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Adsorption and migration of carbon adatoms on zigzag carbon nanotubes

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Abstract

Using density-functional tight-binding and ab initio methods we study the adsorption and migration of carbon adatoms on surfaces of single-walled zigzag carbon nanotubes. We demonstrate that the adatoms form strong covalent bonds with the nanotubes and that the migration is strongly anisotropic. The adatom adsorption energy and migration barrier depend on the nanotube diameter and chirality. The migration barriers, being in the range of 0.6–1 eV, are in a good agreement with the experimental values (about 0.8 eV) reported in the literature.

Keywords: Carbon nanotubes; Ion irradiation; Electron irradiation; Defect annealing

1. Introduction

The outstanding mechanical and electronic properties of single-walled carbon nanotubes (SWNTs) have stimulated much research on their mass production techniques. However, despite a considerable effort, further progress is hampered by the lack of the control over SWNT chiralities and diameters at the growth stage. This is in part due to the insufficient understanding of SWNT growth mechanisms.

A number of microscopic SWNT growth models have been developed [1–6] with growth taking place either at the nanotube edge [1–3] (capped or open) or its root [4–6]. Depending on the temperature range and catalyst used, any of the mechanisms may work. However, whatever the mechanism is, the quantitative understanding of the synthesis process is not possible without knowing how the “building blocks”—carbon atoms and clusters—are supplied to the place where the SWNT growth occurs.

Carbon atoms coming from the feedstock (plasma, gas, etc.) can be captured directly at the end of the SWNT [3], especially if dangling covalent bonds are present. However, it seems to be more plausible that the atoms are first absorbed on the SWNT surface and then they migrate to the SWNT growing end [1,2]. The adsorbed atoms (adatoms) can also aggregate and form clusters (amorphous carbon) and detach from nanotube surface. Thus, knowing the adatom migration mechanism and such key quantities like adsorption and migration energies is indispensable for the comprehensive theory of SWNT synthesis.

At the same time, there exists very little knowledge about how carbon adatoms migrate over the SWNT surface. There have been studies on the migration of carbon adatoms on a graphite (flat) surface [1,7] but effects of SWNT surface curvature on the carbon adatom diffusion have not yet been studied by the proper methods. [1] Moreover, the reported values of the adatom migration barrier (about 0.1 eV) [1,7] seem to be much lower than the value (~0.8 eV) obtained in experiments

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[1] This issue has been studied by Shu and Gong [8], but a van der Waals potential has been used in that work to describe the interaction between the adatom and SWNT. Since the adatom-graphite adsorption energy is estimated to be in a range of several eV [1,9,10], the bonding is rather covalent and there is no motivation for such a choice of the potential.

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on the annealing of the irradiation-induced damage in SWNTs [11]. Annealing, similar to the SWNT growth, is governed by the migration of adatoms which play the role of interstitials in SWNTs [12].

In this paper we study the adsorption and diffusion of carbon adatoms on SWNTs. By using two different computational techniques we evaluate the adatom adsorption energy E_a and migration barrier E_m for zigzag SWNTs with various chiralities.

2. Calculation details

In our simulations, we employed density-functional theory (DFT) implemented in the non-orthogonal real-space tight-binding (DFTB) code [13] and the plane wave (PW) basis set VASP [14] code. Although the PW DFT method has very well been established as the leading edge in electronic structure calculations, we were unable to carry out all calculations using this method because of computational limitations. However, as shown below, the DFTB approach in which the parameters of the Hamiltonian are derived from ab initio calculations gives a qualitatively correct picture thus offering a good compromise between accuracy and computational efficiency.

As for the PW DFT method, we used PAW potentials [15] to describe the core electrons and the generalized gradient approximation (GGA) [16] for exchange and correlation. A kinetic energy cutoff of 400 eV was found to converge the total energy of our system to within meV. The same accuracy was also achieved with respect to the **k**-point sampling of the Brillouin zone. The adatom diffusion paths were calculated in a static approximation using the nudged elastic band method [17]. Other details of our DFT PW calculations can be found in [10].

3. Carbon adatom on a graphene sheet

To check the applicability of DFTB to the problem of adatom migration, we started by calculating E_a and E_m for the adatom on small graphene flakes consisting of 60–216 atoms. We found that the equilibrium position of the adatom was a bridge-like structure (the adatom is above the middle of the carbon-carbon bond) with the perpendicular distance to the graphite surface being 1.9 Å. Our recent DFT PW calculations gave exactly the same configuration with a distance of 1.87 Å [10]. E_a (with account for the spin polarization energy correction [2]) was found to be 2 ± 0.3 eV. The uncertainty is due to size-quantization effects in *finite* graphene slabs in the range of the slabs considered. E_a also agrees with the ab initio data (1.4 eV [10], 1.78 eV [1], 2.1 eV [9]).

The adatom migration paths and migration barriers were calculated in a static approximation by evaluating the system total energy as a function of the adatom position (the adatom was allowed to move only in the direction perpendicular to the graphene plane). In perfect agreement with our DFT PW calculations [10], the diffusion path was found to be a nearly straight line between two equivalent adjacent sites bridging carbon atoms. We also calculated the migration barrier dynamically by performing molecular dynamics for 0.2 ns at temperatures in a range of 1000–1500 K. Both methods gave $E_m = 0.4 \pm 0.1$ eV, which is in a very good agreement with a DFT PW value of 0.45 eV. From our molecular dynamics simulations we also evaluated the adatom jump frequency $\nu_0 = (3.7 \pm 0.7) \times 10^{12}$ s^{-1} which proved to be about the experimental value (4×10^{12} s^{-1}) for the jump frequency of carbon interstitial in graphite [18].

Our previous DFT PW calculations [10] showed that the adatom has a finite magnetic moment, but the difference between the triplet and singlet ground states is quite small, about 0.04 eV. Magnetic effects also proved to be of minor importance for the diffusion [10]. Thus, we can conclude that the DFTB model, although being unable to account for magnetic effects, captures the main physics of the carbon adatoms on graphite-like surfaces.

4. Carbon adatoms on zigzag nanotubes

In this work we dwell upon zigzag $(n,0)$ SWNTs which, depending on the SWNT chiral index n, can be metals or narrow-band semiconductors. This made it possible to study effects of not only nanotube curvature, but also electronic structure on the diffusion and adsorption.

In the DFTB calculations, finite SWNTs (having a length of 12.7 Å and composed of up to 200 atoms) with periodical boundary conditions were considered. The same systems were used for the DFT PW simulations. To check how the results depend on the tube length, we also repeated DFTB calculations for (8,0) and (9,0) SWNTs with doubled length. We found no qualitative difference for the absorption geometry, nor the adatom diffusion path. E_a and E_m were dependent on the tube length, but the difference never exceeded 10% of the value.

Similar to adsorption of a carbon atom onto a graphite surface, the adsorption onto a SWNT surface proved to be exothermic. The adatom on the outer surface of the SWNT occupies the bridge position above

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[2] The ground state for the isolated carbon atom is a triplet state with the energy difference between the triplet and singlet states being 1.26 eV, as our DFT PW model indicates.

the C–C bond. However, due to the SWNT curvature, the adatom adsorption onto sites above C–C bonds being parallel and perpendicular to the nanotube axis [3] results in different adsorption energies and local atom arrangements, see Fig. 1(a) and (b). Adatoms inside the SWNT are displaced a little from the bridge position due to curvature-enhanced interactions with the neighbor atoms.

In Fig. 2 we plot adsorption energies E_a as functions of nanotube diameters for SWNTs with $n = 8, 9, \ldots, 16$. It is observable that for adatoms on the outer surface the absolute value of E_a decreases with an increase in the SWNT diameter. This seems to be a general tendency: similar behavior of Al, H [19] and N [20] adatoms on SWNTs has been reported. The adsorption energy is always lower for configurations when the adatom is above the C–C bond oriented perpendicular to the SWNT axis than for the "parallel" configuration. This can be understood from simple carbon bonding considerations: in the "perpendicular" case it is easier for the adatom to pull the two adjacent nanotube atoms apart (notice that the bond is actually broken, see Fig. 1(b)) thus avoiding the energetically unfavorable configurations with four-coordinated carbon atoms. Ab initio simulations for small SWNTs gave qualitatively similar results, but, similar to the case of the flat graphene sheet, the absolute values are shifted by about 0.5 eV. This difference may be due to fitting the TB parameters to local density approximation (LDA) DFT data, since LDA calculations of adatom adsorption energy also gave a lower value for graphene [9] than with GGA. E_a are much higher for adatoms adsorbed onto the inner surface due to unfavorable coordination numbers of the adatoms (see Fig. 1(c)).

It is interesting to notice that the dependencies shown in Fig. 2 proved to be non-monotonic. The curves for E_a corresponding to the "parallel" and "inside" configurations have sawtooth shapes with the minima corresponding to $n = 9, 12, 15$. SWNTs with these indices have metallic properties, whereas the rest are semiconductors. Our analysis of the local density of states and orbital electronic population indicates that the increase in bonding may be due to an additional overlap of the adatom electronic states with the electronic states of metallic SWNTs near the Fermi energy. PW DFT calculations also give a lower adsorption energy (the "parallel" configuration) for metallic (9,0) SWNTs than for semiconducting (8,0) and (10,0) SWNTs.

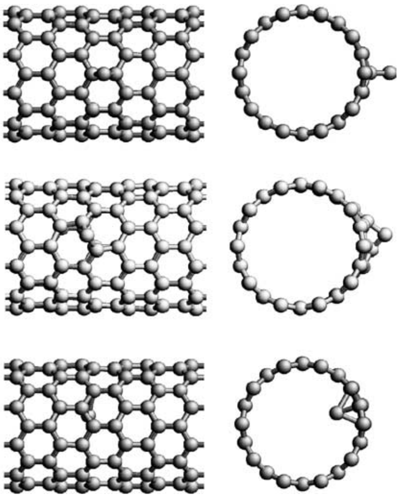

Fig. 1. Ball-and-stick representation of a (10,0) single-walled zigzag nanotube with a carbon atom adsorbed onto the outer and inner surface of the nanotube. The adatom positions correspond to local energy minima.

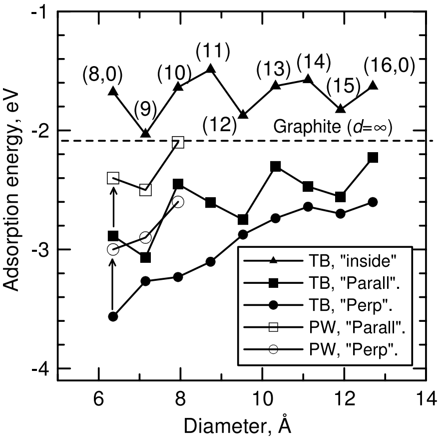

Fig. 2. Adsorption energies of carbon adatoms onto zigzag single-walled nanotubes as functions of nanotube diameters. The arrows visualize the relationship between the corresponding PW and TB results. The numbers stand for the tube chirality indices.

Having evaluated the adatom adsorption energy, we proceed to migration barrier calculations. Analogously to the case of graphene, we evaluated E_m by calculating the total energy of the system as a function of adatom position with constraints. The adatom was allowed to move only in the radial direction, all other atoms were free to move (except for fixed boundary atoms).

We found that adatoms can migrate between equivalent "perpendicular" position on the outer surface of the SWNT via the intermediate "parallel" position with E_m being dependent on the SWNT diameter. E_m as a function of the SWNT diameter is presented in Fig. 3. It is evident that E_m decreases with the tube diameter D approaching the corresponding value for graphite. Notice that the difference between the adsorption energies in "perpendicular" and "parallel" positions is large for nanotubes with small diameters and that the migration

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[3] Strictly speaking, the angle for "perpendicular" bond is exactly 90° in armchair but not zigzag nanotubes, but we use here terms "perpendicular" and "parallel" just to differentiate the bonds.

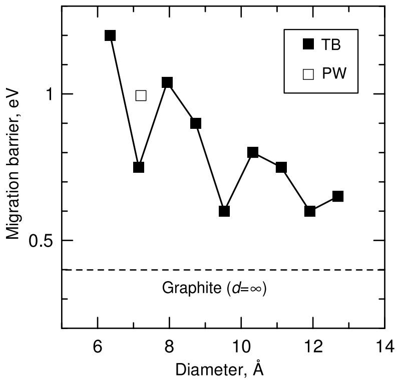

Fig. 3. Energy barrier for adatom migration on the outer surface of zigzag nanotubes as a function of nanotube diameters.

along the axis is always associated with the movement along the SWNT circumference, which explains why E_m is larger for thin SWNTs. Indeed, due to curvature effects (a longer "jump length") and lower adsorption energies for the "perpendicular" configurations, E_m is larger than that on the graphite surface. However, the adatoms are still highly mobile at typical growth temperatures. The time τ needed for the adatom to move a distance L can be evaluated as $\tau = L^2/D_0$ [21], where $D_0 = \nu_0 a^2 \exp[-E_m/kT]$, a is the elementary jump length. Thus if $L = 1$ μm, $T = 600$ °C, $E_m = 0.8$ eV, then $\tau \approx 1$ s.

For all SWNTs considered, adatoms inside the SWNT can easily spiral along the nanotube circumference (along the dark "trenches" with roughly the same potential energy in Fig. 4) with an energy barrier of about 0.1 eV for all the SWNTs considered. The barrier for migration along the tube also depends weakly on the SWNT diameter being in a range of 0.5–0.7 eV.

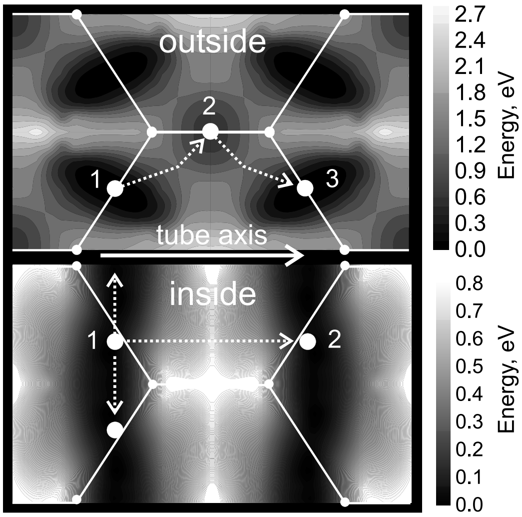

Fig. 4. Potential energy surface for a carbon adatom on a (8,0) nanotube as a function of the adatom position. Darker areas correspond to lower energies. Large circles stand for the adatom, small ones for atoms in the nanotube network. Dotted lines show the migration paths.

5. Conclusion

To conclude, using density-functional tight-binding and ab initio methods we studied the adsorption and migration of carbon adatoms on zigzag nanotubes. We found that the adatoms form strong covalent bonds with the nanotubes and that the migration is strongly anisotropic. The adatom adsorption energy and migration barrier depend on the nanotube diameter and chirality, which should be taken into account in models of nanotube growth and radiation damage annealing. The migration barriers, being in the range of 0.6–1 eV, are in a good agreement with the experimental values (about 0.8 eV) reported in the literature.

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References

[1] Lee YH, Kim SG, Tománek D. Catalytic growth of single-wall carbon nanotubes: An ab initio study. Phys Rev Lett 1997;78:2393–6.

[2] Louchev OA, Sato Y, Kanda H. Morphological stabilization, destabilization, and open-end closure during carbon nanotube growth mediated by surface diffusion. Phys Rev E 2002;66:011601.

[3] Iijima S, Ajayan PM, Ichihashi T. Growth model for carbon nanotubes. Phys Rev Lett 1992;69:3100.

[4] Gavillet J, Loiseau A, Journet C, Willaime F, Ducastelle F, Charlier JC. Root-growth mechanism for single-wall carbon nanotubes. Phys Rev Lett 2001;87:275504.

[5] Fan X, Buczko R, Puretzky AA, Geohegan DB, Howe JY, Pantelides ST, et al. Nucleation of single-walled carbon nanotubes. Phys Rev Lett 2003;90:145501.

[6] Maiti A, Brabec CJ, Bernholc J. Kinetics of metal-catalyzed growth of single-walled carbon nanotubes. Phys Rev B 1997;55:R6097.

[7] Heggie M, Eggen BR, Ewels CP, Leary P, Ali S, Jungnickel G, et al. LDF calculations of point defects in graphites and fullerenes. Electrochem Soc Proc 1998;98:60.

[8] Shu DJ, Gong XG. Curvature effect on surface diffusion: the nanotube. J Chem Phys 2001;114:10922–6.

[9] Nordlund K, Keinonen J, Mattila T. Formation of ion irradiation induced small-scale defects on graphite surfaces. Phys Rev Lett 1996;77:699–702.

[10] Lehtinen PO, Foster AS, Ayuela A, Krasheninnikov AV, Nordlund K, Nieminen RM. Magnetic properties and diffusion of adatoms on a graphene sheet. Phys Rev Lett 2003;91:017202.

[11] Banhart F. Irradiation effects in carbon nanostructures. Rep Prog Phys 1999;62:1181–221.

[12] Krasheninnikov AV, Nordlund K, Keinonen J. Production of defects in supported carbon nanotubes under ion irradiation. Phys Rev B 2002;65:165423.

[13] Frauenheim T et al. Atomistic simulations of complex materials: ground state and excited state properties. J Phys: Condens Matter 2002;14:3015.

[14] Kresse G, Furthmüller J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys Rev B 1996;54:11169.

[15] Blöchl PE. Projector augmented-wave method. Phys Rev B 1994;50:17953.

[16] Perdew JP, Chevary JA, Vosko SH, Jackson KA, Pederson MR, Singh DJ, et al. Atoms, molecules, solids, and surfaces: applications of the generalized gradient approximation for exchange and correlation. Phys Rev B 1992;46:6671.

[17] Jónsson H, Mills G, Schenter GK. Reversible work transition state theory: application to dissociative adsorption of hydrogen. Surf Sci 1995;324:305.

[18] Thrower PA, Mayer RM. Point defects and self-diffusion in graphite. Phys Stat Sol (a) 1978;47:11.

[19] Gülseren O, Yildirim T, Ciraci S. Tunable adsorption on carbon nanotubes. Phys Rev Lett 2001;87:116802.

[20] Zhao M, Xia Y, Ma Y, Ying M, Liu X, Mei L. Exohedral and endohedral adsorption of nitrogen on the sidewall of single-walled carbon nanotubes. Phys Rev B 2002;66:155403.

[21] Meunier V, Kephart J, Roland C, Bernholc J. Ab initio investigations of lithium diffusion in carbon nanotube systems. Phys Rev Lett 2002;88:075506.