2P135

# Theoretical studies on chirality-selective carbon nanotube cap etching

(Nagoya University[†], WPI-ITbM[‡], University of Newcastle[§])

○Ryuto Kimura[†], Yuh Hijikata[†, ‡], Clothilde Eveleens[§], Alister Page[§] and Stephan Irle[†, ‡]

## Introduction

Carbon materials such as graphene and single-walled carbon nanotubes (SWCNTs) are promising advanced materials interesting for many researchers because of their various applicable properties, for instance conductivity, catalysis, and magnetic properties. In the case of SWCNTs, such properties depend much on nanotube chirality, which can be defined by chiral indices, (*n,m*), or chiral angle, $\theta$. A lot of efforts have been devoted to control the chiral SWCNT parameters. For instance, chemical vapor deposition (CVD) with metal clusters are one of the most successful approaches to synthesize them, while limited success has been achieved in experiments so far to control their chirality. Theoretical studies also have revealed the dependency of the chirality in nanotube growth on the metals clusters, however the studies have not mentioned the roles of additive species which are used to activate the metal catalysts.

In this work, we focused on etching effects of $H_2O$, which is one of the typical additive species, on SWCNTs growth. Under CVD, OH and H radicals are formed and they can react with not only the metal clusters but also the nanotubes, which means the radicals etch the nascent caps, possibility chirality-dependent. We theoretically uncover the reactivity of (*n,m*) SWCNTs with the radicals using density functional theory.

## Models and Computational Details

We employed cap structures to focus on the early stage of SWCNTs growth as shown in Figure 1. We considered (*n,m*) = (5,5), (6,5), (7,4), (8,3), (9,2), (10,1) and (11,0) as caps and X = H and OH radicals as etchant species. We evaluated the binding energies ($\Delta E$) of X on the caps after geometry optimizations with the lowest spin states in each system. The $\Delta E$ were defined as follow;

$$\Delta E = E_{\text{cap-X}} - (E_{\text{cap}} + E_{\text{X}}),$$

where $E_{\text{cap-X}}$, $E_{\text{cap}}$ and $E_{\text{X}}$ are state energies of cap-X, cap and X, respectively. All calculations were performed at the B3LYP/6-31G(d) level of theory using Gaussian 09.

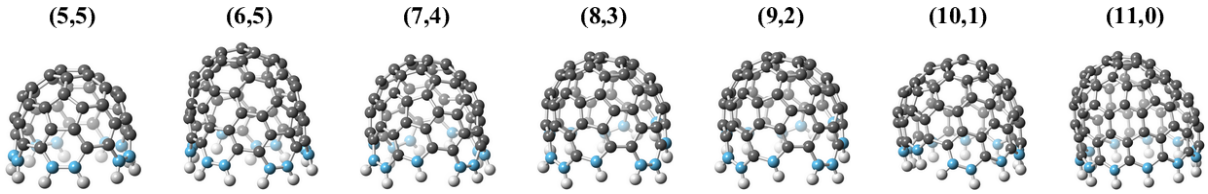


**Figure 1.** Optimized (5,5), (6,5), (7,4), (8,3), (9,2), (10,1) and (11,0) cap geometries. Gray, light blue, and white spheres indicate the carbon of the caps, carbon on the edge, and hydrogen.

## Results and Discussion

Evaluated $\Delta E$ on the all carbons of each cap are shown in Figure 2(a). The $\Delta E$ distributed widely expect the (5,5)-cap case. (10,1)-cap showed the largest range of $\Delta E$, 213 kJmol$^{-1}$. The minimum $\Delta E$ in each cap were basically increased as the chirality angle decreased. Considering the maximum $\Delta E$ in each cap, (9,2)-cap was the most reactive, 300 kJmol$^{-1}$ and (5,5)-cap was the least, 149 kJmol$^{-1}$. The maximum $\Delta E$ increased as the chiral angle decreased from (5,5)-cap to (9,2)-cap. From (9,2)-cap to (11,0)-cap, the maximum $\Delta E$ slightly decreased. The most reactive carbon atoms were located at the edge except for the (5,5)-cap. As a result, their averaged energies ranged from 100 to 150 kJ mol$^{-1}$, which had little dependency on the chirality. However, the average $\Delta E$ of the edge carbons in Figure 2(b) showed the linear relationship. The average increased along with the decreasing of the chirality angle. The ($n$,$m$) SWCNTs can be formed depending on the average $\Delta E$. This results indicate capability of the chiral selective growth. More detailed will be discussed in the poster session.

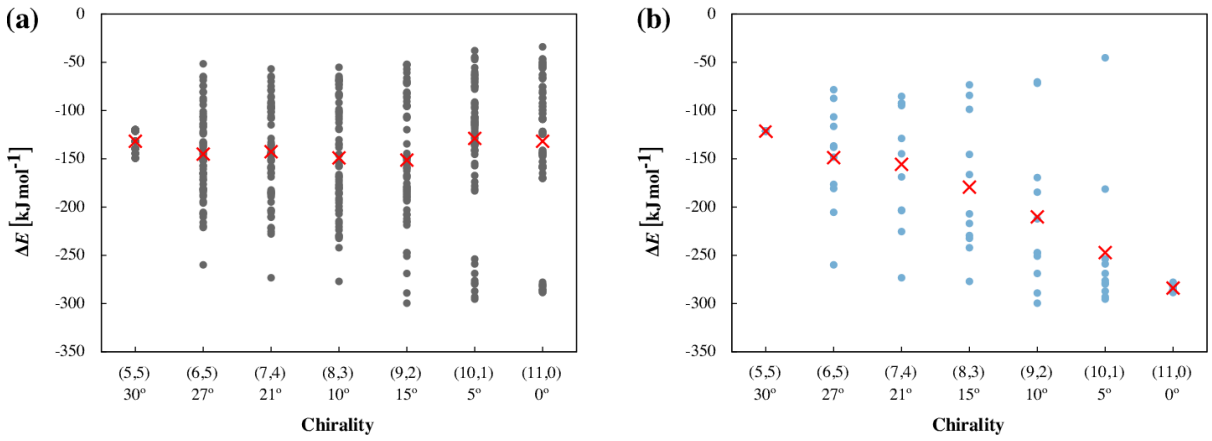


**Figure 2.** $\Delta E$ of OH on the (a) all carbons (gray circle) and (b) the edge carbons (blue circle) and averaged ones (red cross) in each cap.