Fe-encapsulated carbon nanotubes: Nanoelectromagnets

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Existence of chiral current in carbon nanotubes is verified by the presence of inductive phase. The magnetic strength at the center of nanotubes can be magnified by encapsulation of Fe. © 2005 American Institute of Physics. [DOI: 10.1063/1.2138674]

Carbon nanotubes (CNTs) are cylindrical graphenes and \( \pi \)-electrons are transported isotropically via conjugated system. In a three-dimensional (3D) approach, electron wave function is extended vertically to tube surface by 1 Å at Fermi level, and transport mechanism becomes sensitive to electric field. There are two possible conduction pathways in a 3D-structured CNT, i.e., along tube axis (\( J_a \)) and circumference (\( J_c \)) [Fig. 1(a)]. When electric field is applied parallel to the tube axis, electron flux along circumference (\( J_c \)) is diverted into a helix current, similar to nanocoils [Fig. 1(b)]. To date, exploration of magnetic field within a CNT remains a challenge, and a straightforward approach is to introduce Fe into CNTs so magnetic field within the tube is magnified and becomes detectable. In this work, individual Fe-encapsulated CNT bridged tungsten electrodes are verified and measured by the impedance technique. Inductance on the order of mH is detected, thus supporting chiral current in CNTs.

Fe-encapsulated multiwalled carbon nanotubes (Fe-CNTs) were made by pyrolysis of ferrocene in an Ar flow at 900–1000 °C. Length of encapsulated metal varies from tube to tube, normally between 100 and 600 nm [Fig. 2(a)]. Encapsulated metal exhibits clear lattice fringes in conjunction with 002 carbon walls [Fig. 2(b)], and electron diffraction analysis indicates that spot arrays obtained from interior metal are consistent with \( \alpha \)-phase Fe [Fig. 2(c)]. Selective area of scan transmission electron microscopy-energy dispersive x-ray analyses (STEM-EDX) analyses on tube walls show C signal, together with Cu from TEM grid [Fig. 3(a)]. When the beam is moved to the interfacial region between Fe core and tube walls the Fe signal emerges [Fig. 3(b)]. Fe profiles become strong when the beam is targeted on the encapsulated region [Fig. 3(c)].

A permanent magnet is placed around protruding nanotubes 1 cm apart, and clear displacement in response to the magnet is seen [arrows, Figs. 4(a)–4(c)], which verifies selected Fe-CNTs. A second sharpened electrode is then repeatedly brought in contact with protruding nanotubes to extract unwanted particles and branching nanotubes until a better bridging configuration is acquired [Fig. 4(d)]. Impedance of the bridging nanotube was measured by component analyzer (Zentech 3302) connected with a bias current source (Chroma 1320). Total resistance for the nanotube device is equivalent to \( R_t = R_{\.\text{con}} + R_{\.\text{tube}} \), where \( R_{\.\text{con}} \): tube-electrode contact resistance, \( R_{\.\text{tube}} \): intrinsic tube resistance [Fig. 4(e)]. Accordingly, complex impedance \( Z \) can be expressed as

\[
Z = R_t - j \omega C + j \omega L, \tag{1}
\]

where \( R_t \): total resistance, \( \omega \): angular frequency = \( 2 \pi f \), \( f \): frequency, \( C \): capacitance, \( L \): inductance, \( j = -1^{1/2} \). Equation (1) means that \( R_t \) is a constant and does not vary with frequency, whereas passage of alternative current (ac) through capacitors and inductors yields capacitive and inductive reactance \( (\chi_C = 1/\omega C, \chi_L = \omega L) \), respectively, which contribute to \( Z \). In other words, if \( Z \neq R_t \), extra contributions to impedance must either come from \( \chi_C \) or \( \chi_L \). Since CNTs have a charge storage capability, \( \chi_C \neq 0 \) is anticipated. Pure CNTs lack inductive phase so the central issue here is to seek \( \chi_L \) from Fe-CNTs. The resistance of bridging nanotube under a dc field is 11.3 kΩ the value reappears with minor fluctuation between \( \pm 60 \, \Omega \) in an ac field at 1 kHz [Fig. 5(a)]. Resistance variation does not exceed \( \pm 60 \, \Omega \) at higher frequencies between 2 and 10 KHz.

Figure 5(b) shows impedance versus frequency (1–10 kHz), specifically the \( \chi_L \neq 0 \) is present. Profile indicates a consistency between impedance and reactance, namely, a small increment in \( \chi_C \) and \( \chi_L \) between 1–4 KHz promotes inductive phase slightly. Impedance increases with both increasing reactance between 4 and 8 kHz by 1 kΩ. This value is significantly larger than \( R_t \), variation, which also verifies that \( Z \) changes with frequency. Between 8 and 10 kHz, impedance decreases with both reactances. According to Fig. 5(b), averaged capacitance measured between 1–10 kHz is 5–10 nF, which is on the same order of magnitude as value received from single-walled carbon nanotube (SWNT).

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**FIG. 1.** (a) Delineation of electron pathways and (b) a chiral current in nanotube with applied electric field.
ropes. Inductance is 1.6 mH at 1 kHz, it then increases to 3.5 mH at 2–4 kHz, further to 6.7 mH at 6 kHz. Inductance decreases to 1.3 mH between 6 and 10 kHz. Inductance magnitude obtained here is similar to quantum units previously detected at SWNT-metal contact. In an ac field, the

FIG. 2. (a) Close-up TEM image of individual encapsulated-Fe multiwalled carbon nanotubes; scale bar is 30 nm. (b) HRTEM image of encapsulated-Fe multiwalled carbon nanotubes, and (c) corresponding electron diffraction pattern.

FIG. 3. Spatial STEM-EDX analyses on individual encapsulated-Fe multiwalled carbon nanotubes. Beam focusing on (a) carbon walls; (b) boundary between walls and encapsulated metal; and (c) the central region of metal. The corresponding EDX spectra are shown on the right.

FIG. 4. (Color) (a)–(c) Real-time displacements of encapsulated-Fe CNT in response to a permanent magnet. (d) A successful establishment of bridging Fe-CNT between tungsten electrodes, and (e) a representative of corresponding circuit elements for bridging CNT.

FIG. 5. (a) Time-dependent tube resistance measured at 1 kHz. (b) Impedance Z against frequency, together with profiles of inductive and capacitive reactance. (c) Time-dependent tube resistance (R) versus inductance (L).

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Phasor between current and voltage determines characteristics of circuit elements. When voltage leads current an inductive phase emerges; in contrast, a capacitive phase arises as voltage lags current.\(^3\) Nanotube devices made by focused ion beam (FIB) and photolithographic techniques usually create interfacial states at contact, due to stress concentration. The boundary states strongly interact with carriers, resulting in delay of current passage. Quantum inductance therefore arises as a result of phase inconsistency between voltage and current oscillation (i.e., voltage leading to current). Emergence of quantum inductance under ac field depends upon \(\propto T^{-1}\) (\(\propto\) lifetime of quasibound state resonance) and normally appears at frequency higher than 37 kHz.\(^4\) In our study, small fluctuations in \(R\) upon frequency ramping implies that carriers do not localize at tube-electrode contact under alternative field; meanwhile, samples were measured at much lower frequencies (1–10 kHz) and corresponding \(R\) must exceed 500 k\(\Omega\) in order to satisfy the \(\propto T^{-1}\). The \(R\) obtained here is 11.3 k\(\Omega\), significantly lower than the required value. Accordingly, the inductive phase (i.e., \(\chi\neq 0\)) detected here is not due to electronic resonant states at contact, but intrinsic to \(\mathrm{Fe-CNTs}\).

The magnetic field \(\mathbf{B}\) multiplied by \(\mathrm{Fe}\) core within a solenoid is expressed as

\[
L = \mu N^2 A l, \tag{2}
\]

where \(\mu\) = the magnetic permeability (=\(k\mu_s\)), \(k\) = relative permeability of \(\mathrm{Fe}\), \(\mu_s\) = space permeability, \(N\) = winding number, \(A\) = solenoid area, \(l\) = solenoid length. Substitution of \(L = 1.5 \text{ mH}\), \(\mu = k\mu_s = 200 \times 4 \pi \times 10^{-7} \text{Tm/A}\), \(A = 7 \times 10^{-16} \text{ m}^2\), and \(l = 3 \times 10^{-7} \text{ m}\) into Eq. (2) \(N\) appears to be 50,565. This value can be used to estimate chiral arrangement in bridging CNT. Assume that the separation between electrodes corresponds to CNT length \(l = 3 \times 10^{-7} \text{ m}\); then \(l/N\) would be equivalent to pitch along tube axis, which yields \(1/N = 0.006 \text{ nm}\). The circumference current (\(J_0\)) diverted by electric field is expressed as \(\varphi \equiv [90^\circ - \tan^{-1}(D/N)]\), where 90° represents pristine current along circumference and \(D\) is tube diameter. By setting \(D = 30 \text{ nm}\), the diverting angle is \(\varphi = 0.011^\circ\). Substituting \(N = 50,565\) into the equation \(B = \mu N I\), interior magnetic field enhanced by the \(\mathrm{Fe}\) core is 0.012 T (\(=1.2 \times 10^5\) Gauss). This value is significant and is close to data obtained from calculation.\(^2\) A bare CNT solenoid is \(B_0 = \mu_s N I = 6.4 \times 10^{-5} \text{T}\); in other words, encapsulated \(\mathrm{Fe}\) has multiplied the magnetic field by 188 times. This number is comparable with \(\mathrm{Fe}\)-core transformers, which usually have a magnetic multiplication of tens to thousand and winding number of \(10^4\)–\(10^5\).

In Eq. (1), \(R\) is unchanged with frequency; actually, the \(R\) does show a small variation under ac field [Fig. 5(a)]. Although one can neglect this minor fluctuation compared with large change in \(Z\) [Fig. 5(b)], it possibly implies a peculiar transport system in our experiments. Small oscillation of \(R\) with time may be related to modified transport mechanism by interior magnetic field, similar to the magnetoresistance effect. Magnetoresistance of CNT film is negative (\(\Delta R/R_0 < 0\)) and conduction mechanism is dominated by intertube hopping.\(^5\) In our study, the applied magnetic field \(\mathbf{B}\) arises directly from electromagnetic \(\mathrm{Fe-CNT}\) itself, which is parallel to the tube axis \((B_0)\) and field is in alternative change with time. A time dependence of \(R_t L\) profile is shown in Fig. 5(c), which reveals that a small increase in \(R_t\) is accompanied by an \(L\) decrease, and vice versa. According to Fig. 5(c), we have roughly estimated \(\Delta R/R_0\) to fluctuate between \(-0.005\) and 0.005. Alternative change in sign is unlikely due to combination of on-tube localization of carriers (negative) and, the phase consistency between cyclotron orbit and nanotube radius (positive). First, carrier localization by ac field only occurs above the GHz range with least field intensity of \(1 \times 10^7 \text{ V/m}\).\(^7\) The current study was performed at lower frequencies, and electric field intensity along the bridging nanotube is \(1 \times 10^6 \text{ V/m}\). Second, a stronger magnetic field (2 T) is needed for a match between orbit and cyclotron frequency.\(^7\) In a parallel magnetic field CNT resistance is modulated by enclosed magnetic flux on basis of \(\Delta B = (h/2e)/r^2 \pi\) (\(r\) = tube radius, \(h\) = Planck constant, \(e\) = electron charge). When the electron interference period corresponds to \(h/e\) and \(h/2e\), effects are known as Aharonov-Bohm (AB) and Altshuler-Aronov-Spivak (AAS) oscillations, respectively. We were unable to verify the AA or AAS effects from Fig. 5(c), because the profile was recorded in an alternative magnetic field. Nevertheless, weak coupling between \(R_t\) and \(L\) implies a modified transport by enclosed magnetic flux. In theory, magnetic flux should readily vanish in a bridging nanotube, because alternative magnetic field repeatedly changes direction of circulating electrons backwards and forwards. When magnetic field is forward applied to the tube axis, electrons are orbiting in an anticlockwise direction, which produces a positive magnetic moment. In contrast, reverse magnetic field moves electrons clockwise, giving a negative magnetic moment;\(^1\) both cancel each other. Our bridging nanotubes are apparently not in a ballistic regime, due to lattice imperfections, so dephasing of electron pathway occurs and an electron can circulate different routes around CNT in forward and reverse magnetic field. Therefore, two situations occur: first, if forward and backward pathways maintain in phase electrons strongly interfere, hence backscattering. This increases nanotube resistance and magnetic flux approaches zero. Second, if both oscillate out of phase the enclosed magnetic flux does not vanish and tube resistance decreases as a result of band gap reduction by magnetic flux.\(^9\) This is supported by the increase of magnetic flux with resistance decreasing [Fig. 5(c)].

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