

## CARBON MATERIALS WITH ZIGZAG AND ARMCHAIR EDGES

Yasuhiro Yamada<sup>1\*</sup>, Miki Kawai<sup>1</sup>, Hideki Yorimitsu<sup>2</sup>, Shinya Otsuka<sup>2</sup>, Motoharu Takanashi<sup>3</sup>, Satoshi Sato<sup>1</sup>

<sup>1</sup>Graduate School of Engineering, Chiba University, Chiba 263-8522, Japan

<sup>2</sup>Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan

<sup>3</sup>Instrumental Analysis Center, Yokohama National University, Kanagawa 240-0067, Japan

\*Presenting author's e-mail: y-yamada@faculty.chiba-u.jp

### Introduction

Carbonization of PAHs with zigzag edges<sup>1,2</sup> and armchair edges<sup>1,3</sup> has been extensively studied in the past two decades.<sup>4</sup> These works mentioned the presence of zigzag and armchair edges in carbonized structures, but basically only the simplified carbonized structures were exhibited, and the details are still under debate because of the difficulty to characterize the edge structures of these carbon materials without observing structures directly at atomic scale under microscopes.<sup>5</sup> In this work, carbon materials with zigzag and armchair edges were prepared and the structures were determined in detail by using molecular dynamic simulation with a reactive force field (ReaxFF) to narrow down the number of possible structures and Raman spectroscopy and IR spectroscopy combined with computation.

### Materials and Methods

Tetracene and chrysene carbonized in ampoule tubes were analyzed by Raman spectroscopy and diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy (FT-IR-4200) were also conducted and compared with the results of simulated Raman and IR spectra (B3LYP/6-31G(d), Gaussian 09). 100 Molecules of tetracene and chrysene were randomly positioned and heated in ReaxFF (Force field: "dispersion/CHONSSi-ig.ff" Method: Velocity Verlet + Berendsen.).

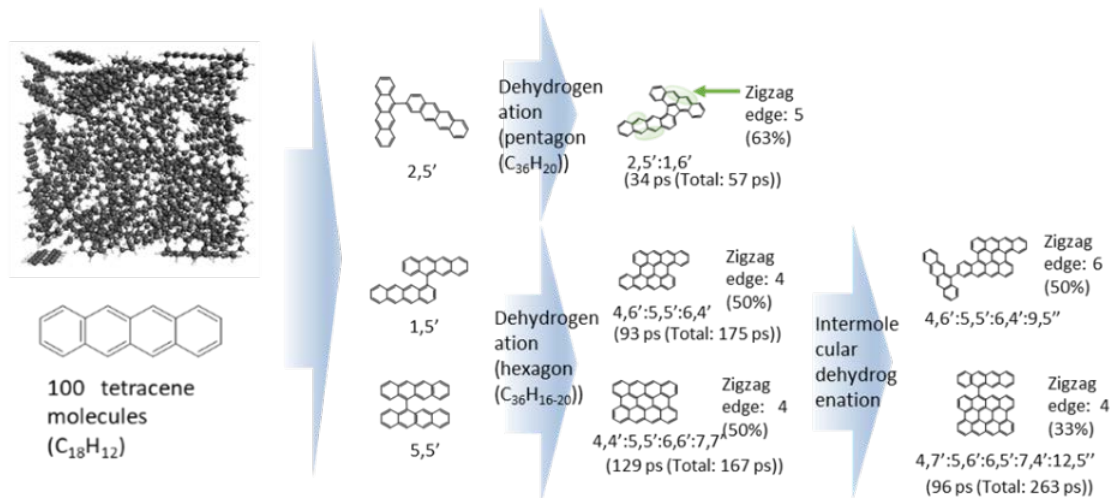


Figure 1. Structures of tetracene heated at 3000 K in ReaxFF.

## Results and Discussion

**Figure 1** shows the calculated results of heat treatment of tetracene at 3000 K in ReaxFF. Reactive positions such as position 5 reacted first, and other positions also reacted by dehydrogenation reaction, and carbonization reaction proceeded. Chrysene tended to retain the percentage of armchair edges even after carbonization, whereas tetracene tended to reduce the percentage of zigzag edges after heat treatment by formation of new edges such as armchair edges. Structures obtained by ReaxFF were used to simulate Raman and IR spectra (**Figure 2**) of carbonized tetracene and chrysene. The presence of these edges was confirmed by simulated Raman and IR spectra combined with experimental Raman and DRIFT spectra. Tetracene was dehydrogenated via the formation of  $sp^3C$  at 693 K and carbonized via elimination of  $sp^3C$  at 853 K (not shown). On the other hand, chrysene was dehydrogenated without formation of  $sp^3C$  at 853 K and carbonized at 893 K, which is much higher than the carbonization temperature of tetracene. Especially, for tetracene with zigzag edges, this precursor molecule has a linear structure with  $sp^2C-H$  on zigzag edges as well as  $sp^2C-H$  at para positions. The presence of  $sp^2C-H$  at para positions significantly enhanced the reactivity of tetracene. In addition, it was revealed that armchair edges were easier to retain their edge structures than zigzag edges after carbonization.

## Conclusions

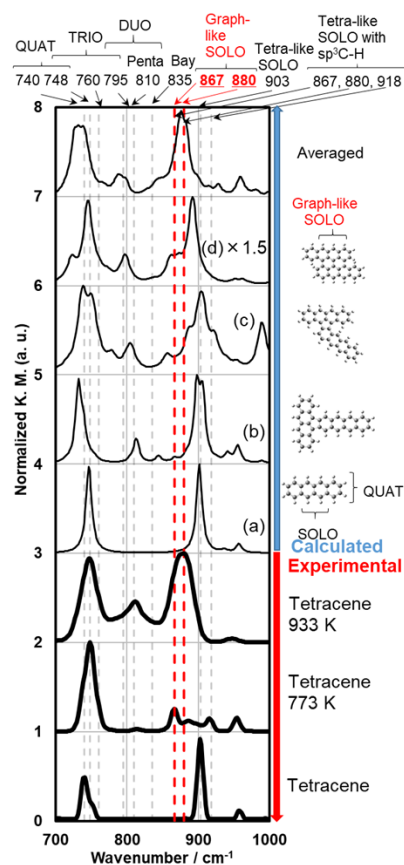
Detailed carbonization mechanisms could be revealed by experimental and calculated Raman and IR spectra combined with ReaxFF. This type of detailed research of carbonization of aromatic compounds has not been reported elsewhere. The result of this work helps to synthesize carbon materials with different edge structures and understand the complicated structure of general carbon materials in the future.

## Acknowledgment

This work was supported by JSPS KAKENHI Grant Number JP18K04833.

## References

1. Sasaki T., Jenkins R. G., Eser S., Schobert H. H. (1993) Carbonization of anthracene and phenanthrene. 2. Spectroscopy and mechanisms. *Energ. Fuel.* 7, 1047-1053
2. Tamai K., Nakamizo M. (1984) Carbonization Processes of Some Aromatic Hydrocarbons. *Tanso* 1984, 30-34
3. Wang G. (2005) Molecular Composition of Needle Coke Feedstocks and Mesophase Development During Carbonization. Ph.D. Dissertation, The Pennsylvania State University, 249-250
4. Yamada Y., Gohda S., Abe K., Togo T., Shimano N., et al. (2017) Carbon materials with controlled edge structures. *Carbon* 122, 694-701
5. Sasaki T., Yamada Y., Sato S. (2018) Quantitative analysis of zigzag and armchair edges on carbon materials with and without pentagons using infrared spectroscopy. *Anal. Chem.* 90, 10724-10731



**Figure 2. Experimental and calculated IR spectra of carbonized tetracene.**