

Band gap sensitivity of bromine adsorption at carbon nanotubes

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Abstract

We report results of our first-principles investigation on the energetics and electronic structures of bromine-adsorbed carbon nanotubes. While the bromine molecule binds preferentially to the outer wall of metallic nanotubes, the binding energy of adsorbed atomic bromines are found to depend on the radius as well as the energy gap. A recent experiment on the nanotube separation using bromines is discussed based on our computational data. The formation of strong C–Br chemical bonds at the zigzag edge of graphite demonstrates a close relationship between the density of states at the Fermi level and the binding strength.

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The carbon nanotube [1] has prompted intensive research activities because of their unique electronic structure [2–4] and unprecedented mechanical and chemical robustness. The one-dimensional geometry and the ballistic transport property of carbon nanotube could be exploited for various types of nanoscale devices. Despite many successful advances in the field of nanotube-based electronic devices [5], however, a breakthrough toward the practical application has been hampered by difficulties related to controlling physical properties of individual nanotubes. In this regard, one of the prime issues is the selection of nanotubes depending on the electronic properties, i.e., metallic or semiconducting. For most of applications, it is ideal to employ nanotubes with a uniform electronic property.

Since most of the current synthetic methods for single-walled nanotubes produce an entangled assembly of metallic and semiconducting nanotubes, the post-synthesis technique to separate one component from

the other is a viable approach. A handful of promising sorting techniques have been proposed to date. For instance, an ac-dielectrophoresis method separated the metallic nanotubes from the semiconducting nanotubes in virtue of the disparate dielectric constants [6]. As another intriguing approach, Chen et al. [7] achieved sediment of the metallic nanotubes from the nanotube bundles that originally included a large fraction of semiconducting nanotubes. It was claimed that the preferential adsorption of the bromine (Br) atom on the metallic nanotubes increased their mass substantially compared to the semiconducting nanotubes, which thereby makes the separation procedure feasible. A theoretical support was also provided for small radius nanotubes [7]. In the ensuing works, they found that the destabilization of Triton X-100 surfactant is a more direct explanation for their observations [8,9].

In this Letter, we investigate the electronic structure and the energetics for the Br-adsorbed ($n, 0$) carbon nanotubes ($n = 8, 9, 10, 17, 18$) in an effort to provide an extensive picture of band-gap sensitivity of the bromine binding. We consider both atomic and molecular

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forms of the bromine. The calculations are based on the density-functional theory [10] with a local density approximation (LDA). The ionic potential is described by the norm-conserving pseudopotential [11]. We use the Ceperley–Alder exchange–correlation energy functional [12]. The energy cutoff for the plane wave basis is set to 50 Ry.

The model geometries used in this work are presented in Fig. 1. The bromine atoms and molecules are located outside or inside (not shown) the zigzag nanotube. The nanotubes are placed in a two-dimensional supercell with lattice parameters taken to be large enough that atoms in different supercells are separated by more than 10 Å. The lattice parameter along the axial direction of the nanotube is twice the unit length of the pristine nanotube. For the Brillouin zone integration, we sample evenly-spaced five k points along the direction of the nanotube axis including the Γ point. The geometry is relaxed until the Hellmann–Feynman forces are less than 0.025 eV/Å.

The relaxed geometry of the adsorbed Br₂ molecule at the equilibrium shows that it is aligned along the axis of the carbon nanotube, bridging two C–C bond as shown in Figs. 1a and b. The distance between the Br₂ molecule and the nanotube wall, d_M , is a typical van der Waals value of 3.4 Å. The interatomic distance (2.32–2.39 Å) of the adsorbed Br₂ molecule is found to be slightly longer than that of the isolated Br₂ molecule (2.30 Å) computed with the same computational framework. This indicates that a small amount of the electronic charge transfers from the nanotube to Br₂. On the other hand, the Br atom is most stable when it is adsorbed just

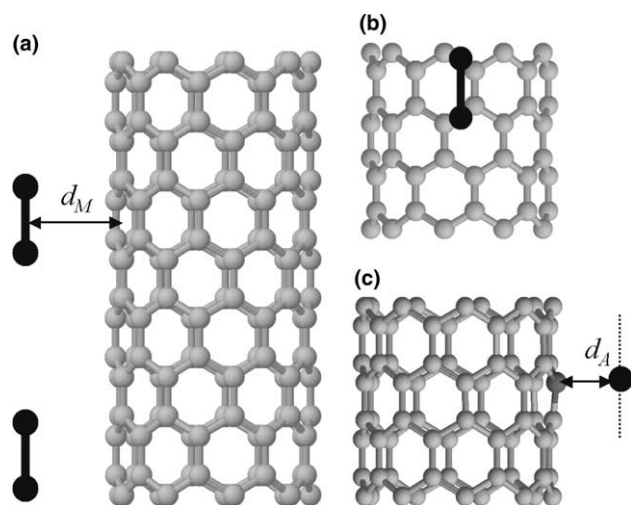


Fig. 1. Model geometries for the bromine adsorbed carbon nanotube. The Br₂ adsorbed (9,0) nanotubes are seen from (a) the side and from (b) the top of the Br₂ molecule, respectively, (c) shows the side view of the Br adsorbed (9,0) nanotube. Grey spheres represent carbon atoms and larger black spheres represent bromine atoms. The slightly darker sphere in (c) is the nearest carbon atom to the adsorbed Br atom. In (a), the twice of the unit cell is shown.

above a carbon atom, compared to sites above the center of hexagon or above the middle point of the C–C bond. The equilibrium distance between the Br atom at the top site and the nearest carbon atom, denoted by d_A in Fig. 1c, is about 2.4 Å, which implies that the character of adsorption is inbetween the chemisorption and the physisorption. (The sum of covalent and van der Waals radii of Br and C atoms are 1.91 and 3.55 Å, respectively.) The carbon atom at the site of the adsorption (the darker ball in Fig. 1c) protrudes slightly toward the Br atom, a trace of sp³ bonding character.

Next, we look into the electronic structure of each system. In Figs. 2a and b, the band structures of the (10,0) nanotube with or without the adsorbed Br₂ molecule are shown, respectively. The almost flat band in the energy gap of the nanotube in Fig. 2b corresponds to the lowest-unoccupied-molecular-orbital (LUMO) of the Br₂ molecule with a bonding character of ppσ*. The highest-occupied-molecular-level (HOMO) of the Br₂ molecule, which is doubly degenerate ppπ*, is located around –2 eV as indicated by an arrow in Fig. 2b. The substantial splitting of the nanotube bands around the HOMO of Br₂ can be found and it is attributed to the wave function overlap between the bromine molecule and the nanotube. We find that the LUMO of Br₂ is at about 0.2 eV higher than the Fermi level of the metallic nanotubes or the valence edge of the semiconducting nanotube. This level could induce hole-doping of the carbon nanotube at elevated temperatures.

The band structures of the (10,0) nanotubes with Br atoms adsorbed at inner or outer walls are presented in Figs. 2c and d, respectively. The Br atom is most stable at the center of the tube when situated inside the (10,0) nanotube. Therefore, the cylindrical symmetry of the nanotube is maintained and the band structure of the nanotube remains almost intact in Fig. 2c. The energy levels indicated by the arrow in Fig. 2c are threefold degenerate p-orbital states of Br atom. When the Br atom is adsorbed outside of the nanotube, the doubly-degenerate nanotube bands as well as the threefold p-orbital states of the Br atom are split significantly as indicated by arrows in Fig. 2d.

The binding energies on the wall of the nanotube, defined by $E_b = E_T(X/CNT) - E_T(CNT) - E_T(X)$, are compiled in Table 1. Here, X represents Br or Br₂ and E_T is the total energy at the optimized geometry. We observe that the metallic nanotubes ((9,0) and (18,0) nanotubes) uniformly provide a stronger binding than the semiconducting nanotubes. With the increased density of states (DOS) at the Fermi level, the metallic nanotubes allow for the enhanced electron transfer from the nanotube to the LUMO of the adsorbate, contributing to the stronger binding. In addition, the difference in the binding energy between the metallic and semiconducting nanotubes decreases as the diameter of the

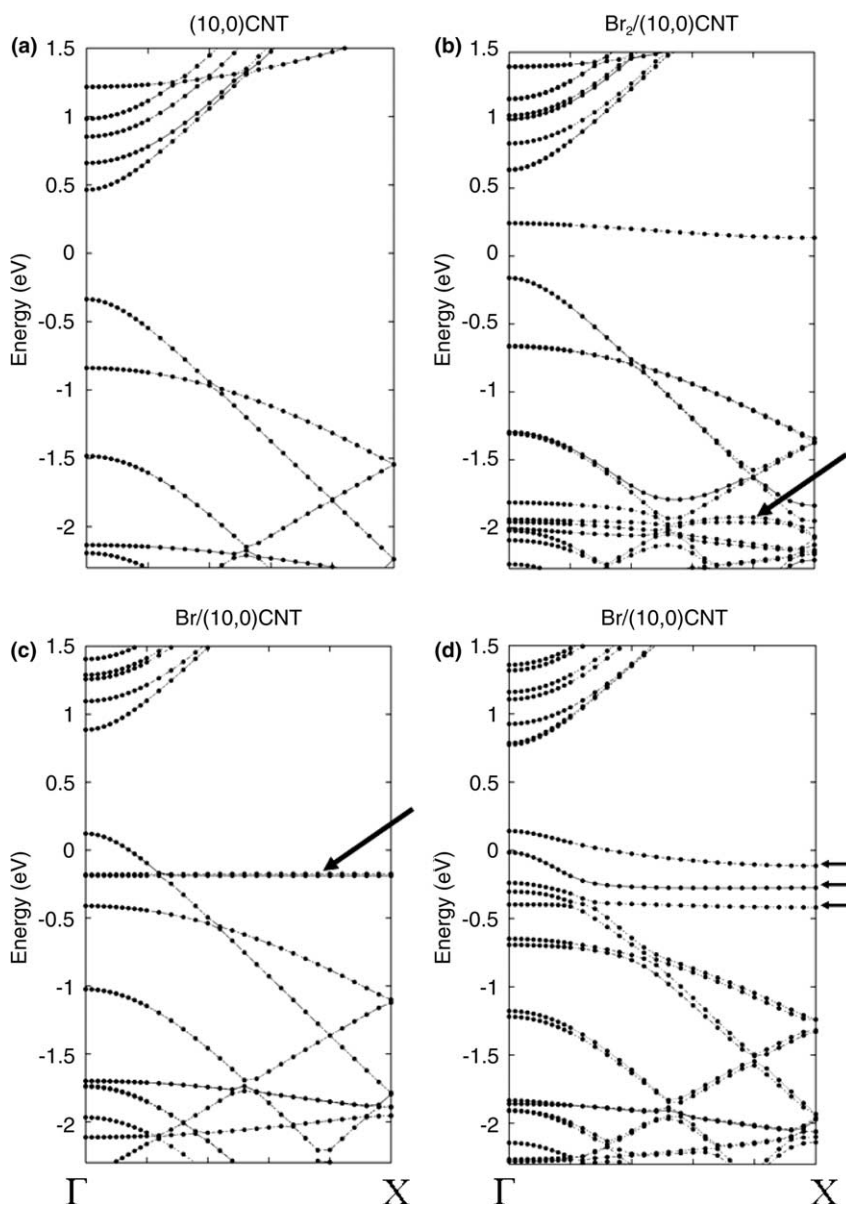


Fig. 2. Band structures of (a) the (10,0) nanotube, the (10,0) nanotube (b) with the adsorbed Br₂ on the outer wall, (c) with the Br atom on the inner wall, and (d) with the Br atom on the outer wall. The arrows indicate molecular or atomic states (see text).

Table 1
The binding energy (eV) of the adsorbate (Br₂ or Br) to the outer wall of the nanotube

	(8,0)	(9,0)	(10,0)	(17,0)	(18,0)
Br ₂ /CNT					
<i>E_b</i> (eV)	-0.16	-0.22	-0.17	-0.19	-0.23
<i>d</i> (Br–Br)	2.32	(-1.20) 2.37	(-0.72) 2.33	(-0.32) 2.35	(-0.33) 2.39
Br/CNT					
<i>E_b</i> (eV)	-1.18	-1.33	-1.26	-1.40	-1.45
<i>d</i> (C–Br)	2.27	(-2.47) 2.41	(-1.68) 2.43	(-1.42) 2.35	(-1.45) 2.34

The values in the parenthesis are the binding energy to the inner wall of the nanotube.

nanotube increases. This is consistent with the fact that the band gap decreases as the diameter of the semiconducting nanotube increases. When the Br₂ molecule is encapsulated inside the nanotube, the binding becomes much stronger and has a strong tendency that the binding energy becomes weaker as the diameter increases. This will be discussed in the next paragraph.

We now look into the binding energetics for bromine atoms. It is noticeable in Table 1 that the larger (17,0) semiconducting nanotube provides a stronger binding than the smaller (9,0) metallic nanotube despite a significantly larger energy gap (0.56 eV). This is due to another tendency in the binding energy that the adsorption in the outer (inner) wall of the nanotube becomes stronger (weaker) as the diameter increases (see Table 1). This could be ascribed to the van der Waals interaction which is enhanced as the interface area between two interacting systems increases. Aforementioned binding energetics for the encapsulated Br₂ molecule could be interpreted in a similar way. It is widely accepted that the LDA description of the small overlap of two decaying charge densities addresses the van der Waals energy fairly well [13,14]. As the curvature decreases, the charge overlap increases between the Br atom and the flattening nanotube surface. The opposite relation applies to the Br atom placed inside the nanotube. To be consistent with this, the van der Waals interaction between the nanotube and the fullerene is maximized when the fullerene is encapsulated inside the nanotube rather than adsorbed outside the nanotube [14].

In [7], it was originally claimed that the observed selectivity originated from the different binding energies of Br atoms between metallic and semiconducting nanotubes. They provided computational results on nanotubes with diameters ≤ 1 nm, in fair agreement with data in Table 1. However, we find that the selectivity is less obvious when the results on larger nanotubes (such as (17,0) and (18,0) nanotubes) are taken into account. Considering the Boltzmann factor at thermal equilibrium, the amount of Br atoms adsorbed at the side wall of nanotubes will largely depend on the diameter, rather the energy gap, of the nanotubes. As explained in the above, this is because the diameter-dependent van der Waals interaction becomes comparable to the difference of electron affinity between metallic and semiconducting nanotubes. We note that the diameter distribution of single-walled nanotubes usually has maximum peaks between 1.0 and 1.3 nm [7,15] and the diameter of (17,0) and (18,0) nanotubes are 1.33 and 1.41 nm, respectively. In fact, later publications by the same group indicate that the destabilization of Triton X-100 surfactant is a key factor for the sedimentation of metallic nanotubes [8,9]. To elucidate this, we carry out calculations on Br atoms intercalated into the (11,0) and (12,0) nanotube bundles. The equilibrium

geometry shows that the covalent Br–C bonding does not exist and Br atoms are at the equal distance from surrounding nanotubes. This is similar to the case where Br atoms are incorporated inside the nanotube. The calculated binding energies are -0.83 and -1.3 eV/Br atom for (11,0) and (12,0) nanotube bundles, respectively. This is a sizeable difference that can give rise to a noticeable effect in experiment. The lower binding energy for metallic bundles implies that the Br atoms will enhance the aggregation of metallic nanotubes, counterbalancing the effect of surfactant. Such a role of Br atoms should be related to the experimental observation of selective sedimentation.

The close relationship between the binding energy and the charge transfer implies that the increase of DOS at the Fermi level may amplify the binding affinity of Br or Br₂. It is well-known that the flat energy bands developed at the zigzag edge of graphene sheets increase the DOS at the Fermi level [16]. From the geometry relaxation of the Br₂ molecule adsorbed at the isolated graphitic zigzag edge, we find that the Br–Br bond initially expands by 0.5 Å from the equilibrium distance of the isolated Br₂ molecule (see Fig. 3a). The binding energy of the adsorbate in this case is found to be -0.35 eV, which is much lower than those for the nanotubes (see Table 1), and the distance to the edge carbon atom, indicated by the dotted arrow in Fig. 3a, is 2.68 Å. A further relaxation followed by a small perturbation results in the complete dissociation of the Br₂ molecule. The adsorption energy of the fully dissociated Br₂ molecule shown in Fig. 3b is as low as -1.89 eV, with the C–Br bond length of 2.04 Å. This indicates that desorption of the Br₂ molecule is an exothermic process at the zigzag edge while it is endothermic on the outer wall of carbon nanotubes. In fact, the experiment in [17] implied a substantial suppression of the edge-inherent π -states at the Fermi level upon the bromine adsorption. This could be ascribed to the formation of C–Br chemical bond at the zigzag edge like Fig. 3b.

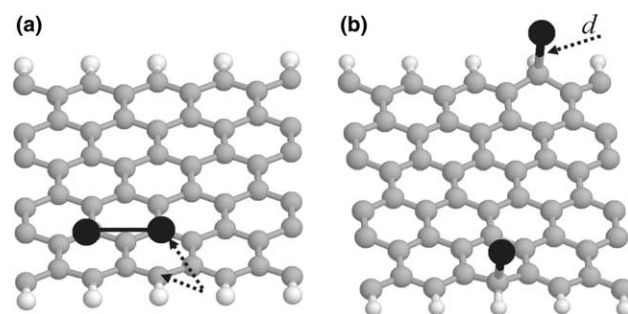


Fig. 3. The optimized geometry of (a) Br₂ molecule adsorbed on the zigzag edge of graphite and (b) two bromine atoms on the opposite edges of the graphitic edge. Grey, white, and black spheres represent carbon, hydrogen, and bromine atoms, respectively. Shown in (a) and (b) are the unit cells with the periodic boundary condition used for the calculations.

In conclusion, we have investigated the energetics and electronic structures of the bromine adsorbed carbon nanostructures. The binding of the adsorbates to the metallic nanotubes is stronger than that to the semiconducting nanotubes with similar diameters. As the diameter of the nanotube increases, the distinction between metallic and semiconducting nanotubes is rather obscured. We find that the bromine can be strongly adsorbed at the graphitic zigzag edge, demonstrating the direct relationship between DOS at the Fermi level and the binding strength.

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