

Size-Dependent Bond Dissociation Enthalpies in Single-Walled Carbon Nanotubes



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ABSTRACT

Carbon nanostructures mixed in the form of nanocomposites are currently used for building materials and heat protective coatings. Therefore their thermodynamic stability is important in order to enhance the lifetime of these materials and prohibit their degradation due to excess mechanical forces and thermal vibrations, respectively. The average bond dissociation energy (BDE) can be used as a descriptor of the thermodynamic stability of such materials.

We find that all carbon-structures with π -conjugation (i.e. C₆₀, nanotubes-CNT, carbon nanocones-NC, and graphene nanoribbons-GNR) have BDE for the C-C bond in the range of, BDE_{CC} = 432 kJ mol⁻¹ - 541 kJ mol⁻¹. In SWCNTs this BDE decreases linearly (i) as a function of $-1/\text{radius}^2$ of the SWCNT due to decrease overlap of the p_z-p_z orbitals and (ii) as a function of $-1/\text{length}$ of the SWCNT due to emergence of metallic properties.

METHODOLOGY

- Model: periodic DFT calculations in VASP 5.4.1
- Basis: Γ -point centered 2x2x2 MP grid, E_{cut} = 600 eV
- XC: revPBE-D3 Convergence of forces: 0.01 eV/Å

INTRODUCTION

- Change in enthalpy for the formation of a PAH

$$\Delta H \cong E_{PAH} - n_C E_C - n_H E_H + ZPV_{PAH} \quad (1)$$

- the zero-point vibrational energy

$$ZPV_{PAH} \cong \frac{hc}{2} \left(\sum_{i=1}^{n_{CC}} \nu_{CC,i} + \sum_{j=1}^{n_{CH}} \nu_{CH,j} \right) \quad (2)$$

- The enthalpy of atomization of the PAH

$$\Delta H_{atom} = n_{CC} BDE_{CC} + n_{CH} BDE_{CH} \quad (3)$$

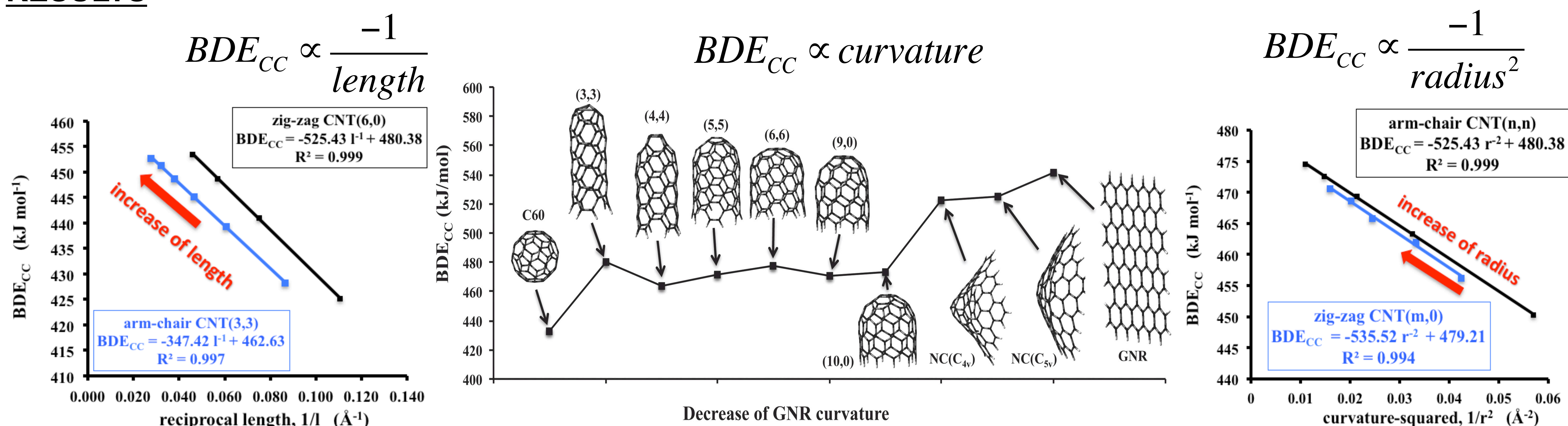
- The change in enthalpy for the formation of the PAH is equal to the negative atomization energy

$$\Delta H = -\Delta H_{atom} \quad (4)$$

- Therefore after combination of equations 1-4, the average BDE per C-C bond in an arbitrary PAH becomes

$$BDE_{CC} \cong \frac{1}{n_{CC}} \left[\begin{aligned} & -E_{PAH} + n_C E_C + n_H E_H \\ & - \frac{hc}{2} \left(\sum_{i=1}^{n_{CC}} \nu_{CC,i} + \sum_{j=1}^{n_{CH}} \nu_{CH,j} \right) \\ & - n_{CH} BDE_{CH} \end{aligned} \right] \quad (5)$$

RESULTS



CONCLUSIONS

- Graphene Nanoribbons contain the most stable form of carbon with average BDE of 541 kJ mol⁻¹
- Graphene Nanocones are slightly lower in stability (BDE = 523 - 525 kJ mol⁻¹) and their stability depends on how wide the apex angle is
- Carbon nanotubes follow in stability with BDE in the range of 464 - 481 kJ mol⁻¹. The capped CNT(3,3) was found to be the most stable among the SWCNTs whereas, the least stable was the CNT(4,4)
- Fullerene-C₆₀ was found to have the lowest BDE (432 kJ mol⁻¹) which can be attributed to the spherical shape which forces the planar five- and six-member carbon rings out of planarity and reduces the p_z-p_z orbital overlap

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References: [1] Constantinos D. Zeinalipour-Yazdi, Eriketi Z. Loizidou, Study of the cap structure of (3,3), (4,4) and (5,5)-SWCNTs: Application of the sphere-in-contact model, *Carbon*, 115 (2017), 819-827

[2] Constantinos D. Zeinalipour-Yazdi, Eriketi Z. Loizidou, Corrigendum to "Study of the cap structure of (3,3), (4,4) and (5,5)-SWCNTs: Application of the sphere-in-contact model", *Carbon*, 146 (2019), 369-370

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