First-principles study of the electronic and thermal transport properties of carbon chains

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ABSTRACT

We studied the thermal and electron properties of covalent one-dimensional (1D) monatomic linear chains of carbon, particularly *carbyne*. We found the α-carbyne (Polyyne, alternating single and triple C-C bond co-existing) is more stable than β-carbyne (Equally-spaced based on C-C double bond) energetically. As investigation of electron density of states (EDOS), polyyne and cumulene had different electronic characteristic, which corresponding metallic and semiconducting respectively. We also calculate the phonon dispersion, phonon density of states (PDOS) and phonon transmission of carbynes.

INTRODUCTION

Since allotropes of carbon is identified in 1985, 1D atomic chain (*sp* hybridization), 2D graphene structure (sp^2 hydridization) and 3D diamond (sp^3 hydridization) have been extensively studied and developed as a possibles to be molecular architectures due to its adventages toward electronics and thermoelectrics devices [1]. Linear carbon chains have fascinated theoretically its simplicity and investigation of physical phenomena. Several previous theoretical studies have reported that cumulene had zero-gap semi-metallic or metallic, hence, polyyne had few eV bandgap [2,3]. Recently, Zhao et al. [4] fabricated linear carbon single atomic chain with double-walled carbon nanotubes and reported Raman peak shift have observed (1790 to 1860cm^{-1}). Electronic transmission properties have been extensively studied both theoretically and experimen-

tally [5-7]. For the thermal transmission properties, however, there have been few studies. In this work, we focused on phononic properties of the carbyne structures and also calculated electronic properties. This work will be fundation of further studies on thermal transport properties of carbon-based materials.

MODELS & METHODOLOGY

Our simulation models we considered in this work are infinite 1D carbon atomic chains (Fig. 1). Here, we performed density functional theory (DFT) calculation and non-equilibrium Green's function (NEGF) for electron transport calculation implemented in SIESTA package [8]. For the exchange-correlation (XC) parts of electron-electron interactions, we adopted Perdew-Burke-Ernzerhof parameterization of the generalized gradient approximation (GGA). Double-zeta-plus-polarization quality of Gaussian basis sets were adopted to represent the atomic orbitals of the valance electrons. We also applied small displacement method [9] to obtain the phonon properties of carbon atomic chain. We used SIESTA-FC method [8] to calculate phonon dispersion and PDOS. For the phonon transport calculation, we used in-house code developed on the basis of the NEGF methods [10] This code utilizes dynamical matrix generated by Phonopy [11]. We confined the range of force interactions of carbon atoms as second nearest neighbors due to the technical problems in developing this in-house code.

Small displacement method is finding eigenvalues of the dynamical matrix constructed by the force constant

matrix. This force constant stems from the calculated force from given atomic strcuture. The equation of motion is given by,

$$\sum_{j',\beta} D_{\alpha,\beta}(j, j', q) e_\beta(j', q, \nu) = m_j [\omega(q, \nu)]^2 e_\alpha(j', q, \nu) \quad (1)$$

where α and β are Cartesian coordinates, j and j' as atom indices, m as mass of an atom. The dynamical matrix is defined as

$$D(j, j', q) = \frac{1}{\sqrt{m_j m_{j'}}} \sum_l \Phi_{\alpha,\beta}(j, 0, j', l') \exp(iq[r(j', l') - r(j, 0)]) \quad (2)$$

where l is unit cell index. Force constant matrix is defined as variation of the force acting a selected atoms induced by finite displacement of another atom. The force constant matrix is

$$\Phi_{\alpha,\beta}(j, 0, j', l') = \frac{\partial^2 V}{\partial r_\alpha(j, l) \partial r_\beta(j', l')} = -\frac{\partial F_\beta(j', l')}{\partial r_\alpha(j, l)} \quad (3)$$

Where V and F are potential energy and forces acting on atoms, respectively.

RESULT & DISCUSSION

1. Electronic properties

We performed DFT and DFT-based transmission calculation for two types of carbon atomic chains. Fig.2 shows calculated electronic band structures, EDOS, and corresponding transmission curves. We observed that cumulene and polyyne shows metal and semiconductor-like behavior, respectively. This results agree with theorectical model for an ideal 1D chain and previous results [12]. Bond-Length Alternation (BLA, the bond length between the single and triple bonds) is twice the differences between C-C length of cumulenenic and polyynic carbon chain. The bandgap of polyyne chains is known to be strongly dependent on BLA [15]. Our calculation showed the small bandgap (Eg=0.3eV) compared to the experimental value (Eg=2.3~2.4eV) [13]. The most stable configuration in this work had BLA of 0.048. Although this value is one-third of reported value [14], but quite well matched with Peirls theorem [13]. Besides this geometry effect, typical bandgap underestimation of GGA functionals is another cause of the small bandgap [15].

2. Phononic properties

We applied small displacement method for two types of carbon atomic chains. Fig.3 shows calculated phonon dispersion, PDOS, and corresponding transmission curves. Because of the limitation on treatable size of

calculation, we confined supercell dimension as (2,2,5) along the unitcell vector 1, 2, and 3. This restriction may effect on the desciption of long-range phonons. As a result, the shape of the LO band in polyyne was different from previous studies. Since we used different simulation package to calculate transmission (Phonopy), there were little discrepancy of the frequency range. For the cumulene phonon dispersion, imaginary modes were observed around Γ, which indicates unstablitiy of the cumulene strucure. For the polyyne phonon dispersion, a small gap was appeared between LO and TA. This feature is reflected in corresponding PDOS and transmission curves. The main difference between PDOS and transmission was that there are no transmission values in the TA reigon. Since we used very small displacement of 0.04 bohr, this feature may originate from very small strength of coupling between longitutional and transverse force constrant matrix components.

CONCLUSION

We studied phononic properties of carbyne structures and also calculated electronic properties. We performed DFT and DFT-based NEGF calculations. We also applied small displacement method and adopted DFT as a force calculator to evaluate phonon properties. We obtained a dynamical matrix from this procedure and calculated phonon transmission. Our results of electronic properties was well-matched with previous works. For the phonon part, our results of the phonon dispersion and PDOS shows acceptable features. However, we observed mismatch between PDOS and calculated transmission. We expect to understand the origin of this discrepancy by more accurate description of force constants.

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