,\text{cm}^{-1}$). After bromine doping (Fig. 1), the inner tube $T$ band remains at $1581\,\text{cm}^{-1}$, whereas the outer tube $T$ band vanishes (consistent with the results for the SWNT comparison sample).

The effects of bromine doping on the Raman $T$ bands of the inner and outer carbon nanotubes can also be observed with 514.5 nm excitation (Fig. 2). The RBM region is omitted here, because the stretching frequency of bromine vapor at $\sim320\,\text{cm}^{-1}$ overlaps with the RBM frequencies of the inner tubes. The data of Fig. 2 were collected with a JY-ISA HR460 spectrometer ($2\,\text{cm}^{-1}$ resolution). The upper (lower) pair of the spectra show the SWNT (DWNT) results before and after doping. The details of the SWNT $T$ band are better resolved with 514.5 nm excitation, fitted by a sum of four Lorentzians. The $T$ band of the doped SWNT sample is well fit by a simple $18\,\text{cm}^{-1}$ rigid up-shift of the undoped spectrum. We can fit the DWNT $T$ band similarly: The pristine DWNT spectrum is fit by a relatively weak, unresolved $T$-band Lorentzian at $1580\,\text{cm}^{-1}$ for the inner tube, plus the same four Lorentzians used to fit the 514.5 nm SWNT spectrum. After Br doping, the $T$ bands shift and become very weak (note the $40 \times$ scaling of the signal). To fit the doped DWNT $T$-band spectrum, consistent with the analysis of the 1064 nm results, we simply superimpose the $1580\,\text{cm}^{-1}$ Lorentzian band for the inner tube with an outer tube $T$ band represented by the four-line fit to the undoped SWNT spectrum, but rigidly
up-shifted by 16 cm⁻¹. The T-band and R-band analyses indicate that the positive charge in our cylindrical molecular capacitor is deposited almost completely on the outer tube of the double-walled pair. Freezing the liquid bromine in the attached bulb with liquid N₂ only partially reverses the doping. Consistent with previous Raman scattering [4] and resistivity results [22] on bromine-doped SWNTs, the T band down-shifts to 1603 cm⁻¹ (compared to 1592 cm⁻¹ in pristine material). We did not try to fully reverse the doping; the sample remained at ~27 °C while the bromine vapor was cryopumped; heating would most likely have driven ωᵣ closer to 1592 cm⁻¹. Interestingly, for alkali metal doping of SWNTs, some groups have reported a small initial up-shift of the T band, followed by the expected down-shift [7]. Our bromine-SWNT system, on the other hand, has a monotonic increase in the T-band frequency over the entire doping range.

We model the system as a three-layer cylindrical capacitor with the bromine anions forming a shell around the outer nanotube. The total energy contains three terms: the band structure energy of the inner and outer tubes and the electrostatic energy $E_{es}$ of the trilayer charge distribution:

$$E = \sum_{i,k} E_{i}^{\text{inner}}(k) + \sum_{i,k} E_{i}^{\text{outer}}(k) + E_{es}. \quad (1)$$

The indices $i$ and $k$ label the occupied bands and wave vectors for the inner or outer tubes. For simplicity, we use a one-orbital tight-binding model with rigid bands and a nearest-neighbor $\pi$ overlap $\gamma_0 = 2.90$ eV [20]. This model ignores the small $1/R^2$ curvature-induced band gap of $n \neq m$ tubes and nonrigid band effects. However, the model captures the primary physical effects relevant here: (i) the distinction between metallic and large band gap semiconducting tubes with radially dependent band gaps and (ii) the cylindrical electrostatics. The smallest diameter tube considered has $d = 0.63$ nm, approaching the size where rehybridization becomes relevant [23]. Subband filling is relatively modest, so a rigid band approximation is a reasonable starting point for the essential physics.

We assume that the excess charge on each shell is uniformly distributed in an infinitely thin wall at the nuclear radius of that shell. The resulting electrostatic energy of the triple-walled capacitor is

$$E_{es} = \frac{1}{2} \frac{e^2 L}{2 \pi \varepsilon_0 n_{inner}^2} \ln \left( \frac{R_{outer}}{R_{inner}} \right) + \frac{1}{2} \frac{e^2 L}{2 \pi \varepsilon_0 n_{outer}^2} \ln \left( \frac{R_{outer}}{R_{inner}} \right), \quad (2)$$

where $e$ is the electron charge, $\varepsilon_0$ is the permittivity of free space, $L$ is the unit cell length of the outer tube, and $n_{inner}$ ($n$) is the linear density of excess holes for inner tube (both tubes). $R_{inner}$, $R_{outer}$, and $R_{Br}$ are the respective radii. We fix the charge per unit length in the Br shell (i.e., a theoretical dopant coverage with an attendant average charge per Br atom), and we minimize the total energy with respect to $n_{inner}$.

We consider DWNTs with inner and outer diameters in the ranges (0.63 < $d < 0.79$ nm) and (1.3 < $d < 1.5$ nm) [16]. The resulting wall indices are (5,5)@10, (5,5)@13, (8,2)@14, (6,4)@10, (6,4)@11, (8,0)@12, (7,3)@12, (7,2)@13, (8,1)@16, and (9,2)@11, where the metallic tubes are in boldface. Two physical effects act in concert to segregate most of the holes onto the outer nanotube. First, the band gaps of the smaller diameter tubes tend to be larger, so they empty last. Second, the cylindrical geometry preferentially raises the electrostatic potential at the inner tube. Only the charge on the inner tube affects the potential difference between the two layers.

Figure 3 shows the results of the energy minimization. Two families of curves for $n_{inner}$ vs $n$ are obtained, one when the inner tube is semiconducting, and the other when it is metallic. The vertical scale ($n_{inner}$) is 10 times smaller than the horizontal scale ($n$); most of the positive
charge appears on the outer tube, in agreement with the experimental results. The lower family of curves is associated with two nested semiconducting tubes, except for (6,4)@**10, 10** and (9,2)@**11, 11**, which have an outer metallic tube. In this family, the outer tubes alone are doped until the Fermi energy \(E_F\) cuts the valence band in the inner tube and then a cusps appears. For the (6,4)@**10, 10** tube, the first cusp is at \(n = 0.14\) holes/Å, where \(E_F\) first cuts the valence band of the (6,4) layer, and the next cusp occurs at \(n = 0.21\) holes/Å, when \(E_F\) reaches the second valence band of the outer **10, 10** layer.

Within the second (upper) family of curves, all of the inner tubes are metallic. The **(5, 5)**@**10, 10** and **(5, 5)**@**13, 7** are metallic pairs, so both tubes dope simultaneously. For **(8, 2)**@**14, 6**, the outer tube is semiconducting. Even though the inner tube dopes first in this case, the charge distribution rapidly begins to favor the outer tube as electrostatic effects begin to dominate. For the metallic **(5, 5)**@**10, 10** and **(5, 5)**@**13, 7** DWNTs, a cusp appears as \(E_F\) approaches the second valence band of the outer tube at \(n = 0.22\) holes/Å, while for **(8, 2)**@**14, 6** the cusp occurs at a smaller value of \(n = 0.0126\) holes/Å, when \(E_F\) cuts the first valence band of the outer tube. Although some of these tubes are really small-gap semiconductors due to curvature-induced hybridization, the electrostatic effects dominate and therefore the small curvature-induced gap would have only a small effect on the overall charging behavior.

The charge transfer between the dopant (bromine) and the DWNT may be defined as the charge per host carbon atom transferred to the dopant, denoted as \(f\). We can estimate \(f\) using the relation \(\Delta \omega (\text{cm}^{-1}) = 460 \times f\) obtained previously for the up-shift of the Raman-active \(E_{2g}\) modes (\(\sim 1582\) cm\(^{-1}\)) during electrochemical charging of graphite-H\(_2\)SO\(_4\) [4]. For the saturation doped DWNT-bromine system, we observe a \(\sim 16\) cm\(^{-1}\) up-shift of the \(T\) band in the outer tube relative to the undoped system (Fig. 2). Consistent with our tight-binding model, we assume that \(\sim 90\%\) of these holes reside on the outer tube. Therefore, \(f = 1 / (29 \times 0.9) \approx 1 / 26\); saturation bromine doping creates one hole in the DWNT per 26 carbon atoms, or 0.6 holes/Å. \(E_F\) is then depressed by 1.2 to 1.4 eV [depending on \((n, m)\)], uncovering states at the top of the third valence band of the semiconducting outer tubes. As a result, resonant Raman scattering from these outer tubes using 514.5 nm (or 2.41 eV) excitation should be dramatically reduced, in agreement with experiment. Theory (i.e., \(<10\%\) of the charge on the inner tube) predicts a 1–2 cm\(^{-1}\) up-shift of the inner tube \(T\) band, near the limit of our experimental resolution.

Similar issues arise in higher stage index \((n > 3)\) graphite intercalation compounds (GICs), where the bounding carbon layers adjacent to the charged intercalate layers are thought to contain most of the compensating charge. For example, optical reflectance studies of potassium GICs, showed that \(\sim 90\%\) of the charge in the carbon layers was on the two bounding layers, and only \(10\%\) on the interior layers [24]. This charge distribution is similar to that obtained here in a double-tube cylindrical geometry, even though the electronic band structure for cylindrical graphene is very different from that of planar GICs. Recent results on DWNTs with BN outer walls and C inner walls [25] should exhibit a similar interplay of electrostatics and band filling, with an electrostatic favoritism to doping the outer layer.

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