Extreme hydrogen sensitivity of the transport properties of single-wall carbon-nanotube capsules

Antonis N. Andriotis,[1,*] Madhu Menon,[2,3,†] Deepak Srivastava,[4,‡] and George Froudakis[5]
[1]*Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas, P.O. Box 1527, 71110 Heraklio, Crete, Greece*
[2]*Department of Physics and Astronomy, University of Kentucky, Lexington, Kentucky 40506-0055*
[3]*Center for Computational Sciences, University of Kentucky, Lexington, Kentucky 40506-0045*
[4]*NASA Ames Research Center, CSC, Mail Stop T27-A1, Moffett Field, California 94035-1000*
[5]*Department of Chemistry, University of Crete, P.O. Box 1470, Heraklio, Crete, Greece 71409*
(Received 6 March 2001; published 9 October 2001)

I-V characteristics of single-wall carbon nanotubes are calculated and shown to be extremely sensitive to H adsorption. Furthermore, this sensitivity manifests oscillating characteristics in both metallic and semiconducting nanotubes and can be attributed mainly to the changes in the transmission function induced by H adatoms and not to the charge transfer. The results are in good agreement with a recent experimental study of hydrogen storage in single-wall carbon nanotubes.

DOI: 10.1103/PhysRevB.64.193401 PACS number(s): 73.50.−h, 73.23.Hk, 73.61.Wp, 81.10.Aj

The electronic structure of single-wall carbon nanotubes (SWCNs) can be either metallic or semiconducting, depending on both the diameter and chirality which can be uniquely determined by the chiral vector (n,m), where n and m are integers.[1] More recent experiments, however, suggest the electronic properties to have extreme sensitivity to a chemical environment. In particular, exposure to gaseous molecules such as oxygen, NO_2, or NH_3 results in orders of magnitude change in the electrical resistivity of semiconducting nanotubes.[2,3] Some small-band-gap semiconducting nanotubes were even observed to become metallic upon oxygen dosing.[2] While exposure to NO_2 molecules increased the conductance of the SWCN sample by about three orders of magnitude, conductance of the SWCN sample was observed to decrease $\approx$100-fold after exposure to NH_3.

A number of factors have been attributed to be responsible for this including charge transfer and the presence of defects. In particular, it has been argued that the interaction of Cu with metallic SWCNs leads to a gap opening at E_F, affecting, thus, the conduction properties of the SWCN.[4] Similarly, charge transfer induced by NO_2 and NH_3 adsorption on semiconducting SWCNs is thought to alter the change in the SWCN conductance.[3] Theoretical calculations performed on oxidized semiconducting nanotubes suggest weak hybridization between carbon and oxygen, resulting in conducting states near the band gap.[5] Furthermore, a small charge transfer of 0.1 electron from the nanotube to each oxygen molecule was predicted.[5]

Interestingly, changes in the resistivity of SWCNs were also observed in cases where the gas adsorption (i.e., N_2, He, H_2) does not induce any charge transfer.[6,7] In such cases the resistivity change upon gas adsorption was tentatively assigned to changes in the electron and hole free carrier lifetimes. Along this line of approach, we have shown recently that Ni adatoms on metallic SWCNs induce changes in the electron scattering time which can account for the anomalous temperature dependence of the SWCNT resistivity.[8]

Despite all these considerations, no satisfactory explanation of the transport changes induced by adatoms on SWCNs has been given yet. It is reasonable to expect the effect of adatoms on the electronic and transport properties of SWCNs to be an outcome of a delicate interplay among various factors including the charge transfer, possible pinning of the Fermi energy, the creation of the impurity band and its location relative to E_F (Fermi energy), etc. However, the contribution of each one of these factors to the transport properties of SWCNs has not been established yet. It is apparent that a quantitative understanding of their contributions to the electronic and transport properties of SWCNs is essential and timely for understanding their true intrinsic properties.

In the present work, we perform a quantitative study of the effect of H adsorption and charge transfer on the transport properties of SWCNs by calculating *I-V* curves for both bare and H adsorbed (5,5) and (10,0) tubes. Our system consists of finite-length (5,5) and (10,0) SWCNs containing 150 and 164 C atoms, respectively. Both tubes are capped at both ends to avoid the influence of dangling bond effects. The SWCNs are placed between two paramagnetic transition metal leads (Ni with its $\langle 001 \rangle$ orientation parallel to the tube axis) which act as terminals between which a bias voltage is applied. The H-adsorbed SWCN systems investigated consisted of up to 12 H atoms on SWCNs. The length of the tubes chosen is sufficiently large enough to isolate the influence of H adsorption on conductance while avoiding interactions between H atoms and metal leads.

Although most previous theoretical works on quantum conductivity have primarily dealt with infinite-length nanotubes on account of the simplification offered in the formalism, recent experimental works have provided evidence for transport through finite-length nanotubes.[9] Rapid advances in experimental techniques will soon enable measurements on nanotube systems consisting of a few hundred atoms as in the present work. Theoretical studies dealing with SWCNs of approximately the same size as the one used in the present work have already appeared in the literature.[10–14]

We use the familiar Landauer expression to obtain conductivity from the transmission function $T(E)$,[15] which, in turn, is obtained using the Green's function formalism. A realistic treatment of SWCNs interacting with metal leads

 ©2001 The American Physical Society

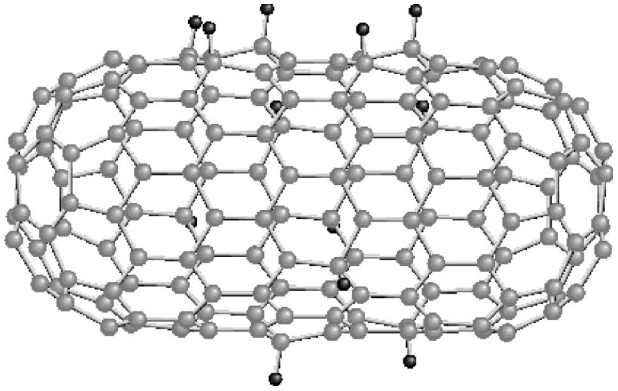

FIG. 1. Relaxed geometry of (10,0) SWCN ''capsule'' with 12 H atoms adsorbed. The relaxation results in the underlying carbon atom going from a planar (sp^2 type) to a pyramidal (sp^3 type) configuration.

must involve a judicious construction of the Green's function. We use the tight-binding (TB) formulation for both the Hamiltonian and the Green's function. The TB Hamiltonian consists of $N_{at}N_{orb}\times N_{at}N_{orb}$ matrices, where N_{at} is the number of atoms in the embedding subspace and N_{orb} is the number of orbitals on each atom. Contrary to previous works on quantum transport which use only one π-electron orbital per atom, we use $N_{orb}=4$ for carbon, which includes $1s$ and $3p$ orbitals. Additionally, we use $N_{orb}=9$ for Ni (taken to be the material of the leads), which includes $1s$, $3p$, and $5d$ orbitals. This Hamiltonian has been used with success in the treatment of transition metal systems as well as their interactions with carbon fullerenes and nanotubes.[16–20]

We use the TB Hamiltonian to perform full symmetry unconstrained molecular dynamics relaxation for the H-adsorbed SWCN system. Consideration of the atomic relaxation is essential since the interaction between the nanotube and hydrogen is fairly strong and can give rise to gap-opening deformations.[21,22] In Fig. 1 we show the relaxed configuration of 12 H atoms on a (10,0) tube. As seen in the figure, the H chemisorption results in the underlying carbon atoms going from a planar (sp^2 type) to a pyramidal (sp^3 type) configuration. The TB calculations are complemented by accurate *ab initio* calculations performed using the density functional theory (DFT) based GAUSSIAN 98 program.[23] The *ab initio* method is used to calculate total energies of all the relaxed structures considered in the present work as well as for calculating the highest-occupied molecular orbital (HOMO) and the lowest-unoccupied molecular orbital (LUMO) energy differences (see Refs. 20 and 24 for more details). Our *ab initio* calculations estimate the binding energy of the H atom on the (10,0) SWCN to be 1.98 eV.

For calculating quantum conductivity we use the Green's function formalism to embed the SWCN in a host lattice consisting of transition metal atoms forming semi-infinite leads at the two ends.[25] A boundary surface **S** separates the embedded system (tube) from the host lattice (leads) with the Green's function of the host satisfying the Dirichlet's boundary condition on **S**.[26] The lead-tube interaction is incorporated through the introduction of an electron self-energy term in the formalism. There are two self-energy terms, one for each metal lead. Although it is desirable to have the calculations performed self-consistently, the size of the system (number of atoms as well as the use of nine orbitals for each atom) makes this prohibitively expensive. We note that previous calculations, when done self-consistently, involved only very-small-size systems (typically less than 15 atoms).[27,28] The purpose of the present work is to gain an understanding of the effect of H adsorption on the transmittance and quantum conductance of SWCNs while keeping other factors fixed. The novel feature of the present method is that the Hamiltonian used in calculating the conductivity is identical to the one used in performing tight-binding molecular dynamics simulations for relaxing all structures considered as well as the use of nine orbitals for each atom that includes *d* electrons of the transition metal atoms. All our results of the TB calculations are checked by *ab initio* ones.

In Fig. 2 we show I-V curves for the semiconducting

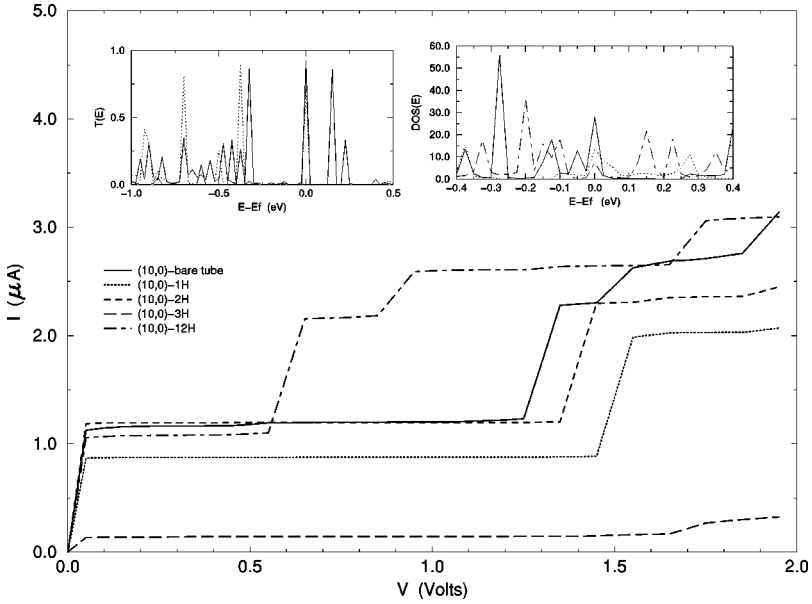

FIG. 2. The I-V curves for a semiconducting (10,0) nanotube with up to 12 adsorbed H atoms. The same legend is used for both insets.

TABLE I. HOMO-LUMO gap values for H-adsorbed (10,0) tube obtained using *ab initio* calculations. All structures are fully relaxed.

Structure	HOMO-LUMO gap (eV)
SWCN+0H	0.75
SWCN+1H	0.12
SWCN+2H	0.18
SWCN+3H	0.06
SWCN+12H	0.10

(10,0) nanotube with up to 12 chemisorbed H atoms.[29] The *I-V* characteristics of the bare tube are denoted by the solid line. The steplike features seen in the *I-V* curves are now well understood; it is the outcome of the resonant scattering, attributed to the resonance structure of $T(E)$ resulting from scattering at the lead-tube contacts. In this picture, finite changes in the bias voltage result in additional electron bands becoming available for transmission,[30] thus giving rise to abrupt changes in the current as the bias voltage is changed. The resonance structure of $T(E)$ can be attributed to the metal-tube interaction as well as to confinement and interference effects which can lead to Breit-Wigner and Fano resonances and antiresonances.[31,32] As seen in Fig. 2, for low values of the applied voltage (<2 V), the current versus voltage curves show oscillations as the number of adsorbed H atoms increases. The initial drop in the current for 1 H atom adsorption is followed by a significant drop in the current for 2 H atom adsorption, while the value of the current for 3 H atoms is very close to the bare tube case for most of the range of the voltage. There is a substantial increase in the current for 12 H atom adsorption.

The extreme sensitivity exhibited in quantum conductivity on H chemisorption can be better understood by studying the behavior of the transmission function $T(E)$ and density of states (DOS) in the vicinity of E_F, shown in the insets of Fig. 2. In these, $T(E)$ and the DOS of the system consisting of a bare SWCN nanotube plus the Ni leads is compared with the DOS resulting from the adsorption of 1 and 12 H atoms in the vicinity of E_F. As seen in the DOS figure, additional peaks are introduced in the gap as a result of H adsorption when compared to the bare SWCN case. For the purposes of clarity, only the results for zero, 1 H, and 12 H atoms are shown for DOS. The resonance peaks below E_F of the bare SWCN are shifted farther downward on H adsorption. These modifications cause the *I-V* characteristics of the H-adsorbed tube to exhibit a high sensitivity in the current at low bias voltages as compared to the corresponding current values of the H-free tube. Furthermore, it can be inferred that the qualitative trend found here is identical to the one obtained using our *ab initio* calculations presented in Table I which contains the HOMO-LUMO gap values for H adsorption for SWCNs. The *ab initio* results show an oscillation in the HOMO-LUMO gap on H adsorption.

In order to study the effect of chirality on H adsorption, we calculate the conductance of metallic (5,5) tube, also with up to 12 chemisorbed H atoms. The *I-V* curves for this system are shown in Fig. 3. As seen in the figure, in contrast to the (10,0) case, there is an increase in the current for 1 H atom adsorption followed by a further increase in the current for 2 H atoms for the most of the range of the bias voltage. There is a smaller increase in the current on 3 H atom adsorption over the bare tube value, while the current for 12 H atoms is close to the bare tube value. Overall, the *I-V* characteristics are similar to that in Fig. 2, showing oscillations with increased H adsorption. The insets show the corresponding transmission function T(E) and DOS for the 150-atom SWCN ''capsule'' plus Ni atoms in contact with the carbon atoms of the SWCN. For the purposes of clarity, again, only the results for 1 H and 12 H atoms are shown for the DOS in Fig. 3. The transmission function $T(E)$ for the 1-H- and 12-H-atom cases differ significantly from the (10,0) tube case. As seen in the figure, the chemisorption of H causes the destruction of most resonances below E_F when

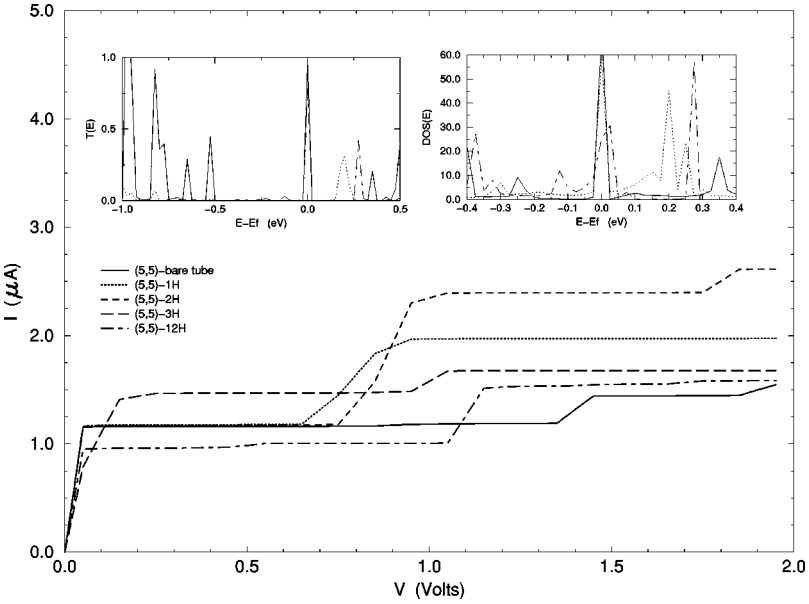

FIG. 3. The *I-V* curves for a metallic (5,5) nanotube with up to 12 adsorbed H atoms. The same legend is used for both insets.

compared with the H-free case. This explains why no significant increase in the current is observed for the 1-H- and 12-H-atom adsorption.

We have also performed *ab initio* calculations for the HOMO-LUMO gap values for neutral and charged nanotubes. For metallic tubes, the charge transfer (positive or negative) tends to develop a gap, while for semiconducting tube the existing gap is decreased on charge transfer (positive or negative), with the positive value of charge transfer (to the nanotube) being more influential in decreasing the gap. The *ab initio* calculations give a small charge transfer of $0.25e$ from each H to the nanotube for all cases studied, making the SWCN anionic. Since, for a metallic tube, the tendency of charge transfer is to develop an energy gap at E_F, it should contribute towards suppression of the current in the metallic tube. The reverse should be true for the semiconducting tube; charge transfer decreases the energy gap, providing an enhancement in the conductivity. Since the conductivity shows oscillations, regardless of the chirality of the SWCN, it is reasonable to attribute the changes in the *I-V* curve of the H-adsorbed tube mainly to the H-induced changes in the resonance structure of $T(E)$ of the H-free tube rather than to charge transfer effects. A similar explanation may be applicable in the case of contrasting behavior observed in the conductance of nanotubes upon NO_2, NH_3, and oxygen adsorption reported in recent experiments.[2,3]

We have also studied the same systems using the transfer Hamiltonian[33] approach (THA) which is the weak-coupling version of the present scattering approach. The results[34] obtained using the THA were qualitatively identical to the present results providing an independent verification of the oscillating behavior of the conductivity on H adsorption on metallic and semiconducting nanotubes.

Interestingly, a very recent experimental paper by Sumanasekera *et al.* dealing with the study of hydrogen storage in SWCNs (Ref. 7) shows the electrical resistivity of SWCNs to depend sensitively on H adsorption. In the absence of significant charge transfer found in the experiments, the resistivity change upon H adsorption is attributed to additional impurity scattering induced by H. This is exactly the same as the conclusion of the present work.

It is also worth considering the effect of localization caused by the H induced sp^3 defects as shown in Fig. 1 and their effects on conductivity. Recent reports[35,36] have shown that armchair nanotubes are insensitive to disorder-induced localization (Anderson localization), therefore justifying the exceptional ballistic transport properties of the these nanotubes. The present study, therefore, is valid for (5,5) nanotubes even though localization effects are not explicitly taken into account. Although these effects may be valid for the (10,0) nanotube, we do not expect localization effects to prevent the extrapolation of our results to larger tube lengths.

In summary, our calculations show extreme sensitivity of the quantum conductance on H adsorption on carbon nanotubes. This has been explained to be caused by additional resonances induced by H adsorption. Furthermore, while the semiconducting SWCN exhibits a significant increase in conductivity on large H adsorption, the conductivity remains essentially unchanged for metallic SWCNs on large H adsorption. These contrasting tendencies present an intriguing possibility of using H-rich environments for identifying metallic and semiconducting nanotubes.

The present work is supported through grants by the NSF (98-62485, 99-07463, MRSEC Program under award No. DMR-9809686), DEPSCoR (99-63231 and 99-63232), DOE Grant No. 00-63857, NASA Grant No. 00-463937, and the University of Kentucky Center for Computational Sciences.

*Electronic address: andriot@iesl.forth.gr
†Electronic address: super250@pop.uky.edu
‡Electronic address: deepak@nas.nasa.gov

[1] R. Saito, M. Fujita, G. Dresselhaus, and M.S. Dresselhaus, Phys. Rev. B **46**, 1804 (1992).
[2] P.C. Collins *et al.*, Science **287**, 1801 (2000).
[3] J. Kong *et al.*, Science **287**, 622 (2000).
[4] K. Kong *et al.*, Phys. Rev. B **60**, 6074 (1999).
[5] S.H. Jhi *et al.*, Phys. Rev. Lett. **85**, 1710 (2000).
[6] G.U. Sumanesekera *et al.*, Phys. Rev. Lett. **85**, 1096 (2000).
[7] G.U. Sumanasekera *et al.*, (unpublished).
[8] A.N. Andriotis *et al.*, Phys. Rev. B **61**, R13393 (2000).
[9] M. Bockrath *et al.*, Science **275**, 1922 (1997).
[10] D. Orlikowski *et al.*, Phys. Rev. B **63**, 155 412 (2001).
[11] Y. Ma *et al.*, Phys. Rev. B **63**, 115 422 (2001).
[12] G. Froudakis, Nano Lett. **1**, 179 (2001).
[13] K.N. Kudin *et al.*, Phys. Rev. B **63**, 045 413 (2001).
[14] C.W. Bauschlicher, Jr., Chem. Phys. Lett. **322**, 237 (2000).
[15] R. Landauer, Z. Phys. B **68**, 217 (1987).
[16] A.N. Andriotis *et al.*, Chem. Phys. Lett. **301**, 503 (1999).
[17] A.N. Andriotis and M. Menon, Phys. Rev. B **60**, 4521 (1999).
[18] M. Menon *et al.*, Chem. Phys. Lett. **320**, 425 (2000).
[19] A.N. Andriotis *et al.*, Phys. Rev. B **62**, 9867 (2000).
[20] A.N. Andriotis, M. Menon, and G.E. Froudakis, Phys. Rev. Lett. **85**, 3193 (2000).
[21] C.L. Kane and E.J. Mele, Phys. Rev. Lett. **78**, 1932 (1997).
[22] L. Yang and J. Han, Phys. Rev. Lett. **85**, 154 (2000).
[23] M.J. Frisch *et al.*, computer program GAUSSIAN 98, Revision A.6 (Gaussian, Inc., Pittsburgh, 1998).
[24] A.N. Andriotis and M. Menon, J. Chem. Phys. **115**, 2737 (2001).
[25] J.E. Inglesfield, J. Phys. C **14**, 3795 (1981).
[26] A.J. Fisher, J. Phys.: Condens. Matter **2**, 6079 (1990).
[27] N.D. Lang and Ph. Avouris, Phys. Rev. Lett. **84**, 358 (2000).
[28] M. Di Ventra *et al.*, Phys. Rev. Lett. **84**, 979 (2000).
[29] The current is calculated according to the following formula:
$$I=(2e/h)\int T(E)[f(E-V/2)-f(E+V/2)]dE.$$
[30] C. Dekker, Phys. Today **52(X)**, 22 (1999).
[31] G. Breit and E. Wigner, Phys. Rev. **49**, 519 (1936).
[32] U. Fano, Phys. Rev. **124**, 1866 (1961).
[33] J. Bardeen, Phys. Rev. Lett. **6**, 57 (1961).
[34] A.N. Andriotis *et al.* (unpublished).
[35] P.L. McEuen *et al.*, Phys. Rev. Lett. **83**, 5098 (1999).
[36] C.T. White and T.N. Todorov, Nature (London) **393**, 240 (1998).