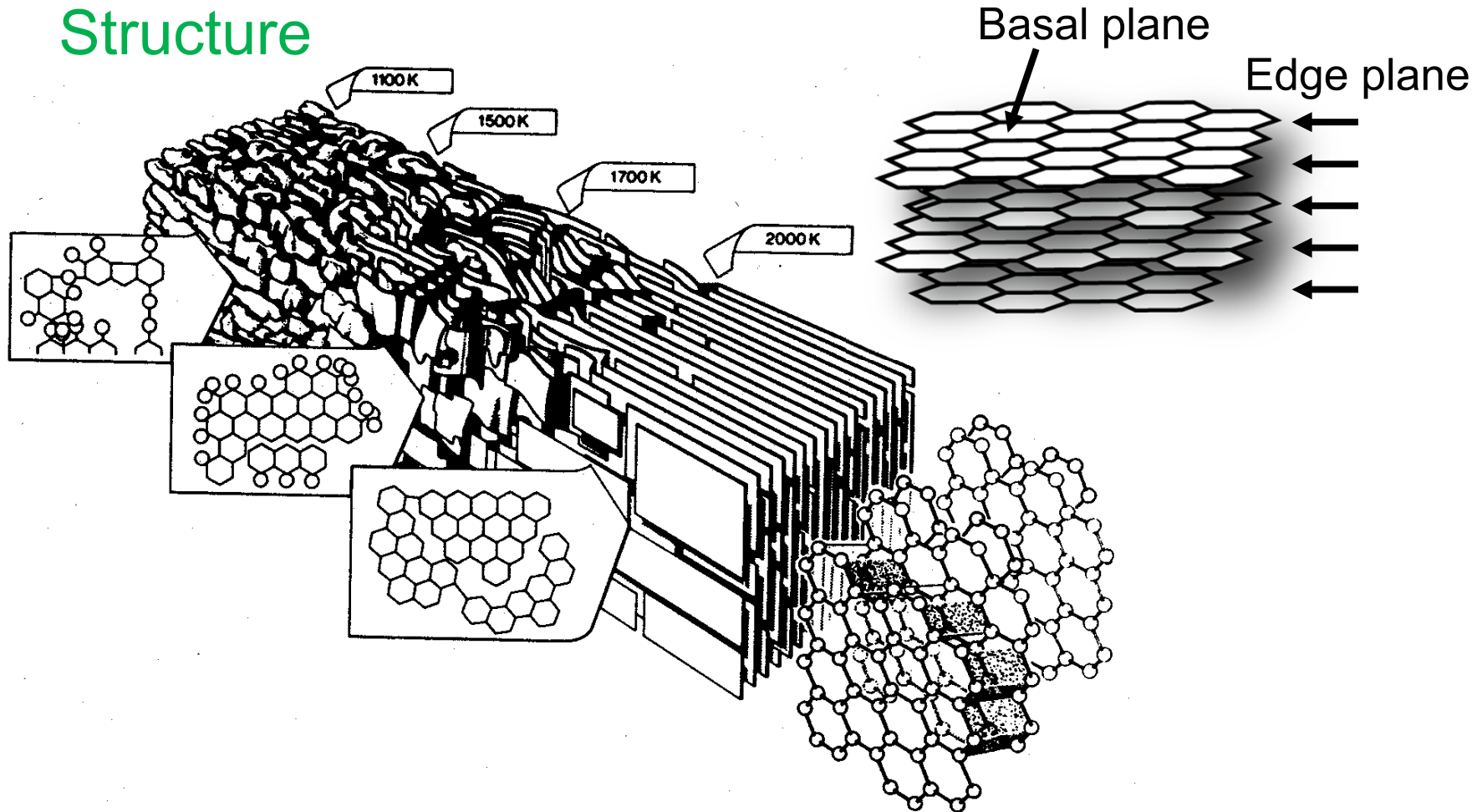

A quantitative analysis of trace amounts of hydrogen and surface oxygen complexes for graphites and high-temperature treated carbons in relation to their molecular structures

Takafumi Ishii (Gunma University)

- Introduction
- **Development of techniques** for analyzing the trace amounts of carbon edge sites
- **Characterization of graphite and high temperature treated carbons**
 - ✓ A quantitative analysis of the edge sites
 - ✓ The carbon structure understood from the amounts of edge sites
- Conclusion

Structure

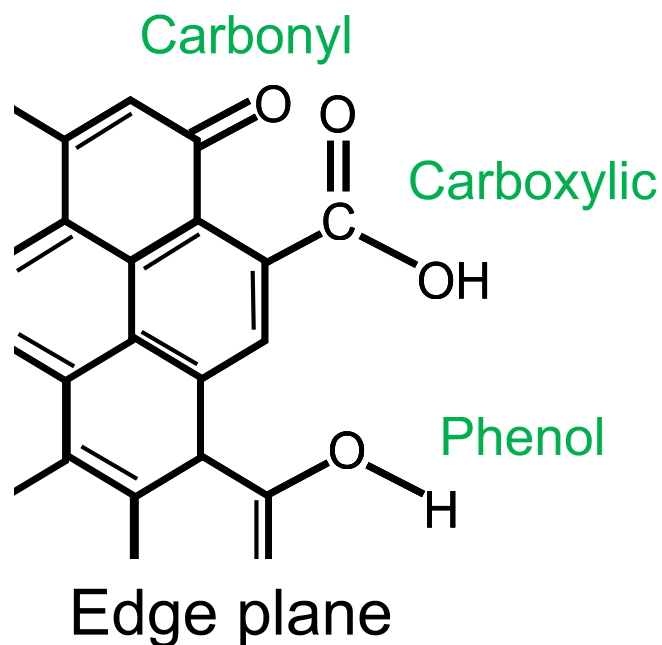


Layer structure of carbon sheets

(Marsh and Griffiths, 1982)

Edge Sites of Carbon Materials

Surface oxygen complexes and hydrogens on the edge sites



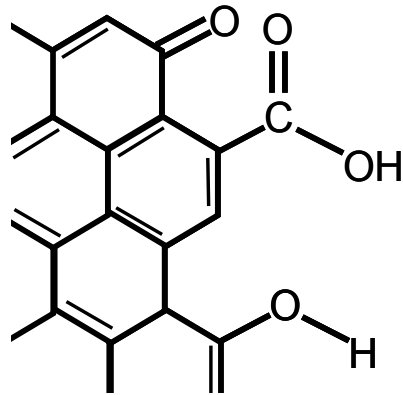
Surface characteristic

wettability, sorbability, electrochemistry...

Analyses of the amounts and nature of edge sites are important for understanding the carbon chemistry.

Surface oxygen complexes and hydrogens on the edge sites

How to analyze ?



Surface oxygen complexes

Infrared Spectroscopy

X-ray Photoelectron Spectroscopy

Temperature-programed desorption

Hydrogen

Combustion analysis

However...

Such analyses are not an easy task for **Graphite materials.**

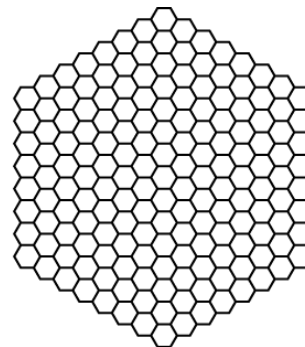
Because, the edge sites are **too small**
due to the structure.

Objective in This Work

1. Development of techniques for analyzing the trace amounts of carbon edge sites

2. A quantitative analysis of carbon edge sites and the estimation of graphene sheet size from the number of edge sites in graphite materials.

Average size of graphene sheets



Edge site: Carbon = 1:1

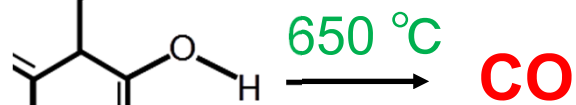
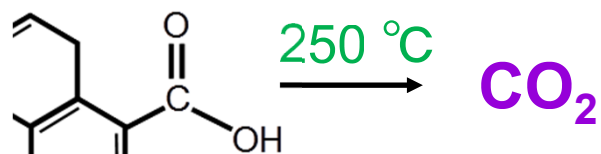
1:3

1:8

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Surface Oxygen Complexes

Temperature-programmed
desorption (TPD)



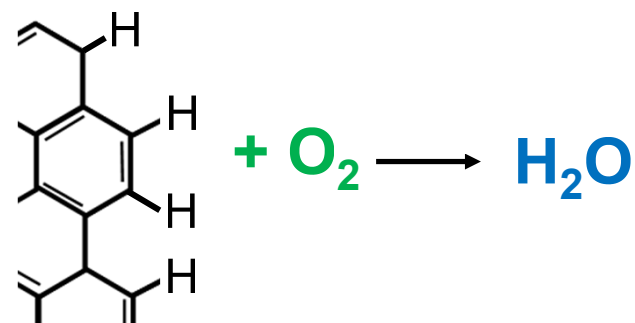
Desorption
gases

Challenges for the apparatus

- High sensitivity
- Reaching a high temperature

Hydrogen

Combustion analysis

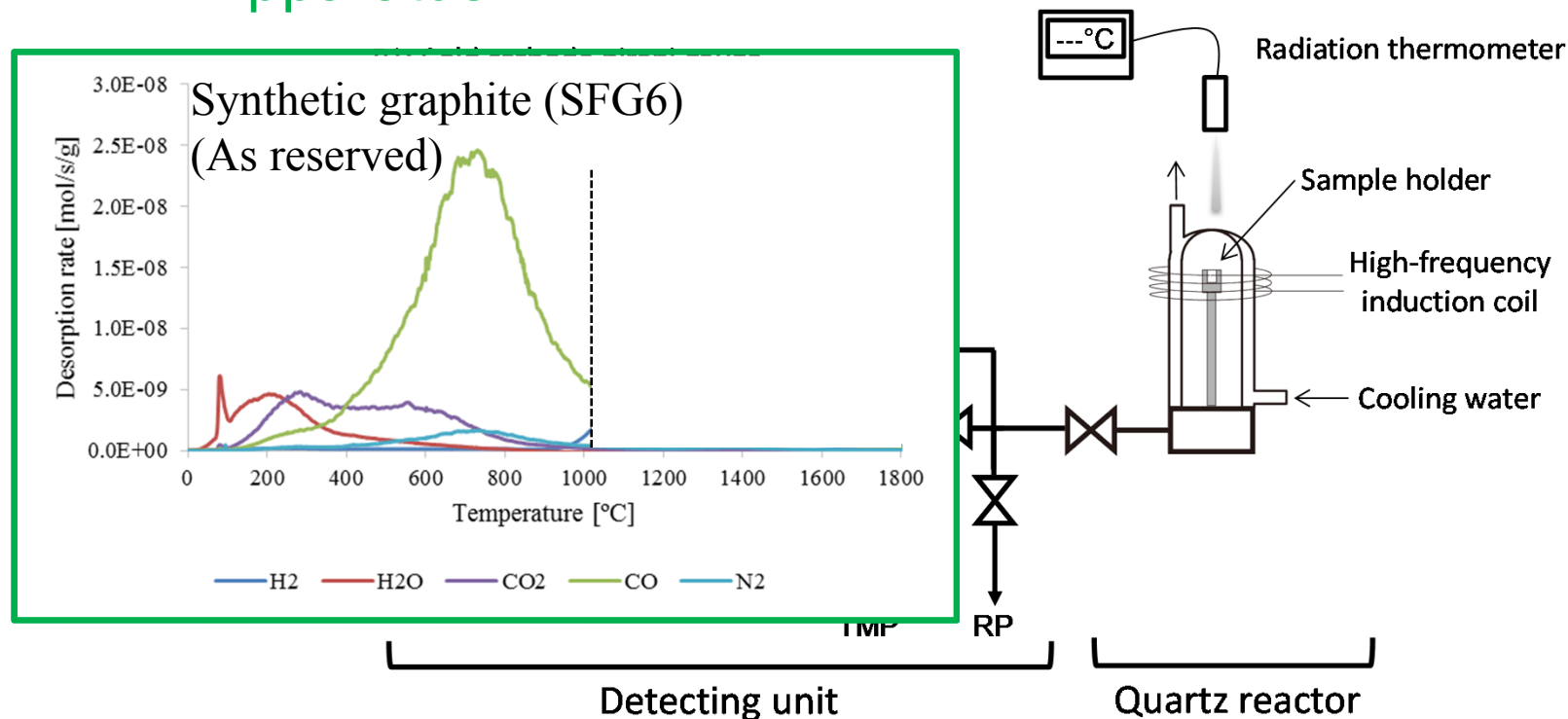


Challenge for the apparatus

- High sensitivity

Experimental Setup for TPD Analysis

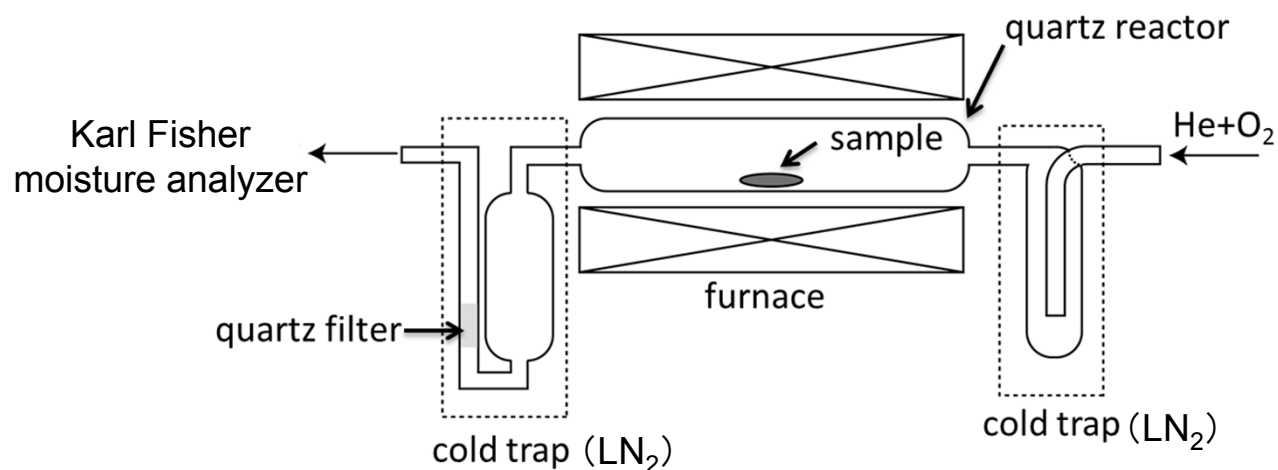
TPD Apparatus



Features of the apparatus

1. Wide temperature range of TPD measurement is achieved by heating graphite sample holder by using a high frequency induction heating method.
 - The temperature range is RT ~ 1800 °C
2. Sensitized by the resistance between QMS and TMP.
 - Its sensitivity is 100 times as high as a common TPD apparatus.

Gasification Apparatus



Karl Fisher moisture analyzer

Trace amounts of H₂O formed during carbon gasification are trapped in the cold trap. After that, it can be quantitated by using Karl Fisher moisture analyzer.

Features of the apparatus

High detection limits of hydrogen content less than 0.1 μmol/g.
→ Its sensitivity is 100 times higher than common apparatus.

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Graphitized carbon

○Graphite materials

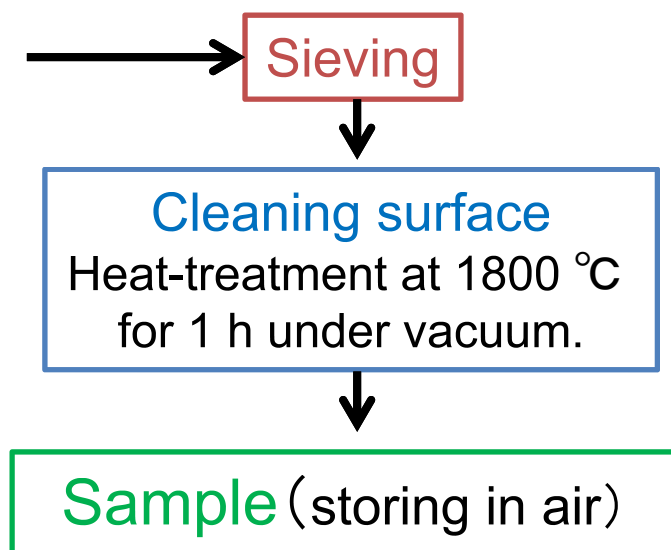
Natural graphite (Alfa Aesar, Purity; 5N)

Synthetic graphite (Alfa Aesar, Purity; 5N)

○Coke carbons

Gilsonite coke heat-treated @2400 °C

Gilsonite coke heat-treated @2800 °C



Carbon samples

Sample ID	Sample	Heat treatment temperature [°C]	Particle size [μm]
NG(50)	Natural Graphite	n/a	50
NG(160)	Natural Graphite	n/a	160
SG(70)	Synthetic Graphite	n/a	70
SG(170)	Synthetic Graphite	n/a	170
GC24	Gilsonite Coke	2400	500
GC28	Gilsonite Coke	2800	600

Quantitative analyses results of edge sites

Sample	TPD analysis	Combustion analysis	Total edge site
	Oxygen groups [$\mu\text{mol/g}$]	Hydrogen [$\mu\text{mol/g}$]	N_{edge} [$\mu\text{mol/g}$]
NG(50)	0.28	0.41	0.62~0.74
NG(160)	0.10	<0.10	0.15~0.20
SG(70)	0.16	0.28	0.40~0.46
SG(170)	0.09	0.16	0.22~0.26
GC24	0.11	0.85	1.12~1.15
GC28	0.11	0.57	0.89~0.91

Surface oxygen complexes ··· NG(50) has the largest amount

Hydrogen ··· GC24 has the largest amount
NG(160) has the smallest one

The amounts and nature of edge sites for graphitized carbon are different from one sample to another.

Quantitative analyses results of edge sites

Sample	TPD analysis	Combustion analysis	Total edge site
	Oxygen groups [$\mu\text{mol/g}$]	Hydrogen [$\mu\text{mol/g}$]	N_{edge} [$\mu\text{mol/g}$]
NG(50)	0.28	0.41	0.62~0.74
NG(160)	0.10	<0.10	0.15~0.20
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GC24	0.11	0.85	1.12~1.15
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Cases of other carbon materials reported in previous studies

Sample	Oxygen content [$\mu\text{mol/g}$]	Hydrogen content [$\mu\text{mol/g}$]
PFA, PVC carbons*	0.8 ~ 11.3	36 ~ 1190
Graphite materials ^[1]	-	5 ~ 200
Graphite (SLX50) ^[2]	1.3-5.2	-
Graphitized Carbon	6 ~ 80	

* T. Ishii et al., *Carbon*, **80**, 135 (2014)

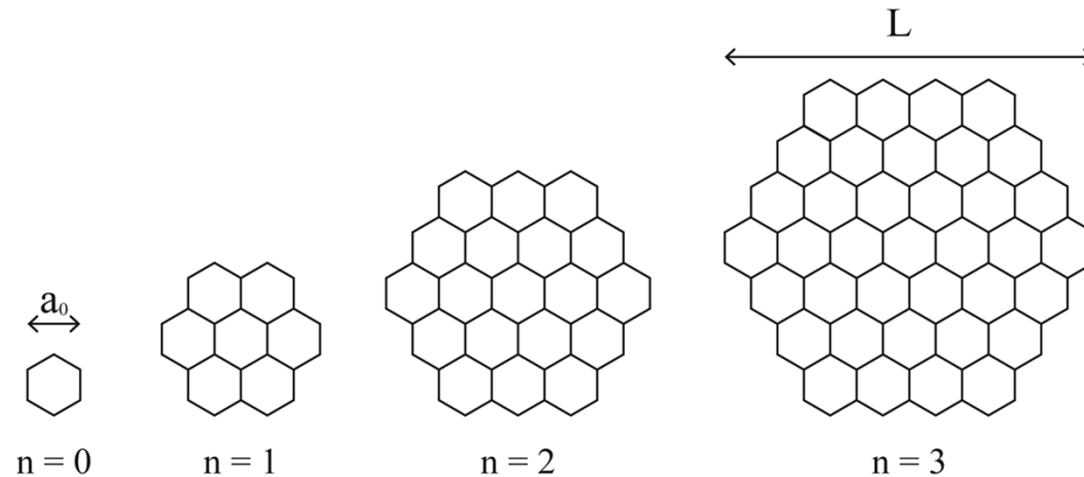
^[1] M. S. P. T. et al., *Carbon*, **44**, 252 (2006)

^[2] S. L. X. et al., *Carbon*, **44**, 300 (2006)

98)

1, 451(1964)

The trace amounts of edge sites in graphitized carbons can be estimated



$$N_{edge} = \text{free sites} + \text{hydrogen} + \text{carbonyl} + \text{ether} + 2 \cdot \text{anhydride} + 2 \cdot \text{lactone}$$

$$L = a_0(2n + 1) \cong \frac{2Ca_0}{N_{edge}} \quad (C \gg \text{other species})$$

Coronene-Base-Model

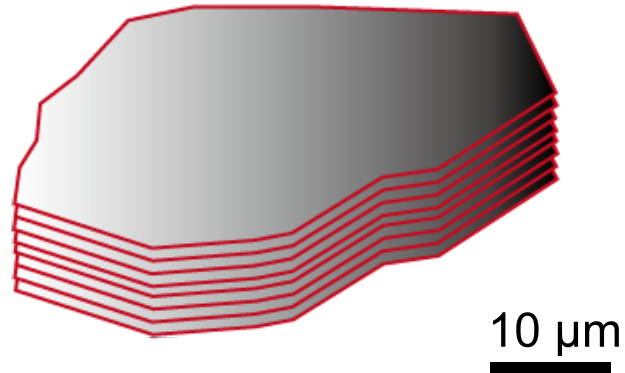
In the equations, N_{edge} , a_0 , *free sites*, *H*, *C*, *ether*, *carbonyl*, *anhydride* and *lactone* correspond to the total number of edge sites, the lattice parameter of a-axis (0.2461 nm), the numbers of free sites, hydrogen atoms, carbon atoms, ether, carbonyl, acid anhydride and lactone groups per unit weight of each carbon sample, respectively

Average Size of Graphene Sheets (L)

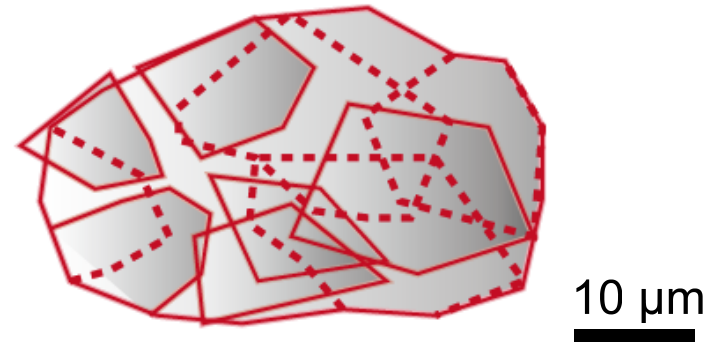
The amounts of total edge sites and the average sizes of graphene sheets (L) calculated based on the coronene-base-model

Sample	Total edge site N_{edge} [$\mu\text{mol/g}$]	L [μm]	particle size [μm]
NG(50)	0.62~0.74	55~66	↔ 50
NG(160)	0.15~0.20	207~271	↔ 160
SG(70)	0.40~0.46	89~102	↔ 70
SG(170)	0.22~0.26	160~184	↔ 170
GC24	1.12~1.15	36~37	500
GC28	0.89~0.91	45~46	600

- In the case of graphites,
 L correspond to their particle sizes.
→ There is no edge sites inside graphite's particles.
- In the case of coke carbons,
 L are smaller than their particle sizes.
→ Edge sites exist inside and outside their particles.



Graphite



Coke carbon (2400~2800 °C)

The schematic images of edge sites in carbon particles

Graphites: The edge sites exist only on the surfaces of the particles
Coke carbons: The edge sites exist inside and outside the particles

Our accurate analysis make it possible to investigate the edge sites of graphitized carbons

In this work, for analyzing the trace amounts of edge sites, highly sensitive TPD technique and carbon gasification apparatus are developed. These technique make it possible to quantify oxygen and hydrogen contents in carbon materials with remarkable accuracy.

Quantitative analyses of edge sites in graphitized carbons are carried out by means of our techniques. It was found from these results that the amounts and nature of edge sites in graphitized carbons are different from one sample to another.

Moreover, the average sizes of carbon layers in these carbons are estimated from the total number of edge sites. These analyses reveal that the actual sizes of graphite samples are essentially the same as their particle sizes. This structural information about highly developed carbons such as graphite has not been obtained so far, but only the present experimental techniques developed in this study make such analysis possible.