Work function of small radius carbon nanotubes and their bundles

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Carbon nanotube work functions can deviate from that of graphene due to geometric and structural factors. The authors have systematically investigated the work functions of various forms of small radius carbon nanotubes and their derivatives by density functional calculations. They considered and compared the work functions of tubes and tube bundles in order to understand the effects of chirality, tube length, and capping condition. Systematic trends are unraveled and discussed. © 2007 American Institute of Physics. [DOI: 10.1063/1.2723682]

Since the discovery of carbon nanotubes, their unusual properties and great potentials for technological applications have attracted the attention of many theoretical and experimental research groups. Because of the unique high aspect ratio as well as the mechanical and chemical stabilities, carbon nanotubes may be used as field emitters for flat panel displays. The work function is a key factor in controlling the field emission properties. Some investigators obtained work functions of about 4.8 eV for single-walled carbon nanotube (SWCNT) bundles and 2.4 eV for Cs-intercalated SWCNT bundles using ultraviolet photoelectron spectroscopy, and 4.6–4.8 eV for individual multiwalled carbon nanotubes (MWCNTs) using transmission electron microscopy technique, and values of 4.95 and 5.05 eV for MWCNTs and SWCNTs using photoelectron emission method. On the other hand, some theoretical works have also demonstrated that the structure of the tip of SWCNTs will affect their work function, and the work function of individual SWCNTs does not have significant structure dependence, and the work functions of small tubes increase dramatically as the diameter of the tube decreases due to the curvature effect. Up to now, there has been no systematic study of the effect of tube length, tube-tube distance, and tube tip on the work function of SWCNTs, and this will be the focus of this article.

The calculations are done within the framework of local density approximation (LDA). LDA can determine the atomic structure and electronic charge density from first principles. We used ultrasoft pseudopotentials with a plane-wave cutoff of 358 eV and the Ceperley-Alder form of exchange-correlation functional. Supercell geometries are used to calculate the work function. For a large enough unit cell, the Fermi energy can be determined relative to the vacuum level, and that allows us to find the work function. For the case of SWCNTs of a finite length with various tube-tube distances (the center to center distance is called $D_x$), the nanotube is put into a supercell, as shown in Fig. 1. The lattice constant of the supercell along the $z$ axis is given by $L + D_v$, where $L$ is the length of the tube and $D_v$ is the vacuum thickness along the tube axis, which is set to be 20 Å for all calculations. A nanotube bundle is the nanotube array configuration that minimizes the total energy of the system, and it is known that the tubes have a hexagonal arrangement inside a bundle. We also calculated the work function of SWCNTs of infinite length. The lattice constant along the tube axis is determined by minimizing the stress of the system, and the in-plane lattice constant is chosen such that the nearest intertube distance is about 20 Å. Such a distance ensures the calculated work function corresponds to that of an isolated tube. The $k$-point sampling is $1 \times 1 \times 1$ for SWCNTs of finite length, $4 \times 4 \times 1$ for SWCNTs bundles of finite length, and $1 \times 1 \times 80$ for SWCNTs of infinite length. All atoms are fully relaxed until the magnitude of the force is less than 0.02 eV/Å. The work function is determined from the difference between the Fermi level and the average potential in the vacuum region where it approaches a constant.

One of the interesting properties of nanotubes is the dependence of the properties on the radius and chirality, and...
mizes the energy of the system. We see from Fig. 2 that for ranged in a hexagonal array and the tube-tube distance mini-
mation in two dimensional, the tubes in the bundle are ar-
energy when the tubes are arranged in a close-packing for-
tances, with the tubes arranged in a square array, mimicking
of tubes in the growth of an array, we have a system with
gether, meaning that if we can control the length and density
the same type of tube, the work function actually depends on
the length of the tube and on the way they are packed to-
to an electric field pattern that depends on the length and the
tubes can be explained qualitatively by the fact that there
is a dipole at the tip of each SWCNT. For an array of finite
SWCNTs, there is an array of dipoles which give rise
is a dipole at the tip of each SWCNT. For an array of finite
calculation, we just consider the potential along the line join-
ing the dipoles in the bundle. This explains the trend for capped
pristine tubes, such that the work function increases with
diminishing the energy of the system. We see from Fig. 2 that for
the same type of tube, the work function actually depends on
the length of the tube and on the way they are packed to-
together, meaning that if we can control the length and density
of tubes in the growth of an array, we have a system with
very tunable electronic properties.

The dependence of the work function of SWCNTs on the
density of tubes (which depends on $D_c$), and the length ($L$) of
the tubes can be explained qualitatively by the fact that there
is a dipole at the tip of each SWCNT. For an array of finite
length SWCNTs, there is an array of dipoles which give rise
to an electric field pattern that depends on the length and the
distance between tubes. For H-terminated nanotubes, the di-
poles at the tips are positive, since carbon attracts electron
from hydrogen; and for capped pristine nanotubes the di-
poles are negative at the tips, since the electrons spill out into
the vacuum at the tips. In a bundle, the dipoles at the tips will
form an array, which become effectively a dipole layer. For
positive dipoles at the surface, electrons will gain energy as
they pass through the dipole layer, and thus the work func-
tion should decrease. The higher the density of the dipoles
(corresponding to smaller intertube distances $D_c$), the lower
would be the work function. This explains the observation
that for the H-terminated tubes of the same length, the work
function decreases with decreasing $D_c$ as a smaller intertube
distance $D_c$ implies a higher density of positive dipoles at the
tips, reaching the lowest work function in the bundles. For
negative dipoles at the tip, the electron has to do extra work
to exit the tube, and thus the work function will become
higher, and the higher density of dipoles (corresponding to
smaller intertube distance $D_c$), the higher would be the work
function of the bundle. This explains the trend for capped
pristine tubes, such that the work function increases with
decreasing $D_c$ since we have an array of negative dipoles,
reaching a maximum at the bundle limit.

The dependence on the tube length ($L$) is more subtle. From
Fig. 2(a), we observe that the work function for a given
intertube distance $D_c$ decreases as $L$ increases ($1/L$ de-
creases). In Fig. 3, we plot the Coulomb potential as seen
from an electron for a two dimensional array of dipoles with
negative charges facing “out”, which emulates the simulation
of an array of capped tubes for Fig. 2(a). For a qualitative
discussion, we just consider the potential along the line join-
ing the dipoles (Fig. 3) since we assume that the electrons are
confined in the tube, and the tube diameter is small compared
with the tube-tube distance. We see that the dipole layer for
capped tubes gives a potential barrier for electrons to climb
from the interior to the outside. However, for shorter tubes,
the Coulomb potential seen by an electron at the interior of
the tube is lower than that of longer tubes since the potential
from the positive charge is not fully balanced by the negative
charges in short tubes. This effectively means that for an
array with the same $D_c$, electrons from shorter tubes have
a bigger barrier to climb, and hence the smaller $L$ (larger $1/L$)
tubes have higher work functions. Thus, the dependence on $L$
as shown in Fig. 2 can be traced to classical dipole effects,
although the results come from quantum mechanical
calculations.

We see from Fig. 2(a) that dependence on $L$ is getting
less conspicuous as $D_c$ decreases, and for the case of
bundles, the work function is essentially independent of $L$.
This is because the tubes are metallic and when the nano-
tubes are closely packed, the screening is good and thus the
dipole field cannot penetrate into interior, except for a small
penetration depth of a few angstroms. This is similar to the
case of a metallic surface where the surface dipole fields are
confined to the surface, and thus the work function quickly
converges with the film thickness.

We see from Fig. 2 that the work function varies roughly
linearly with $1/L$, with a small oscillation due to the quan-
tum size effect. This simple trend allows us to extrapolate
to $1/L \to 0$, which will give the work function for a “long”
tube. These results are shown in Fig. 4 for various values of

FIG. 2. (Color online) Work functions of (a) capped (3,3), (b) H-terminated
(3,3), (c) capped (5,0), and (d) H-terminated (5,0) SWCNTs of various tube-
tube distances $D_c$ vs the inverse tube length $1/L$. The straight lines are the
linear fit of the corresponding data. Limit extrapolation to the $(1/L) \to 0$ limit yields work function of “long” SWCNTs of various $D_c$ shown in
Fig. 4.

FIG. 3. (Color online) (b) Coulombic potential for periodic dipole arrays
[shown schematically in panel (a)] along the line joining the dipoles (with
positive and negative charges at 1 Å apart). Blue and red are results for 20
and 40 Å. Note that the shorter tube has a lower potential inside, leading to
a higher potential difference from interior to outside.
The array of exposed tips gives a high density of positive excitons at the tips constituting the surface of the “solid” SWCNT system. However, the density is dependent on chirality. For the case of bundles, the dependence of work function on the tube terminations becomes weaker and weaker as the intertube distance increases.

We note for a bundle of tubes, the work function depends markedly on the condition of the cap, but is only weakly dependent on chirality, though we focus on small radius tubes, those phenomena that are related to the tip dipoles should also be associated with larger diameter tubes.

In summary, we see here that the work function can exhibit significant variations depending on the length of the tubes and the way they are arranged, and we trace the phenomena to the sign of the dipoles formed at the tips of the tubes (which is inherently determined by quantum mechanics) and the geometry (which governs the density of dipoles). It is interesting to see that for isolated tubes, the tip dipole does not affect the work function, but the density and the sign of the dipole become the crucial factor when the tubes form a bundle. We thus have, in principle, a system that has tunable work functions if the length and the packing density of the tubes can be controlled by growth procedures. Although we focus on small radius tubes, those phenomena that are related to the tip dipoles should also be associated with larger diameter tubes.

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