The Interaction between Boron-carbon-nitride Heteronanotubes and Lithium Atoms: Role of Composition Proportion

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Abstract

A series of Li@BCN models were systematically investigated to explore the physical origin of the interaction between lithium atoms and BCNs. Theoretical results show that the crucial electron population in the BCNs of Li@B-BCN and Li@N-BCN series is dramatically different. As results, the first hyperpolarizability of Li@B-BCN series increases with the increase of carbon proportion whereas that of Li@N-BCN series significantly decreases with the increase of carbon proportion. The results indicate that the physical properties of Li@BCN models are significantly dependent on the different chemical environment of the tube edge.

Introduction

Boron nitride nanotubes (BNNTs), representative analogous of carbon nanotubes (CNTs), have attracted increasing numbers of attentions [1-6] since they were first synthesized in 1995 by Chopra and co-workers [7]. Comparing with metallic or semiconducting CNTs [8], BNNTs are known as permanent semiconductors with a wider band gap (almost insulator), which is not sensitive to the chirality and morphology of the tubes [5, 9]. The excellent high-temperature stability and neutron radiation shielding capability of BNNTs makes them leading candidates as enabling materials for sensors and devices in the extreme environments [6, 10, 11]. For example, D. Golberg *et al.* found that a stable nanoscale oxygen generator could be formed by encapsulating unstable MgO_2 within BNNT [12]. Recently, Kang and co-workers showed the experimental electroactive characteristics of BNNTs in novel multifunctional electroactive nanocomposites [13]. Up to now, two mainly types of BNNTs have been widely investigated, namely zig-zag and armchair BNNTs [1, 5]. One of the distinctive characters of zig-zag BNNTs is the different chemical environment between the two edges (B-rich edge and N-rich edge), which is fascinating and different from CNTs or armchair BNNTs. For example, we investigated two typical models Li@B-BNNT and Li@N-BNNT that is designed by encapsulated the Li atom to the two edges of BNNT respectively [14, 15]. Results show that the electron distribution of Li@N-BNNT is more diffuse than that of Li@B-BNNT and corresponding static first hyperpolarizability (β_0) are significantly larger. It is worthy of note that β_0 is an important microcosmic parameter of the second nonlinear optical (NLO) response of macroscopic materials [16, 17].

Boron-carbon-nitride nanotubes [18-21] (BCN) are expected to be novel candidates of nano materials due to the diversity of structure, which might break through the limitation of CNTs and BNNTs. Generally, these heteronanotubes are considered as the substitution of CNT segments by BN segments with a suitable formation proportion [22-28]. Recently, our study indicates that the N-connecting pattern of the BN-segment linking to the C-segment is an efficient way to decrease

the transition energy which might be a suitable strategy to enhance the NLO response of heterojunction nanotubes [29-31]. However, it is worthy of note that the investigation on the interaction between BCN and metal atoms is rare up to now. Paying further attention to the mechanism of the modification on the heteronanotubes might open new perspectives for further development of their applications in nanotechnology.

In this work, to reveal the physical origin of the interaction between lithium atoms and the two edge of zig-zag BNNT, Li@B-BNNT and Li@N-BNNT were designed by doping the lithium atoms interacting with pristine zig-zag BNNT. Furthermore, on the basis of Li@B-BNNT and Li@N-BNNT, a series of BCN models (Li@B-BCN and Li@N-BCN) were obtained by substituting some proportion of the boron/nitride atoms at another terminate with carbon atoms (Figure 1). The structures, electronic properties and corresponding first hyperpolarizabilities have been systematically studied. Results show that the first hyperpolarizabilities of Li@B-BCN series increase with the increase of carbon proportion, whereas that of Li@N-BCN series significantly decrease with the increase of carbon proportion. The new discovery on the electronic properties of Li@BNNTs and Li@BCNs might provide important information for the design and preparation of high performance NLO nano-materials in the future.

Figure 1. The optimized structures of Li@BNNT and Li@BCN models (the carbon proportion is 50% and hydrogen atoms is used as passivated atoms on the periphery that is not shown)

Computational Details

For theoretical investigations, selecting a suitable model is the key link to understand relationship between the results and physical properties [32-35]. In this work, a zig-zag BNNT (5, 0) fragment with a suitable length (1.2 nm) is chosen as the fundamental model. The interaction between the BNNT/BCN and Li atoms is a relatively weak noncovalent interaction. The global hybrid generalized gradient approximation M06-2X functional [36, 37] is recommended by Truhlar and co-workers for calculation applications involving main-group thermochemistry, noncovalent interactions, and electronic excitation energies to Rydberg states. Correspondingly, a test calculation with the two DFT methods shows that the trend of the β_0 values of Li@B-BNNT (See Table S1 in SI) obtained by M06-2X is similar to the other functionals. In this work, we choose the results of M06-2X functional to discuss corresponding properties and their variation. For the basis set, the multiple-split valence basis set is capable of showing the expansion and contraction of valence atom orbitals in the molecular environment and is suitable for calculation of the (hyper)polarizabilities. In this context, the optimized geometric structures and corresponding properties were all based on the results of the M06-2X/6-31+g* level except for special emphasis, which is sufficient for our purpose. The corresponding interaction energy (E_{int}) is evaluated to get an insight into the interaction between the lithium atom and BNNT/BCN fragment. Besides, the counterpoise (CP) procedure was used to calculate the interaction energies qualitatively to correct the basis set superposition error [11] (BSSEs). The E_{int} is calculated as the difference between the energy of the complex (Li@BNNT or Li@BCN) and the sum of the energies of the lithium atom and BNNT or BCN. For example, the E_{int} in Li@BNNT is defined as the following formula:

$$E_{\text{int}}(\text{Li@BNNT}) = E(\text{Li@BNNT})_{\text{Li@BNNT}} - (E(\text{Li})_{\text{Li@BNNT}} + E(\text{BNNT})_{\text{Li@BNNT}}) \quad (1)$$

The first hyperpolarizability is defined as the following equation:

$$\beta_0 = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \quad (2)$$

$$\text{Where } \beta_i = \frac{3}{5}(\beta_{iii} + \beta_{ijj} + \beta_{ikk}), i, j, k = x, y, z \quad (3)$$

All of the calculations were performed with Gaussian 09 program package [38] except for special emphasis.

Results and Discussions

The optimized structures of all the isoelectronic models are shown in Figure 1, and the main geometrical parameters and natural population analysis (NPA) charges are listed in Table 1. The shortest distance between lithium and boron atoms (Li-B in Figure 1) of Li@B-BNNT is 2.643 Å, which is longer than that (2.252 Å) of Li-N of Li@N-BNNT. Furthermore, results show the lithium atom is closer to the N-rich edge than the B-rich edge that is not dependent on the carbon proportion. On the other hand, the natural population analysis shows that the charge (0.783) of lithium atom in Li@B-BNNT is larger than that (0.526) of Li@N-BNNT. It indicates that the 2s valence electron of Li interacting with B-rich edge is more ionized than that interacting with N-rich edge. For the Li@BCNs models, the NPA charges of lithium atom in Li@N-BCN series are larger than that of Li@N-BNNT, while that of the Li@B-BCN series varies slightly decrease with the increase of carbon proportion. On the other hand, the corresponding interaction energy (E_{int}) is evaluated to get an insight into the interplay between the lithium atom and different edge of BNNT fragment. As shown in Table 1, the E_{int} in Li@B-BNNT is -30.05 kcal/mol, which is almost twice of that (-16.71 kcal/mol) in Li@N-BNNT. Interestingly, the E_{int} increase with the increase of carbon proportion, which is independent on the B/N-rich edges. According to the above comparisons, two main points is emphasized as the following: 1. The interaction between the B-rich edge and the lithium atom is stronger than that of N-rich edge. 2. With the increase of carbon proportion, the corresponding properties of Li@BCNs might be significantly different from pristine Li@BNNTs models, which are related on the different periphery of BNNT/BCN. The increasing of carbon proportion enhances the stability of lithium doped nano-compounds, which shows the interaction between lithium atom and BCN are larger compared with BNNT. More details about the corresponding discuss on electronic and optical properties are shown in as the following.

Table 1. Main geometrical parameters ($\text{\AA}$), natural population analysis (NPA) charge of crucial atoms (q_{Li} , q_{B} , q_{N} , au) and interaction energy (E_{int} , kcal/mol) of Li@BNNT and Li@BCN models (33.33% and 50% represents the carbon proportion in the BCN models) optimized at the M06-2X/6-31+g* level

	Li@B-BCN			Li@N-BCN		
	Li@B-BNNT	33.33%	50%	Li@N-BNNT	33.33%	50%
Li-B/N	2.643	2.654	2.535	2.252	2.233	2.220
D_{B}^*	3.913	3.894	3.738	4.034		
D_{N}	4.352			4.380	4.337	4.338
D_{C}		4.114	3.957		3.980	3.826
q_{Li}	0.783	0.701	0.719	0.526	0.709	0.696
q_{B}	0.747	0.748	0.624	0.874		
q_{N}	-1.200			-1.181	-1.188	-1.187
E_{int}	-30.05	-33.14	-66.47	-16.71	-34.60	-50.79

* D_{B} means the diameter ($\text{\AA}$) of the boron-rich termination, D_{N} means the diameter of the nitrogen-rich termination and D_{C} means the diameter of the carbon-rich termination of Li@BNNT and Li@BCN models

The comparison on electronic properties of the four structures is interesting. As listed in Table 2, the α_0 value of Li@N-BNNT is 1.03×10^3 au, about twice of that (5.11×10^2 au) of Li@B-BNNT. Results show the polarizability of the model obtained by lithium atom interacting with N-rich edge is obviously larger than that of B-rich edge. Besides, the α_0 value of Li@B-BCN increasing with carbon proportion while that of Li@N-BCN is decreasing. On the other hand, the relationship between the carbon proportion and static first hyperpolarizabilities (β_0) in different Li@BCN models are intuitively shown in Figure 2. The β_0 (1.51×10^5 au) of Li@N-BNNT is about two order of magnitude larger than that (3.68×10^3 au) of Li@B-BNNT. Besides, two distinct variation trends are revealed for the Li@BCNs models when increasing carbon proportion. As shown in Figure 2, the first hyperpolarizability of Li@B-BCN series increases with the increase of carbon proportion, whereas that of Li@N-BCN series significantly decreases with the increase of carbon proportion. In this context, the electronic properties of Li@BCNs are also related on the

different chemical environment between the two different edges interacting with lithium atom. The reasons for the origin of the difference would be unearthed and the details are discussed as follows.

Figure 2. The relationship between the static first hyperpolarizabilities and carbon proportion in different Li@BCN models

According to an approximately two-level expression [39, 40], the β_0 value is mainly dependent on three important factors: excitation energy (ΔE), oscillator strength (f_0) and the difference of dipole moment between the crucial transition states ($\Delta\mu$). To provide an origin understanding about the BN segment doped effects on the first hyperpolarizabilities of heteronanotubes, we focused on the transition states of these models. In this paper, the transition energy of all models are estimated at TD-M062X/6-31+g(d) level and the results are listed in Table 2. The ΔE value of Li@B-BNNT is 2.37 eV, which is obviously larger than 0.59 eV of Li@N-BNNT. Significantly, the transition energy is the decisive factor in determining the β_0 values of Li@BNNTs. On the other hand, the ΔE of Li@B-BCN series decreases with the increase of carbon proportion, whereas that of Li@N-BCN series significantly increases with the increase of carbon proportion. In this context, the order of ΔE^3 is inversely proportional to that of β_0 values as the two-level expression. Correspondingly, as we mentioned above that the α_0 value of Li@B-BCN increasing with carbon proportion while that of Li@N-BCN is decreasing. The origin of the

variation of the α_0 is also related to the inverse variation of their ΔE . Comparing with the variation of the β_0 , the variation of the α_0 is relaxative because β_0 is inversely proportional to the third power of ΔE while α_0 is inversely proportional to the second power of it. It is worthy of note that the polarizability is related to the capability of electron distortion when a molecule is influenced by the external environment. The capability of electrons distortion would enhance when the corresponding excitation energy decrease [16].

Table 2. The polarizability α_0 (a.u.) and first hyperpolarizability β_0 (a.u.) at the M06-2X/6-31+g* level, the oscillator strength f_0 and the transition energy ΔE (eV) at the TD-M06-2X/6-31+g* level

	Li@B-BNNT	Li@B-BCN		Li@N-BNNT	Li@N-BCN	
		33.33%	50%		33.33%	50%
β_x	3.68×10^3	-1.45×10^4	-1.56×10^4	1.51×10^5	-1.06×10^5	-8.36×10^3
β_y	7.73	-3.42×10^3	2.42×10^2	14.62	92.31	3.91×10^3
β_z	-42.77	-2.79×10^3	2.09×10^3	-51.78	26.41	-3.06×10^2
β_0	3.68×10^3	1.51×10^4	1.58×10^4	1.51×10^5	1.06×10^5	9.24×10^3
α_0	5.11×10^2	6.04×10^2	7.27×10^2	1.03×10^3	7.16×10^2	7.13×10^2
f_0	0.11	0.25	0.27	0.13	0.11	0.17
ΔE	2.37	2.07	1.91	0.59	0.93	1.92

Furthermore, the population of the crucial electron is considered to get an insight into the varied trend of static first hyperpolarizability. As shown in Figure 3, the singly occupied molecular orbital (SOMO) of Li@B-BNNT is significantly different with that of Li@N-BNNT. According to our previous study [14, 15], the SOMO of Li@B-BNNT is mainly contributed by the periphery-boron clusters. It indicates that the 2s electron ionized by the lithium atom is bounded by the B-rich periphery. However, an excess electron is shown in Li@N-BNNT, which is formed through the lone pairs of nitrogen atoms of N-rich edge pushing out the 2s electron of the Li atom. As mentioned in our previous work [41-46], the excess electron plays a pivotal role in the large first hyperpolarizability of Li@N-BNNT. Correspondingly, the transition energy of Li@N-BNNT is 0.59 eV, which is significantly lower than 2.37 eV of Li@B-BNNT. On the other hand, the

SOMO of Li@B-BCN is partially distributed on the carbon fragment when increasing the carbon proportion. As result, the transition energy of Li@B-BCNs decrease with the increase of carbon proportion, which is the origin of the variation trend of β_0 of Li@B-BCN series. However, the feature of excess electron is disappeared in the Li@N-BCNs. As shown in Figure 3, the SOMO of Li@N-BCN is mainly distributed on the carbon fragment, which shows more characteristics of pristine BCNs. Correspondingly, the transition energy of Li@N-BCN series increase with the increase of carbon proportion, which is distinctly different with Li@B-BCN series. Therefore, the β_0 of Li@N-BCN series significantly decreases with the increase of carbon proportion.

Figure 3. The singly occupied molecular orbital (SOMO) of Li@BNNT and Li@BCN models

(green and brown color represents the different phases (+/-) of wave function)

Conclusion

In summary, a series of Li@BNNT and Li@BCN models were systematically investigated to explore the physical origin of the interaction between lithium atoms and the BCNs. The corresponding structures, natural population analysis charge, interaction energy, first hyperpolarizabilities and transition properties have been studied by DFT and TD-DFT methods. Significantly, the crucial electron population in the BCNs is dramatically different between Li@B-BCN and Li@N-BCN series. As results, the first hyperpolarizability of Li@B-BCN series increases with the increase of carbon proportion, whereas that of Li@N-BCN series significantly decreases with the increase of carbon proportion. The new discovery on the electronic properties

of Li@BNNTs and Li@BCNs might provide important information for the design and preparation high performance NLO nano-materials in the future.

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Graphical Abstract