1P112

Elongation 法によるドープされた BN ナノチューブの電子状態と導電性・NLO 特性

（九大院・総理工[1]，JST-CREST[2]）○Chen Wei[1]，Yu Guang-tao[1]， Pomogaeva Anna[1]，

Gu FengLong[1]，青木 百合子[1, 2]

Single-wall boron nitride nanotube (BN-SWNT) is a wide gap semiconductor because bulk hexagonal boron nitride has a wide gap between 5.5 and 6 eV [1]. Therefore, BN-SWNTs are expected to be promise materials in nanoelectronics or optoelectronics fields. Various theoretical approaches have been employed to determine the stability, feasibility, and the electronic properties of BN-SWNTs [1,2]. However, these quantum chemical methods are expensive because of the large number of atoms. In this work, we report a new method with high efficiency and accuracy--Elongation Method[3] -- to investigate the electronic structures of different type of BN-SWNTs. This work is a first step toward the application of the elongation method to nanotubes.

It is well known that BN nanotubes are usually difficult for methods trying to exploit the local character of electronic structure because of their strong delocalized nature. So, we compare the elongation and conventional results to show the accuracy of the elongation method on the (4,4) and (6,0) BNNTs at HF/STO-3G level. The detail information about errors per atom of the elongation and cutoff method is
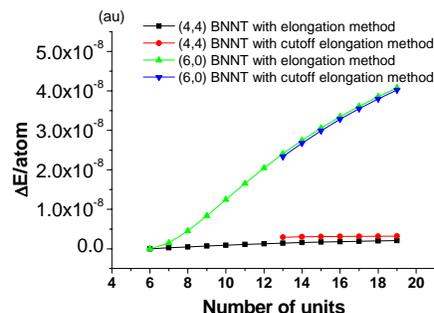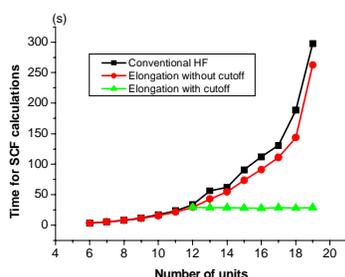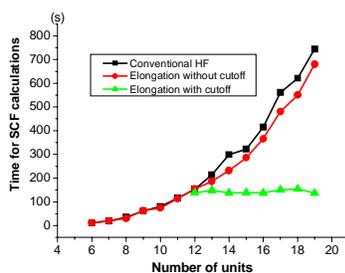

Figure 1. The errors per atom of the elongation and cutoff method for BNNTs

shown in Figure 1. Obviously, the elongation method without and with cutoff technique are accurate for the energy calculations of (4,4) and (6,0) BNNTs. In Figure 2, we compare CPU time to carry out the SCF calculations for (4,4) and (6,0) BNNTs at HF/STO-3G level. It is seen that, for these two systems, the time required by the elongation without cutoff calculation is slightly less than the conventional HF calculation, while the corresponding time consumed by the cutoff technique is almost near to a constant. With the increase of BNNTs' length, the cutoff technique has a large advantage in the SCF treatment comparing with other methods.

(a)

(b)

Figure 2. Total time to solve SCF process
(a) (4,4) BNNT (b) (6,0) BNNT

Besides pure BNNTs, we also investigate the electronic structure of the C-doped BNNTs $[(BN)_xC_y]_m$ (x=1-4, x+y=5) by using elongation method at HF/STO-3G level. The errors per atom are drawn in Figure 3. When N_{st}=6 (N_{st} is the starting cluster size), it is can be seen that errors per atom of four systems are very small, but increase as the carbon content is increased because of more delocalized in carbon's nature. So, for $[(BN)_1C_4]_m$ and $[(BN)_2C_3]_m$, we recalculated their energies by using the larger size starting cluster (N_{st}=10). As a result, errors

per atom are decreased to be 10^{-8} au when Nst=10. Undoubtedly, the elongation method has a good accuracy for the BN/C nanotubes.

To understand the details of the electronic structures, the density of state (DOS) was examined for $[(BN)_xC_y]_m$ (x=1-4, x+y=5) at HF/6-31G level by using Elongation method, as shown in Figure 4. Due to the lack of electron correlation, the 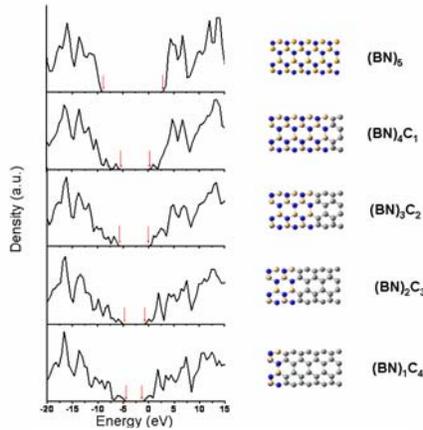calculated energy gaps are larger than the results of Ref. 4. However, the same change trend of energy gaps of several C-doped BN nanotubes is obtained. As the carbon content is increased, the energy gap decreases.

Figure 3. The error per atom for (4,4) $[(BN)_xC_y]_m$

Figure 4. The structures of BN/C nanotubes and their density of states.

To study the effect of carbon doping on the nonlinear optical (NLO) properties of BNNTs, the NLO properties of the pure (4,4) BNNT and C-doped BNNT $(BN)_4C_1$ are calculated by the Elongation Finite-Field method at HF/6-31G level. The results are drawn in Figure 5. Obviously, carbon doping has little effect on the first hyperpolarizability (β), while a large effect on the polarizability (α) and the second hyperpolarizability (γ) is observed. Especially, the γ value of $(BN)_4C_1$ is much larger than that of pure (4,4) BNNT, for example, the γ value of $(BN)_4C_1$ is twice as large as that of (4,4) BNNT when N=20. Undoubtedly, carbon doping can affect the electronic structure and NLO properties of BNNTs.

Our investigation shows that the elongation method has a high efficiency and accuracy to investigate BN and C-doped BN nanotubes.

Figure 5. The NLO properties of (4,4) BN and $(BN)_4C_1$ nanotubes

Reference:

[1] X. Blasé, A. Rubio, S. G. Louie, M. L. Cohen, *Phys. Rev. B* 1995, 51, 6868.

[2] (a)YF. Li, Z. Zhou, JJ, Zhao, *Nanotechnology*, 2008, 19, 015202. (b) W. An, XJ. Wu, JL. Yang, XC. Zeng, *J. Phys. Chem. C*, 2007, 111, 14105-14112.

[3] A. Imamura, Y. Aoki, K. Maekawa, *J. Chem. Phys.*, 1991, 95, 5419.

[4] M. Terrones, J. M. Romo-Herrera, E. Cruz-Silva, F. Lopez-Urias, E. Munoz-Sandoval, J. J. Velazquez-Salazar, H. Terrone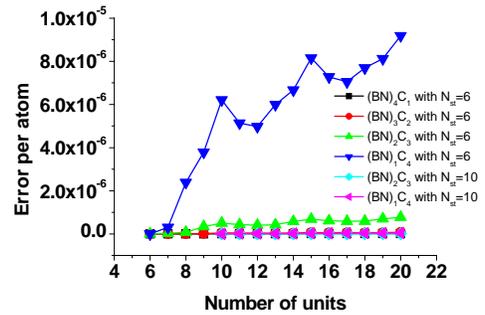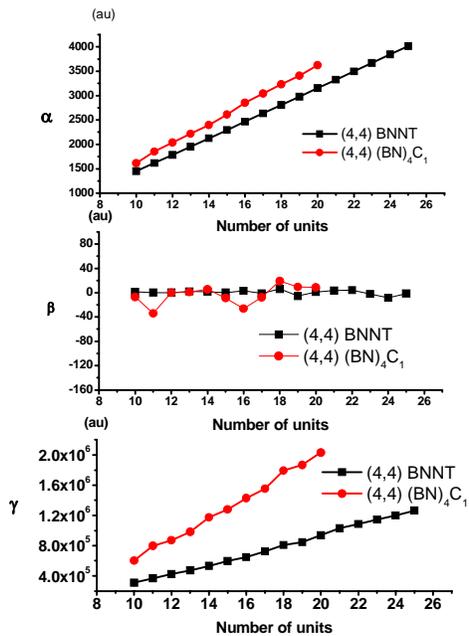s, Y. Bando, and D. Golberg, *materialstoday*, 2007, 10, 30.