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Carbon nanotube self-doping: Calculation of the hole carrier concentration

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The hole carrier concentration of semiconducting carbon nanotubes is calculated as a function of tube diameter based on a self-doping mechanism caused by curvature induced charge redistribution of the bonding orbitals. The results show that nanotube hole carrier concentration is inversely proportional to the tube diameter and agree well with field-effect measurements and Raman spectroscopy on pristine carbon nanotubes.

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Carbon nanotubes (CNT's) are an archetypal class of materials for nanoscale science and technology because their properties can be controllably and significantly altered simply by changing their geometry. This is especially true of their electronic characteristics[1] and has allowed the realization of all-carbon junction devices[2] and molecular-scale logic elements.[3] A crucial factor for the operation of these and future CNT devices is the ability to control the distribution and type of charge carriers within them, i.e., doping levels.

The issue of CNT doping has recieved extensive attention across several areas: Initial demonstrations of field-effect transistors using so-called pristine semiconducting tubes showed they were *p* type, i.e., the majority of carriers were holes[4,5] and subsequent studies verified this behavior.[6] In addition, the effect of chemically doping CNT's with different gas species has been studied[7,8] and used to create nanoscale chemical sensors[9] and intramolecular *p*-*n* junctions.[10] Lastly, electrochemical doping of nanotubes in solution has been used for nanoelectromechanical systems (NEMS).[11]

Despite the considerable experimental progress, a consensus on the underlying mechanism of CNT doping has yet to be reached. In particular, the ubiquitous *p*-type behavior of apparently undoped semiconducting CNT's has been variously ascribed to contact doping,[4,12] processing conditions,[5] atmospheric contamination such as oxygen adsorption,[7] or more recently, to contact barrier characteristics.[13] In this paper, we present a theory of CNT doping that is instead based on the inherent atomic bonding properties of the graphite layer from which a nanotube is formed. We find that hole doping levels in semiconducting CNT's can arise via an intrinsic ''self-doping'' mechanism caused by rehybridization of atomic orbitals which depends critcally on tube diameter. Our results are shown to be consistent with a wide range of experimental data.

Figure 1(a) shows a schematic of the density of states for 2D graphite: The two π bands meet at the Fermi energy typifying a vanishing-gap semiconductor.[14] A small overlap with the σ bonding states is also seen away from the Fermi level. In Fig. 1(b) the corresponding diagram for pristine semiconducting CNT's is shown. The Fermi level is shifted towards the π valence band indicative of *p*-type behavior as observed experimentally. In addition, with decreasing nanotube diameter π-σ mixing increases and becomes appreciable due to the curvature of the graphite layer.[15] These observations naturally lead us to the question of the physical origin of hole doping in CNT's; It has been found that upon rolling a graphite sheet to form a nanotube the tube radius shrinks due to a contraction of the hexagonal rings relative to the planar orientation,[16] consistent with the measured Raman spectra of semiconducting CNTs as compared to graphite.[17] In addition, first-principles calculations on out-of-plane variations of the sp^2 bonding configuration have shown a decrease in bond length caused by an increase in charge on the σ bonds.[18] This type of charge transfer has also been observed for hole-doped graphite intercalates in which electrons are transferred from π to σ orbitals, thereby strengthening the C-C bond and decreasing the bond length.[19] It should be noted that while decreases in bond length on the order of 1% have little effect on CNT electronic band structure,[16] such changes are known to be associated with significant doping levels in graphite-related materials.[20] In CNT's, the overlap of π and σ states inevitably causes a redistribution of charge in the π bonds that make up the valence band.[16,21] Hence, we postulate that the observed *p*-type behavior in semiconducting CNT's is caused by π-σ charge transfer resulting in depletion of electrons in the π valence band (hole doping) and an increase in the strength of the σ bonds making up the nanotube lattice [Fig. 1(c), 1(d)]. The effect we describe is beyond *rigid-band* models thus allowing the charge on atomic orbitals to vary in these types of systems as *ab initio* calculations have previously shown.[18,19] It is plausible to expect this type of charge transfer to occur between electronic states of different symmetry through a hybridization mechanism with π-hole character increasing as π-σ hybridization, shifting the Fermi level towards the valence band.

The separation of charge caused by transfer of electrons from π to σ orbitals results in an effective dipole moment at each lattice site. A proper system Hamiltonian to consider the coupling of such charge transfer to the graphene lattice needs to consist of three terms

$$H = H_C + H_L + H_I . \tag{1}$$

The first term contains the individual energy of electrons and holes at each lattice site and in addition, the direct and exchange Coulomb interaction between them and their neighbors[22]

$$H_C = \sum_{l} B_l^{+} B_l H_{l,l} + \sum_{l,l'} B_{l'}^{+} B_l W\left(\begin{smallmatrix} ll'l'l \\ 1212 \end{smallmatrix}\right), \tag{2}$$

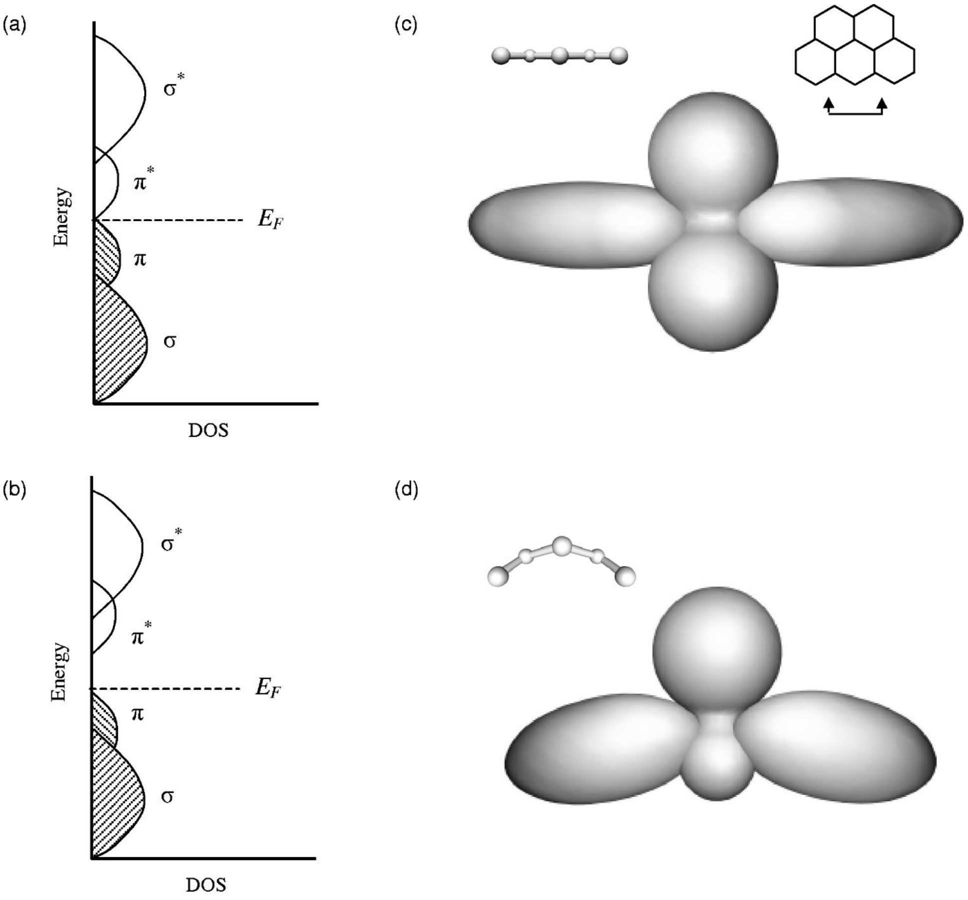

FIG. 1. Schematic density of states (DOS) (a), (b) and corresponding atomic orbital diagrams (c), (d) for 2D graphite and semiconducting CNT's, respectively. Within the self-doping model presented, upon curving the graphite sheet into a nanotube charge is redistributed among the orbitals, depleting the π bond of electrons while increasing charge on the σ bonds.

where B_l^+ is the operator describing electron transfer from a π to σ orbital creating a π-hole at lattice site l. W is defined in general by

$$W\binom{l_1l_2l_3l_4}{j_1j_2j_3j_4}=\int\int d^3x d^3x'\,\phi^*_{j_1}(x-R_{l_1}{}^\circ)\,\phi^*_{j_2}(x'-R_{l_2}{}^\circ)\times\frac{e^2}{\varepsilon_{x,x'}|x-x'|}\,\phi_{j_3}(x'-R_{l_3}{}^\circ)\,\phi_{j_4}(x-R_{l_4}{}^\circ).$$

The superscripts refer to the lattice position and the subscripts stand for π and σ. The $\phi_j(x-R_l{}^\circ)$ are Wannier functions for the two types of atomic orbitals and $\varepsilon_{x,x'}$ is the dielectric function. We consider charge transfer via hybridization of atomic oribitals on the same lattice site. This requires that $l_4=l_1=l$ and $l_2=l_3=l'$. In addition, we neglect cotransfer of electrons, leading to the restrictions $j_3\neq j_4$ and $j_1\neq j_2$. To simplify notation π and σ are represented by 1 and 2, respectively. $H_{l,l}$ is given by

$$H_{l,l}=\sum_i H_{ll,ii}-W\binom{llll}{1221},\tag{3}$$

where

$$H_{lm,ij}=\int d^3x\,\phi_i^*(x-R_l{}^\circ)\left\{-\frac{\hbar^2}{2m}\nabla^2+V_p(x)\right\}\phi_j(x-R_m{}^\circ)$$

describes the kinetic and potential energy of the particles in the field of the atomic nuclei. It is assumed that the operator in curly brackets does not contribute to charge transfer and therefore only terms for which $l=m$ and $i=j$ are included in Eq. (3).

The lattice energy is given by

$$H_L=\sum_{\alpha,q}\hbar\omega_q(b^+_{\alpha,q}b_{\alpha,q}+1/2),\tag{4}$$

where $b^+_{\alpha,q}$ is the creation operator for a phonon with wave vector q and polarization α associated with graphite.

Upon curving 2D graphite into a cylinder the atomic wave functions change shape and charge is redistributed among them. The coupling between charge transfer at each lattice site and nanotube curvature can be described by the following interaction Hamiltonian:

$$H_I=\sum_{\alpha,q,l}\hbar\omega_q u_l(\alpha,q)B_l^+B_l[b_{\alpha,q}+b^+_{\alpha,-q}],\tag{5}$$

where

$$u_l(\alpha,q)=\gamma_{\alpha,q}e^{iqR_l{}^\circ}/\sqrt{2N}$$

in which

$$\gamma_{\alpha,q}=\int d^3x\,\phi_1^*(x-R_l)\,\phi_2^*(x-R_l)[e(\alpha,q)\nabla H_{l,l}]$$
$$\times\,\phi_2(x-R_l{}^{\circ})\,\phi_1(x-R_l{}^{\circ})$$

is the matrix element which describes charge transfer between atomic orbitals, with $\phi_i(x-R_l{}^{\circ})$ and $\phi_i(x-R_l)$ $(i=1,2)$ being the orbitals before and after curvature respectively and $e(\alpha,q)$ the polarization vector; N is the total number of atoms considered. We omit off-diagonal terms in Eq. (5) since we are again considering hybridization induced charge transfer constrained to the same lattice site.

To proceed we perform a unitary transformation of the displacive type[23] on H:

$$\tilde{H}=e^{-S}He^{S},$$

where

$$S=\sum_{\alpha,q,l}u_l(\alpha,q)B_l^+B_l[b_{\alpha,q}-b_{\alpha,-q}^+].$$

The result is

$$\tilde{H}=\sum_l B_l^+B_l(H_{l,l}-\varepsilon_l)+\sum_{l,l'}\sigma_{ll'}B_{l'}^+B_l$$
$$+\sum_{\alpha,q}\hbar\omega_q(b_{\alpha,q}^+b_{\alpha,q}+1/2), \tag{6}$$

where

$$\varepsilon_l=\sum_{\alpha,q}\hbar\omega_q u_l(\alpha,q)u_l(\alpha,-q)$$

is the shift in electronic on-site energies caused by curving graphene into a cylinder and

$$\sigma_{ll'}=\exp\Bigg\{\sum_{\alpha,q}[u_l(\alpha,q)-u_{l'}(\alpha,q)]$$
$$\times[b_{\alpha,q}-b_{\alpha,-q}^+]\Bigg\}W\left(\begin{smallmatrix}ll'l'l\\1212\end{smallmatrix}\right)$$

modifies the Coulomb interaction between neighboring sites. The change in position of the carbon atoms relative to the uncurved lattice can be found from

$$x_l=\langle\tilde{\psi}_l|\eta_{\alpha,q}|\tilde{\psi}_l\rangle,$$

where $|\tilde{\psi}_l\rangle=e^S|\psi_l\rangle$ is the eigenfunction of the transformed Hamiltonian at lattice site l, and

$$\eta_{\alpha,q}=\sum_{\alpha,q}\sqrt{\frac{\hbar}{2MN\omega_q}}(b_{\alpha,q}+b_{\alpha,-q}^+)$$

is the displacement operator, where M is the atomic mass of carbon. Using the expression for S, the calculation of x_l can be pursued analytically[24] leading to

$$x_l=2\sqrt{\frac{\hbar}{M\bar{\omega}}}\,\bar{u}\langle B_l^+B_l\rangle \tag{7}$$

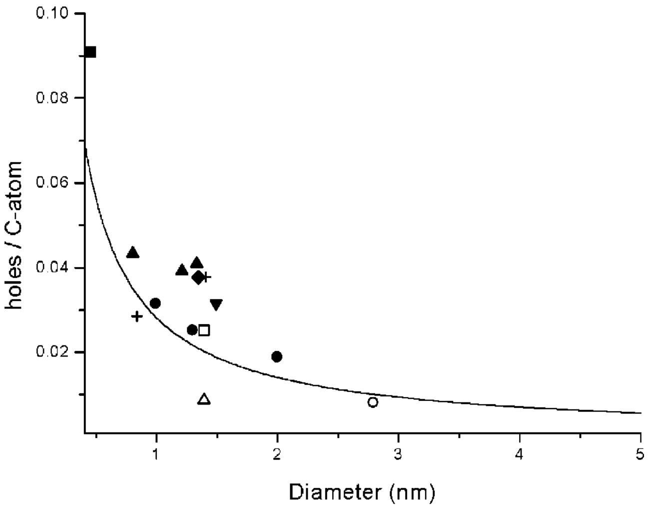

FIG. 2. Diameter dependence of hole concentration for self-doped semiconducting CNT's. Experimental data from field-effect measurements [△ (Ref. 13), □ (Ref. 31), ○ (Ref. 32)] and Raman spectroscopy [◆ (Ref. 17), ▲ (Ref. 33), + (Ref. 34), ● (Ref. 35), ■ (Ref. 36), ∇ (Ref. 37)] is plotted for comparison.

for curvature induced π-σ charge transfer coupled to a lattice whose mean phonon frequency is $\bar{\omega}$; $\overline{u^2}=(1/2N)\Sigma_{\alpha,q}|\gamma_{\alpha,q}|^2$ and $\langle B_l^+B_l\rangle$ is the expectation value for the number of π holes per lattice site formed in the nanotube.

In order to solve Eq. (7) for the CNT π-hole carrier concentration we use the expression $\overline{u^2}\simeq(\sqrt{2}q_De^2/\pi\hbar\bar{\omega})(1/\varepsilon_\infty-1/\varepsilon_0)$, applicable for charge carriers strongly coupled to lattice degrees of freedom,[25] where $q_D=2(\pi/\Omega)^{1/2}$ is the Debye momentum, $\Omega=(3\sqrt{3}/2)a^2$ is the primitive cell area for 2D graphite and ε_∞ and ε_0 are the high frequency and static dielectric constants, respectively. For a given nanotube the value of x_l is uniquely determined by geometry, being inversely proportional to diameter.[26] As a concrete example, we plot the π-hole carrier concentration versus nanotube diameter for $(n,0)$ semiconducting CNT's within our model in Fig. 2 [$\varepsilon_0\gg\varepsilon_\infty\simeq1$ (Ref. 27), $\bar{\omega}=1581\ \mathrm{cm}^{-1}$]. Smaller diameter tubes in which π-σ mixing is greatest are seen to be the most heavily p-type with the hole concentration depending inversely on diameter.

Field-effect measurements on individual semiconducting CNT's have been used to obtain hole carrier concentrations for some nanotube diameters and these are plotted in Fig. 2. In addition, we can compare our model to the phonon shifts observed when CNT's are doped with external acceptor species; It has been found that a general measure of charge transfer in acceptor-type CNT compounds is given by an upshift of Raman-active tangential modes by $\sim320\ \mathrm{cm}^{-1}$/(hole/C atom) introduced into the π band.[28] Using this value, the observed upshift of Raman modes in prisitine semiconducting nanotubes relative to graphite can then be used to infer CNT self-doping levels and compared to our model. This is a valuable comparison to make because the Raman data is free of contributions from electrical contacts. We show hole carrier concentrations inferred from Raman data for different diameter semiconducting CNT's in Fig. 2. The exprimental data agrees quite well with the self-doping model presented here. Since the data is from several sources using differing experimental techniques this lends further credence to our results.

To summarize, a self-doping model of CNT carrier concentration based on charge transfer from π to σ orbitals has been presented. We calculate that the hole carrier concentration is inversely proportional to diameter and find quantitative agreement with experiment. Our results show a tool in the already robust library of geometrically tunable carbon nanotube properties that are attractive for nanoelectronics. In addition, the physical insights gained from our model should allow further more detailed calculations to be carried out. The CNT self-doping phenomenon described here could also have important implications for future NEMS sensors and may be relevant to recent work on superconductivity in small diameter nanotubes.[29,30]

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