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QUANTITATIVE ANALYSIS OF ZIGZAG AND ARMCHIR EDHES ON CARBON MATERIALS WITH/WITHOUT PENTAGONS USINH INFRARED SPECTROSCOPY

Yasuhiro Yamada*, Tatsuya Sasaki, Satoshi Sato

Graduate School of Engineering, Chiba University, Chiba 263-8522, Japan

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

Introduction

Infrared spectroscopy (IR) is one of analytical methods to determine edge structure of carbon materials (**Figure 1**). Out-of-plane sp^2C-H bending vibrations on four types of edge structures have been assigned as SOLO, DUO, TRIO, and QUATRO.[1] In addition, in-plane sp^2C-H stretching vibration has been calculated to define the edge structures.[2] However, the reported work determines the peak positions by only calculation. Our group has recently studied analyses of structurally controlled carbon materials using IR, but the accurate assignment is still necessary.[3] In this work, the peak positions of sp^2C-H bending and stretching vibration of various edge structure were estimated by analyzing reference aromatic compounds composed of either only hexagonal rings or hexagonal and pentagonal rings using IR.

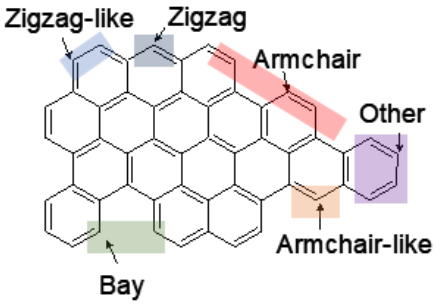

Figure 1. Structure of various edges in carbon materials.

Materials and Methods

Twenty-two aromatic compounds with various edges were used as reference compounds to obtain peak positions of edges and intensities of the peaks for qualitative analyses of diffuse reflectance infrared Fourier transform (DRIFT) spectra and to obtain calibration factors for quantitative analyses. For two-dimensional analyses using combination of two types of vibrations, a geometric mean, $P_{n\_edge\ (bending*stretching)}$ (eq. 1) were obtained by multiplying $P_{n\_edge\ (bending)}$ and $P_{n\_edge\ (stretching)}$. $P_{n\_edge\ (bending)}$ and $P_{n\_edge\ (stretching)}$ are percentages of calibrated peak area of one type of edges, which is an experimental peak area of a certain edge divided by calibration factor (**Figure 2**).

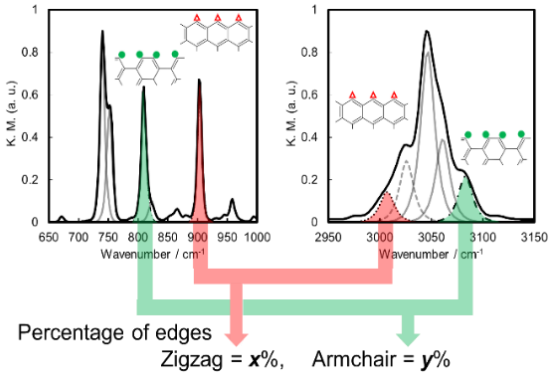

Figure 2. Two-dimensional analyses using two-types of vibrations using DRIFT spectra.

$$P_{n_{edge}(bending*stretching)}\ [\%] = \sqrt[2]{P_{n_{edge}(bendigng)} \times P_{n_{edge}(stretching)}} \qquad \text{eq. 1}$$

, where $P_{n\_edge\ (bending)}$ is the percentage of out-of-plane sp^2C-H bending vibration on one type of edges. $P_{n\_edge\ (stretching)}$ is the percentage of in-plane sp^2C-H stretching vibration on one type of

edges. $P_{n\_edge\ (bending*stretching)}$ is the percentage of a geometric mean for bending and stretching vibration of sp^2C-H on the edges.

Results and Discussion

Table 1 show peak positions for each edge, which were obtained from experimental peak positions in this work. Contrary to the reported work, which exhibited only the calculated peak positions,[2] this work clearly showed the experimental peak positions. Peaks originated from the out-of-plane sp^2C-H bending vibration have been utilized to classify the presence of each edge structure clearly, but correlation coefficients for out-of-plane sp^2C-H bending vibration were lower than those for in-plane sp^2C-H stretching vibration because of the coupled vibration[4] for out-of-plane sp^2C-H bending vibration. Thus, these two vibrations were combined to improve the reliability of quantitative analysis (**Figure 2**).

Table 1. Peak positions of various edges.

Name of edges	Peak positions/ cm^{-1}	
	Out-of-plane sp^2C-H bending	In-plane sp^2C-H stretching
Zigzag	874-904	3001-3014
Armchair-like	813-839	3064-3069
Armchair-like (pentagon)	861-898	3011-3030
Armchair	810-831	3060-3097
Armchair (pentagon)	822-837	3022-3053
Zigzag-like	812-849	3009-3047
Bay	ca. 796	ca. 3096
Other	725-773	3022-3067

Using these methods, this work developed a novel method to quantify the edge structures such as zigzag, armchair, and other edges of carbon materials with/without pentagons using DRIFT by combining peaks originated from out-of-plane sp^2C-H bending vibration and in-plane sp^2C-H stretching vibration. This method could determine edge structures much more accurately than conventional methods using only peaks of out-of-plane sp^2C-H bending vibration.

Conclusions

A novel two-dimensional method to quantify edge structures of carbon materials with/without pentagons was developed by analyzing both out-of-plane sp^2C-H bending and in-plane sp^2C-H stretching vibration. This method could determine edge structures much more accurately than conventional methods using only peaks of out-of-plane sp^2C–H bending vibration because 22 reference compounds with various edges and density functional theory calculation to simulate spectra were used to determine the calibration factor of peaks originating from specific edge structures in this work.

Acknowledgment

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