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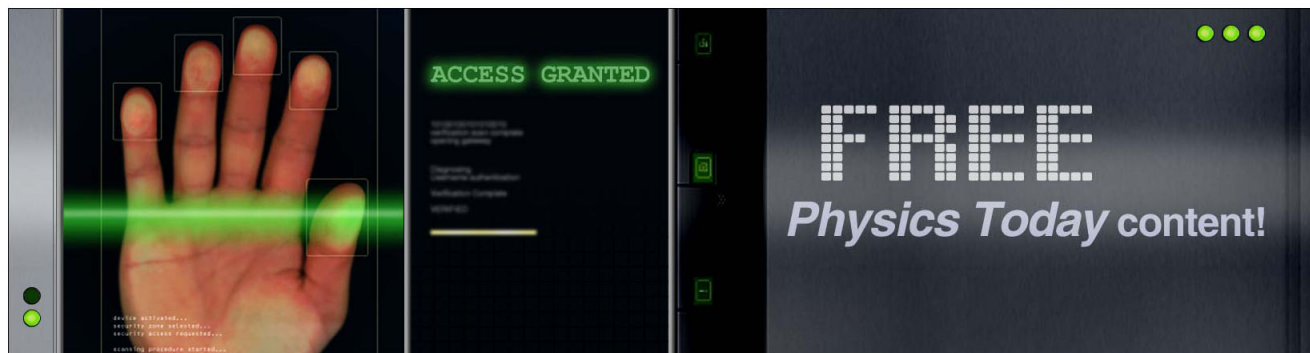
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High subthreshold field-emission current due to hydrogen adsorption in single-walled carbon nanotubes: A first-principles study

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We investigate the effect of hydrogen adsorption on field-emission current from a single-walled carbon nanotube using first-principles calculations. The results show a new emission regime at field values around the field-emission threshold of bare nanotubes, with emission currents comparable to those of the high-field regime. This current enhancement can be explained with the surface dipole created as a result of the difference in electronegativity between carbon and hydrogen that contributes to electron extraction from the nanotube. © 2009 American Institute of Physics.

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Carbon nanotubes (CNTs) have become a central material in nanotechnology with applications ranging from advanced composites¹ to modern capacitive memory cells.² CNTs are made up of one or more rolled-up layers of graphene that create a chemically stable nanostructure with exceptional mechanical and electrical properties. Due to their small size, the electronic structure of CNTs is easily affected by contact with molecules and individual atoms. On the other hand, their chemical stability resists reactions and decomposition. Their atomic structure and its interaction with hydrogen have led to their application for the storage of hydrogen,^{3,4} which is a small molecule and difficult to store safely and effectively at room temperature. Hydrogen chemical sensors have also been implemented by coating or functionalizing CNTs with palladium.⁵⁻⁷ There are a number of theoretical^{8,9} and experimental¹⁰⁻¹³ works on the effect of gases such as nitrogen and hydrocarbons on field-emission from CNTs. However, the study of the effect of hydrogen adsorption on field-emission has been limited in spite of the fact that hydrogen, because of its size, is a difficult molecule to purge even in ultra high vacuum systems. Experimental work by Zhi *et al.*¹⁴ previously demonstrated that hydrogen plasma treatment improves the field-emission properties of CNTs. Using field-emission electron microscopy, Saito *et al.*¹⁵ showed changes in the shape of the emission spot (appearance of localized bright spots on the CNT tip) obtained from a multiwalled CNT once the CNT was exposed to hydrogen. Two theoretical studies by Maiti *et al.*⁸ and Chen *et al.*¹⁶ showed that under an electric field a hydrogen molecule can reduce the ionization potential of CNTs (making it easier to extract electrons), and a similar effect takes place with boron-hydrogen and nitrogen-hydrogen termination of an open ended CNT. The focus of the present work is to calculate the field-emission current from a single-walled CNT under various levels of hydrogen adsorption using a first-principles method.

There are two natural states of adsorption of hydrogen on CNTs: the first is physisorption of a hydrogen molecule on a CNT,¹⁷⁻¹⁹ and the second is chemisorption of hydrogen, which forms a covalent bond with the CNT.^{3,20,21} In this letter, we have considered chemisorption of atomic hydrogen with the relaxed state of hydrogen adsorbates on a CNT,

which is initially determined using molecular dynamics (MD) simulations. This was done using the software NANO-HIVE-1²² with adaptive intermolecular reactive empirical bond order (AIREBO) potentials,²³ which are widely used for hydrocarbon systems.^{24,25}

To study the effect of hydrogen on field-emission, an 8-unit-cell (5,5) CNT, capped with half of a C₆₀ molecule on one end, was used (the other end was terminated with hydrogen atoms to avoid dangling bonds). Field-emission from the capped end of the CNT was investigated. The capped half of the CNT structure was covered with various percentages of hydrogen, namely, 20%, 40%, 60%, 80%, and 100%, with a random distribution of hydrogen on the surface. Each of these structures was then relaxed in NANO-HIVE-1. Further geometry optimization was then performed in the software GAUSSIAN 03.²⁶ The restricted Hartree-Fock method and the 6-31g(d) basis set were used. The electronic structure of the nanotubes with each of the hydrogen coverage levels was calculated under different electric fields using the same method and basis set in GAUSSIAN 03. The current at each value of field was then calculated using a transport solver developed by our group based on a nonequilibrium Green's function approach in the Fisher-Lee formalism²⁷ and using the Landaur-Buttiker formula.²⁸ A detailed description of

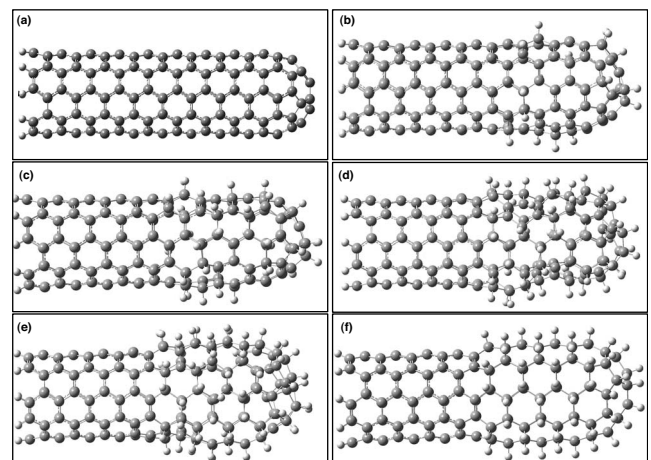


FIG. 1. Relaxed structure of a (5,5) CNT terminated with hydrogen on the left and capped with half of a C₆₀ molecule on the right, and partially covered with: (a) no hydrogen, (b) 20% of hydrogen, (c) 40% of hydrogen, (d) 60% of hydrogen, (e) 80% of hydrogen, and (f) 100% of hydrogen.

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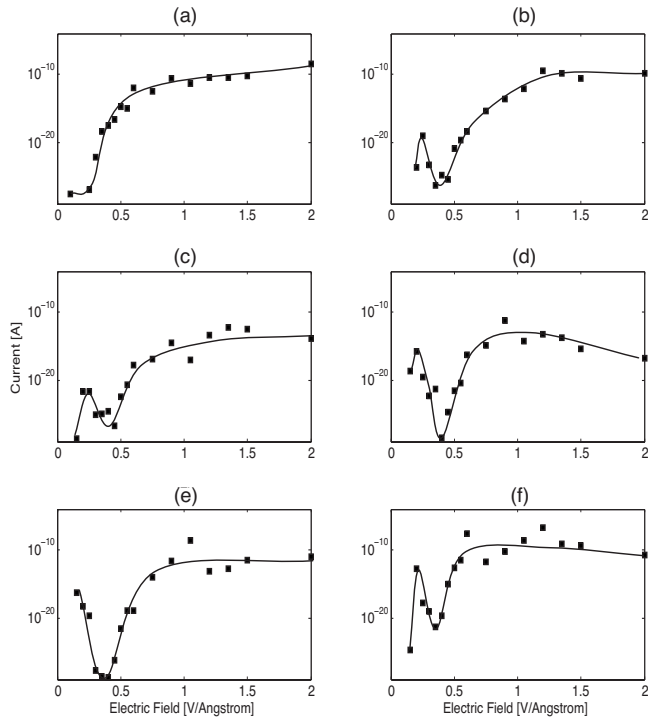


FIG. 2. Current-voltage characteristics of the simulated structure that is partially covered with: (a) no hydrogen, (b) 20% of hydrogen, (c) 40% of hydrogen, (d) 60% of hydrogen, (e) 80% of hydrogen, and (f) 100% of hydrogen.

this methodology and transport solver can be found in Ref. 29.

Figure 1 illustrates the relaxed structure of the nanotube under various levels of hydrogen coverage. The CNT starts to deform drastically for hydrogen coverage above 20%. However, as the adsorption rate increases symmetry is gradually regained. At above 80% coverage the CNT diameter expands significantly, effectively increasing the carbon-carbon bond lengths.

The calculated emission current from these structures as a function of electric field is illustrated in Fig. 2. It is apparent that at high electric fields, the addition of hydrogen does not have a major effect. However, at low electric fields, hydrogen adsorption significantly changes the emission characteristics. A new ON regime is now created at field values slightly below the threshold of emission for the bare CNT. This is consistent with the experimental observations of Zhi *et al.*¹⁴ who demonstrated that as the CNT is exposed for a long duration of time to a hydrogen plasma, the on regime shifts below the threshold of emission for a bare CNT.

In order to understand this enhancement in the field-emission current at low fields, we investigated the charge distribution (Fig. 3) on carbon and hydrogen atoms and the resulting surface dipoles, which are expected due to the difference in electronegativity between carbon and hydrogen. At low electric fields a large dipole moment of $\sim 6.53 \times 10^{-30}$ Cm is created between hydrogen (positively charged) and carbon (negatively charged) at the tip of the CNT. The direction of this dipole is such that it assists in the extraction of electrons from the CNT, effectively reducing the CNT's work function. As the external field increases, it opposes the charge transfer between carbon and hydrogen, reducing the dipole and its electron extracting effect and resulting in a decrease in current. For example, at a field value of 1.35 V\AA^{-1} , the dipole has decreased to $\sim 3.58 \times 10^{-30}$ Cm. The magnitude of this dipole continues to decrease as a function of applied field until it is neutralized, at which point the CNT with hydrogen starts to behave similarly to one without hydrogen.

Another way of looking at this effect is by examining the potential barrier to electron emission at the CNT tip. For example, the barrier width outside of an infinite, planar electron emitter under electric field is $\Phi\epsilon^{-1}$, where Φ is the work function of the material and ϵ is the applied field. As we have previously discussed in Ref. 29, charge accumulation at the tip of a CNT greatly affects the potential barrier that the

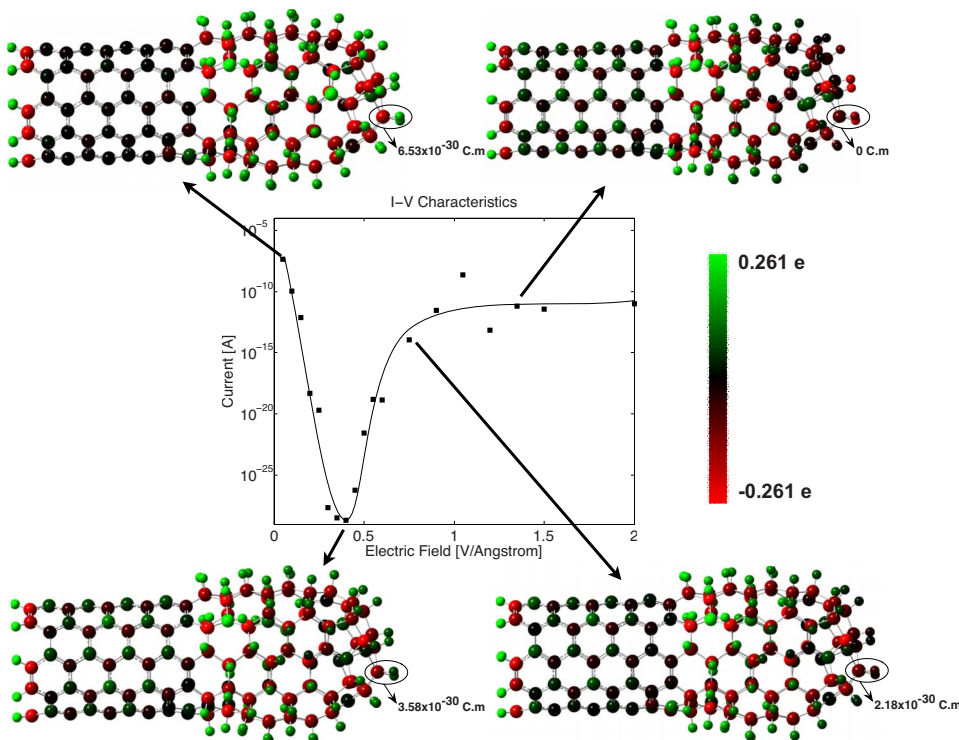


FIG. 3. (Color online) Charge distribution for 80% partial hydrogen coverage at different electric fields. The arrows indicate which part of the I-V curve corresponds to which charge distribution. The dipole moment of a carbon-hydrogen pair at the tip of the CNT, which assists in emitting electrons, is also shown. As the electric field increases, it starts to weaken the dipole. Once the dipole is neutralized, the CNT with hydrogen will start to behave like a CNT without hydrogen.

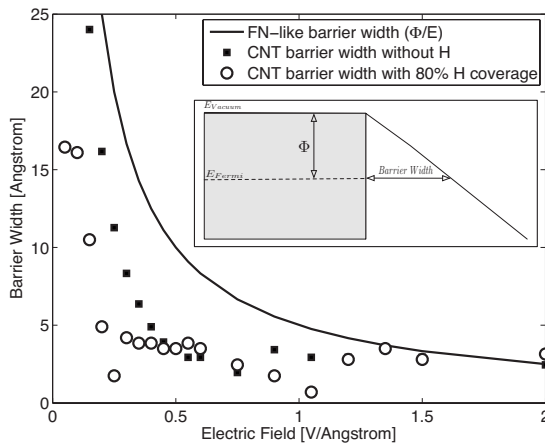


FIG. 4. Potential barrier width for a planar electron source (where ϕ is the work function), potential barrier width for a CNT without any hydrogen coverage, and potential barrier width for a CNT with partial hydrogen coverage of 80%. The inset shows the potential barrier width outside of an infinite planar surface.

electrons inside the CNT face on the way to emission. Figure 4 illustrates the potential barrier width of an infinitely wide surface emitter as a function of applied field (as in the conventional Fowler–Nordheim model³⁰), that of a CNT without hydrogen, and that of a CNT with 80% hydrogen coverage. It is evident that the sharp geometry of the CNT enhances the external field and results in a reduced barrier width compared to that of a flat surface emitter. With the addition of hydrogen, this effect is further enhanced, thereby additionally reducing the potential barrier width at low electric fields. This leads to the high emission current in the new ON regime at low fields. As the applied field increases, it counters this C–H surface dipole by pulling more electrons toward the hydrogen atoms. Eventually the surface dipole due to hydrogen adsorption is neutralized and the potential barrier width follows a trend similar to that of a CNT without hydrogen.

As mentioned before, we have only considered the atomic chemisorption of hydrogen onto a CNT. The reason for this choice was the result of our MD simulations. We found that once a hydrogen molecule gets sufficiently close to a CNT it decomposes and the individual atoms chemisorb onto the CNT. Given that AIREBO potentials (used in our simulations) are well established for the study of reactions in carbon-hydrogen systems, this result justifies our use of atomic hydrogen. Moreover, this result is consistent with the work of Gale and Bilić³¹ who have shown theoretically that chemisorption of hydrogen molecule (which is the separation of hydrogen molecule into atomic hydrogen and forming covalent bonds with the CNT), apart from the onset (the first molecule), is energetically favorable. Also, Nikitin *et al.* have demonstrated the chemisorption of atomic hydrogen on nanotubes experimentally.^{3,20} Nonetheless, we acknowledge that based on the existing literature physisorption of hydrogen on CNTs is also possible. However, we believe the results presented here cover a significant portion of cases of field-emission from hydrogen-decorated CNTs.

In summary, using a custom transport solver based on first-principles calculations, the effect of hydrogen adsorption on the electron field-emission current of a CNT is simulated. The results show a significant enhancement in the emission current at low electric fields, effectively creating a new emission regime. This is believed to be due to the

hydrogen-induced dipole moment that will significantly reduce the tunneling barrier width and height that the electrons in the CNT face. This effect not only has applications in low turn-on-voltage field-emitters (desirable, for instance, in flat-panel displays) but also has potential in hydrogen sensing.

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