Integrated multi-scale study for nanosynthesis in plasma volume

Longtao Han[1,2], Predrag S. Krstic[1]

[1] *Institute for Advanced Computational Science, Stony Brook University, Stony Brook, NY, USA*

[2] *Dept. of Materials Science and Engineering, Stony Brook University, Stony Brook, NY, USA*

Motivation

High flux of active contents (atoms, ions and electrons) in plasma volume suggest different growth mechanisms from other approach. To obtain a better understanding of the synthesis mechanisms in plasma, we conduct multi-scale computational calculations and simulations, specifically addressing following issues:

- Develop evolution process of the plasma and growth of nanomaterials, in terms of their physical and chemical properties
- Recommend optimal plasma parameters for controlled synthesis

Methodology

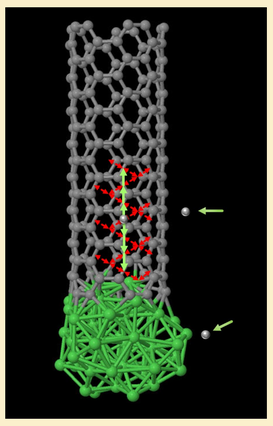
CNT	• First principle density functional theory (DFT) approach is used to analyze many properties such as the energy of binding adatom states, the activation barriers, reaction paths and electron density. • Kinetic Monte Carlo (KMC) simulation is performed to find lifetime of active adatom and distance of adatom migration.
BN	• Quantum classical molecular dynamics (MD) code (SCC-DFTB) is implemented to simulate the growth of boron-nitride nanocages, fulle-renes and nanotubes.

Migration of carbon adatoms at SWCNT surface

Ultimate problem:

Can migration of adatoms over the external surface of SWCNT feed the tube growth in plasma?

- In previous model[1], only catalyst surface can provide C atom for growth, because C comes from hydrocarbon molecules.
- Plasma environment can provide active C atoms, which can also be captured on CNT surface.



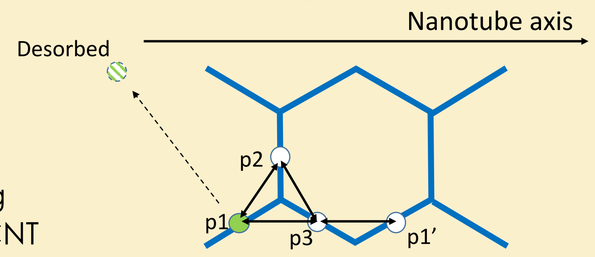
Theory:

Jump length | Vibrational frequency | Energy barrier

$$D = \frac{\lambda^2}{4}\Gamma = \frac{\lambda^2}{4} \cdot \nu \cdot exp\left(-\frac{E_b}{kT}\right)$$

- Migration of adatoms can be described by diffusion theory. All needed properties can be calculated.
- Migration of adatoms terminates with desorption. Its probability can be described by adsorption energy (Ea).
- Charging on CNT can affect the migration and desorption.

Scheme 1: All possible transition processes of adatom during migration on CNT



Results:

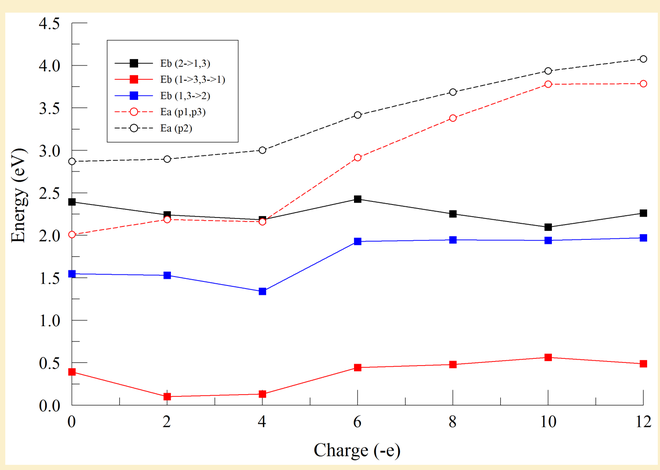


Fig.1 Comparison of migration barriers (Eb) and desorption barriers (Ea) with different charges on CNT

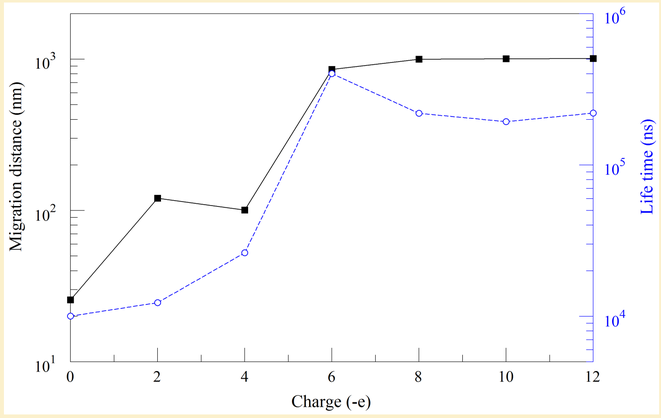
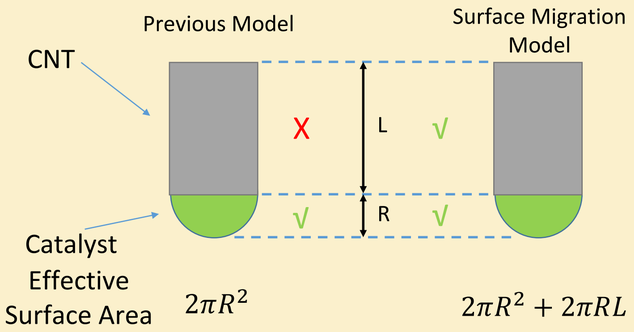


Fig.2 Migration distance and life time of adatom with different charges on CNT

- Migration with small energy barrier exists in (5,5) chirality type, along the nanotube axis direction.
- With increase of charge on CNT, adsorption energy increases while migration barriers remain similar values.
- Carbon atom adsorbed on CNT surface can migrate efficiently through fast migration path. Migration distance increases with increase of charge.



Scheme 2 Enhancement of feeding flux for CNT growth by migration of adatom

- Effective area accepting feedstock C atom increases by (L+R)/R times, which can be as large as 200 times!
- Surface migration can be an important mechanism for CNT synthesis in plasma environment.

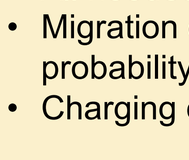
Growth of BN nanostructure

In this project, different approaches are tested to simulate the growth of boron-nitride nanostructure.

X Classical MD: LAMMPS

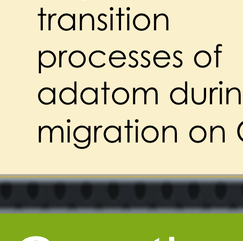
√ Quantum classical MD: SCC-DFTB

BN fullerene:



Boron cluster with different sizes: 36, 96 atoms

Flux: N atoms



Fullerene-like BN structure

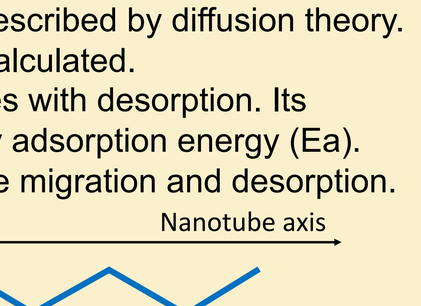


Fig.3 Evolution of Lindemann index and position statistics of B and N atoms at two different growth stage

BN "graphene":

HBNH is used as feedstock molecule. BN "Graphene" can be built with B6 cluster as seed or without seed.

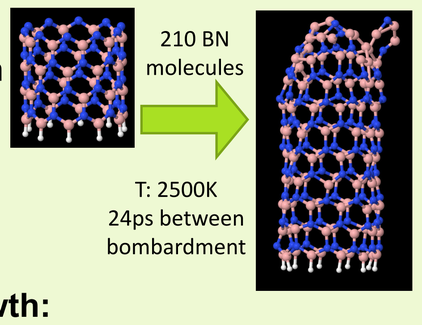
H atoms terminate the boundary of BN nanostructure, which prevents it building into cage.

Conclusion:

- SCC-DFTB is a successful approach to simulate growth of BN nanostructures.
- Seed and feedstock species, temperature, pressure and flux can all affect the structure of product.

BN nanotube:

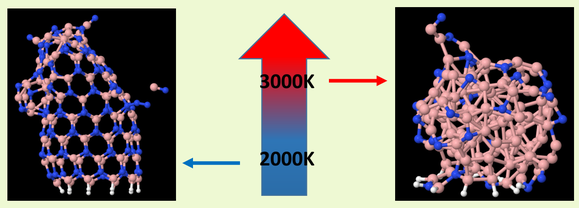
- For the first time, the simulation of BNNT growth is achieved.
- A 0.7nm zigzag type BNNT grows to 2nm under continous bombardment of BN molecules



Two crucial parameters for growth:

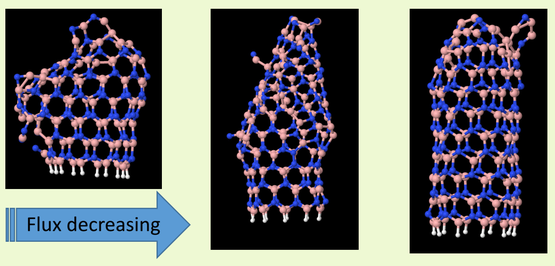
Temperature:

Proper temperature promotes migration of side chains to the top of tube.



Flux:

Low flux of feedstock molecules provides enough time for migration of side chains



References

1. Kumar, Mukul, and Yoshinori Ando. "Chemical vapor deposition of carbon nanotubes: a review on growth mechanism and mass production." *Journal of nanoscience and nanotechnology* 10.6 (2010): 3739-3758.

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