Formation of polybromine anions and concurrent heavy hole doping in carbon nanotubes

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Using density-functional theory calculations, we investigate the atomic and electronic structure of the bromine species encapsulated in carbon nanotubes. We find that the odd-membered molecular structures (Br\textsubscript{3} and Br\textsubscript{5}) are energetically favored than the common Br\textsubscript{2} molecule. The transformation from bromine molecules (Br\textsubscript{2}) into Br\textsubscript{3} or Br\textsubscript{5} is found to be almost barrierless. A strong electron transfer from the nanotube to the adsorbates, which has been doubtful in previous studies, is accompanied by the formation of such odd-membered polybromine anions. We suggest that the tip-opened carbon nanotube samples can be heavily hole-doped after exposure to Br\textsubscript{2} gas.


The fascinating material properties of the carbon nanotube (CNT) have generated immense interest from researchers in various fields. In particular, its intrinsic one-dimensional geometry and excellent transport properties make the nanotube one of the prime candidates for active elements in next generation electronic devices.\textsuperscript{1-3} Examples of the potential CNT applications include CNT-based switching devices, field emitters for flat-panel displays, memory or logic circuits, and sensors.\textsuperscript{4-8} Despite that no method to date has succeeded in the controlled growth of either metallic or semiconducting nanotubes, their selective use has been highly desirable for practical applications. In this regard, controlling the electronic properties of CNT has become a vital issue and thus needs fundamental understanding of its atomic and electronic structure.

Adsorptions of halogen elements on the nanotube have been tried to exploit its electronic structure.\textsuperscript{9,10} Especially, a sharp increase in the conductance was shown to accompany the intercalation of bromine molecules.\textsuperscript{11,12} Theoretical studies have investigated the adsorption energetics and electronic structure of the Br/CNT system.\textsuperscript{13,14} The calculations revealed a large amount of energy gain upon the encapsulation of Br\textsubscript{2} inside the small-diameter CNT [0.72 eV/Br\textsubscript{2} in the (10,0) CNT].\textsuperscript{13} On the surface of the large-diameter nanotube, the adsorption energy was found to be about 0.1 eV/Br, whereas the metallic nanotube showed a slightly larger binding energy.\textsuperscript{13,14} However, these theoretical studies have led to an unexplained question about the reality and possibility of hole doping of the semiconducting nanotube with bromine molecular vapors. Note that the charge transfer from the nanotube to the physisorbed Br\textsubscript{2} molecule was calculated to be very small.\textsuperscript{14}

In this letter we investigate the geometric and electronic structure of the bromine-encapsulated CNTs. We find that encapsulated bromine molecules (Br\textsubscript{2}) transform into the charged polybromine species (Br\textsubscript{3} and Br\textsubscript{5}), rendering the nanotube template heavily hole-doped. Thus the observed conductance increase upon the bromine doping in previous experiments\textsuperscript{11,12} is likely due to the formation of these polybromine anions. Throughout this work, total energy calculations are formed with the local-density approximation (LDA) and the generalized gradient-corrected approximation (GGA) in some limited cases, using the Vienna \textit{ab initio} simulation package (VASP).\textsuperscript{15} The ionic potentials are represented by the ultrasoft pseudopotentials as provided with VASP,\textsuperscript{16} and the energy cutoff for the plane-wave basis is set to 290 eV. The atomic positions are relaxed with residual forces smaller than 0.02 eV/Å.

First, we investigate the molecular structure of the bromine adsorbates inside CNTs of various diameters [from (10,0) to (16,0)]. Figure 1 shows the optimized geometries for Br\textsubscript{2}, Br\textsubscript{3}, Br\textsubscript{5}, and Br\textsubscript{3} encapsulated inside the (16,0) CNT. The unit cell dimensions along the axial direction of the nanotube are set to triple of the minimal unit cell of the zigzag nanotube (12.735 Å) for Figs. 1(a) and 1(b) and to quadruple of that (16.98 Å) for Figs. 1(c) and 1(d). We observe that Br\textsubscript{2} and Br\textsubscript{3} are aligned in the nanotube with the Br–Br bond lengths of 2.361 and 2.532 Å, respectively, as shown in Figs. 1(a) and 1(b). The bond length (2.361 Å) is a little longer than the interatomic distance (2.274 Å) of Br\textsubscript{2} in the vacuum. Two Br–Br bonds (2.575 Å) at the edges of Br\textsubscript{3} in Fig. 1(c) are mostly aligned with the CNT axis, while the central bond (2.582 Å) deviates a little. Noticeably, Br\textsubscript{5} forms a bent molecule as shown in Fig. 1(d), where the bond lengths at the edges of Br\textsubscript{5} are 2.452 Å, whereas those in the
and Br$_5$ encapsulated inside the nanotubes, respectively. The empty dia-
monds from top to bottom, calculated with GGA, correspond to the binding
energies at $N=12$ and $N=15$ imply that bromine adsorbates bind more strongly to the metallic nanotubes. We note that Br$_3$ is more favored than Br$_5$ in smaller nanotubes ($N=10$, 11, and 12), while Br$_5$ is more favored in larger nanotubes. This should obviously be ascribed to the strain imposed on the Br$_5$ molecule inside the small-diameter nano-
tubes. The linear chained Br$_4$ is found to be more stable than Br$_3$ but less stable than the odd-membered species inside the carbon nanotubes.

In these cases the bromine species are bound to the nanotubes by the weak intermolecular force in conjunction with ionic interactions. The weak intermolecular bindings, mediated by the van der Waals interaction, are estimated to be some halfway between the LDA and GGA results. In some cases, authors discussed that the LDA calculation effect-
ively describes the weak intermolecular bindings while GGA greatly fails. For a cross-checking, we perform the GGA calculation only for the cases of Br$_3$, Br$_4$, Br$_5$, and Br$_5$
inside the (13,0) CNT. We find much reduction of the binding strength in the GGA results, as shown in Fig. 2. This reduction should be ascribed to the underestimation of GGA for the weak intermolecular interaction between Br species and CNT. Nevertheless, we observe that the Br$_4$, Br$_3$, and Br$_5$
structures are still much stabilized than Br$_3$ inside the (13,0) CNT. A proper description of the van der Waals interaction may be similar to the LDA results or some halfway between the LDA and GGA results. However, the energetics regarding the formation of the odd-membered bromine species is be-
lieved to be correct, irrespective of density functionals.

We now investigate the electronic structure of the bromine-encapsulated nanotubes to account for the energet-
icss discussed in the previous paragraphs. The projected densities of states (PDOSs) for the CNT and adsorbates are pre-
sented with solid and dotted lines, respectively, in Fig. 3. Despite that bromine has been commonly considered as
more electronegative than CNT, the lowest unoccupied mol-
ecular orbital level of Br$_3$ is found to be in the midgap of the semiconducting CNT, as shown in Fig. 3(a). This means that the electron transfer from the nanotube to Br$_3$ should not be substantial, consistent with the usual physiosorption fea-
ture. However, in the cases of Br$_3$ and Br$_5$ in (16,0) CNT, the singly occupied molecular orbital (SOMO) levels are well below the Fermi level, rendering the valence band of the nanotube to be crossed by the Fermi level. Such features
shown in Figs. 3(b) and 3(c) directly indicate an almost one electron transfer from the nanotube to the adsorbates (Br$_3$ or Br$_5$).

For reference, the total energies of the isolated charge-neutral Br$_2$, Br$_3$, and Br$_5$ structures are calculated with the same density-functional parameters. While Br$_3$ is energet-
ically unfavorable compared to Br$_2$, the energy of the Br$_3$

\begin{align*}
\text{Energy (eV)} & = \frac{1}{n} \left[ E_{\text{tot}}(\text{Br}_n/\text{CNT}) - E_{\text{tot}}(\text{CNT}) \right] - \frac{n}{2} E_{\text{tot}}(\text{Br}_2),
\end{align*}

where $n$ is the number of bromine atoms in the unit cell. The reference energies of Br$_2$, Br$_3$, and Br$_5$
are calculated with the same calculation parameters. Indeed,
we observe that the polyhalogen structures, Br$_2$, Br$_3$, and Br$_5$, are much favored inside CNTs. The drops in the formation en-

$E_{\text{tot}}(\text{CNT})$ for Br$_2$, Br$_3$, and Br$_5$, respectively. We also note that the molecular structures of Br$_3$, Br$_4$, and Br$_5$, as shown in Fig. 1, are consistent with the previously calculated anionic polybromine clusters, in spite of the severe difference in the calculation scheme. Our results, together with the energetics shown below, indicate that such polyhalogen anions could stably exist inside the carbon nanotube.

The binding strength for the bromine adsorbates inside nanotubes with various diameters is investigated
mainly with LDA, as shown in Fig. 2. Here the formation energy is defined as $E = (1/n) \left[ E_{\text{tot}}(\text{Br}_n/\text{CNT}) - E_{\text{tot}}(\text{CNT}) \right] - \frac{n}{2} E_{\text{tot}}(\text{Br}_2)$, where $n$ is the number of bromine atoms in the unit cell. The reference energies of Br$_2$ and isolated CNT are calculated with the same calculation parameters. Indeed,
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structure is found to be lower than that of Br₂, which is largely consistent with the previous discussion.¹⁷ Total energies per atom are 0.0, 0.08, and −0.09 eV for Br₂, Br₃, and Br₅, respectively, with respect to that of Br₂ molecules. These energy values could directly be compared with those shown in Fig. 2. Note that there are partially occupied states, so-called SOMO states, at the Fermi level for the isolated Br₃ and Br₅ molecules, which become fully occupied when Br₃ and Br₅ are inside the nanotube. As noted above, these bromine species do not form chemical bonds with nanotube, and thus the nanotube band structures are almost rigid without disturbing its π electronic structures, upon the electron transfer to the bromine species.

Finally, we investigate the energy barriers in the formation of these odd-membered bromine species. The optimized geometries of three Br₂ molecules and two Br₃ molecules in a row, encapsulated inside the (16,0) CNT, are obtained in a long supercell (25.44 Å). Then, the energetics of the transformation from such three Br₂ molecules into two Br₃ structures is calculated with the nudged elastic band method.²⁴ Initially, three far-separated (6.05 Å) Br₂ molecules approach with a very small energy barrier (∼0.02 eV), which can be easily overcome at room temperature. They transform into the state of a weakly bonded two Br₃ molecules and finally reach the well-separated two-Br₃ state with a small energy barrier (∼0.04 eV). In addition, to estimate the energy barrier in the formation of the Br₅ structure, the Br₃ and Br₂ molecules are separated by the van der Waals distance in a row in the vacuum. The geometry optimization results in the bent Br₃ structure spontaneously. Thus, provided that such Br₂ and Br₃ molecules exist in close vicinity inside the nanotube, their transformation barrier into the Br₅ structure could also be negligible if the CNT diameter is large enough. Since the encapsulation of Br₂ molecules is an exothermic process, as shown in Fig. 2, and since the transformation into the Br₃ or Br₅ species is almost barrierless, an exposure of tip-opened nanotube samples to a bromine partial pressure could result in the formation of charged Br₃ or Br₅ structures.

In summary, we investigated the atomic and electronic structures, upon the electron transfer to the bromine species. This work was supported by Korea Research Foundation Grant funded by Korea Government (MOEHRD, Basic Research Promotion Fund) (KRF-2005-070-C00054), under which the calculations were performed by using the supercomputing resources of the Korea Institute of Science and Technology Information (KISTI). The research was also supported by grants from KOSEF through the Center for Nanotubes and Nanostructured Composites (CNNC). One of the authors (N.P.) would like to acknowledge the support from KISTI under the 7th Strategic Supercomputing Applications Support Program. Two of the authors (N.P. and W.P.) acknowledge the support from the Terra-level Nano Devices, Korea National Research Program.