先端炭素材の調製と応用 II

1. 炭素ナノ繊維(Carbon nanofiber;CNF)の合成と構造
2. CNFの応用

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Characteristics of CNFs

Unique Properties

Problems

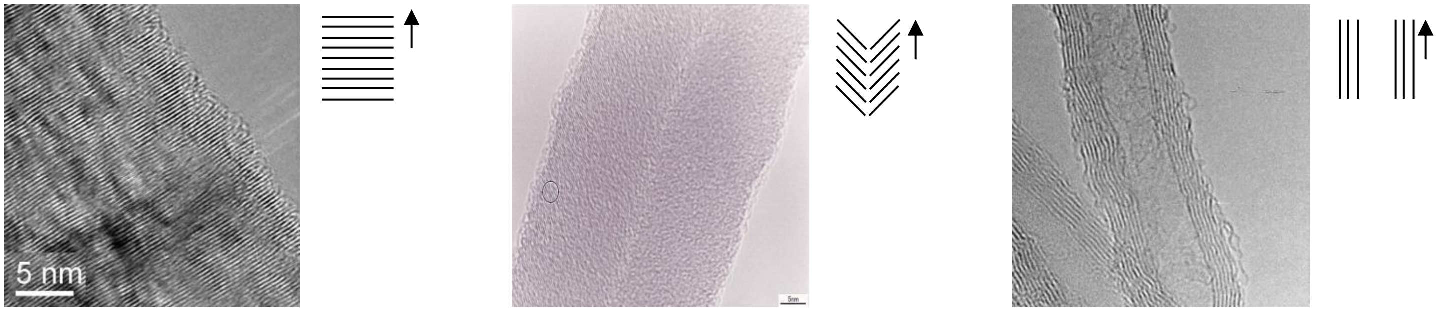
Carbon nanofiber：CNF

Fullerene	Zero dimension Basal surface Nano-size	High price Very limited application Mass-production (Frontier Carbon)
CNT	One dimension Basal surface Nano-size	Relatively high price Patent problems Mass-production Limited application
CNF	One dimension Various surfaces and structures Nano-size	Relatively low price Patent problems Mass-production Various applications Large diameter

Structural variety of CNFs

Typical classification of CNF Structure

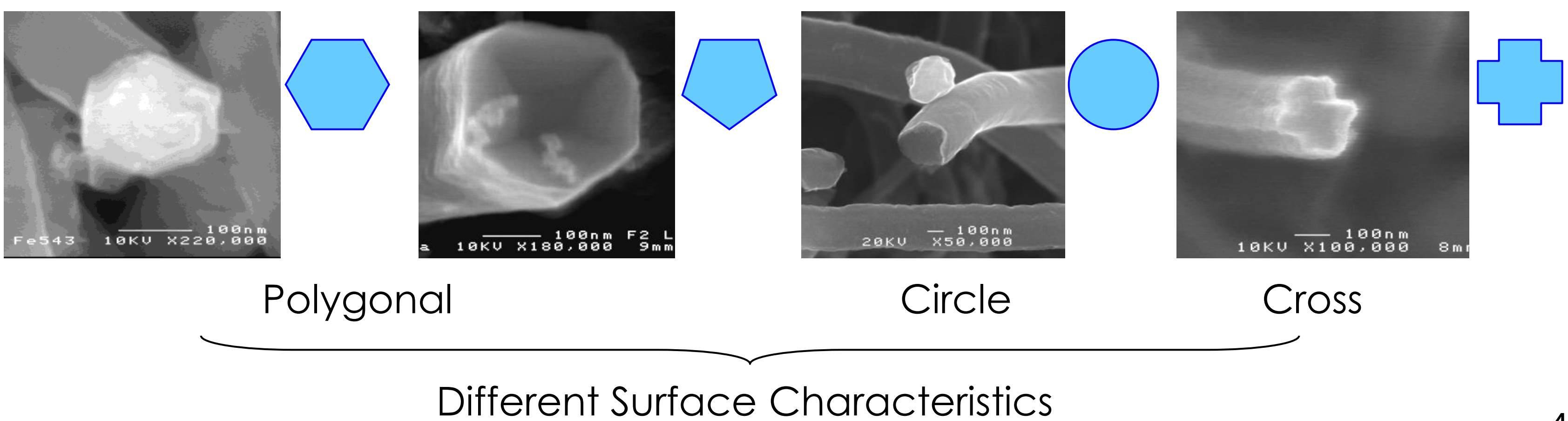
- graphene ((002) layers) alignment to the fiber axis, TEM observation



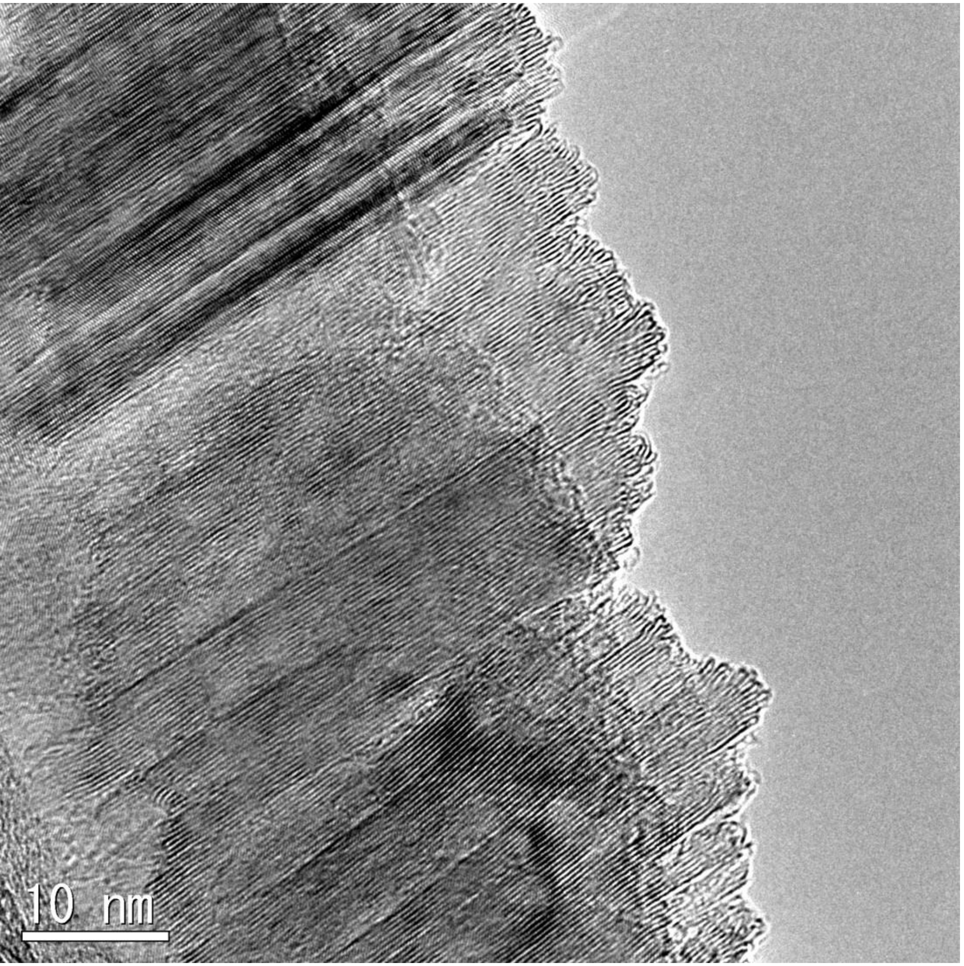
< Simple cases of CNF structure >

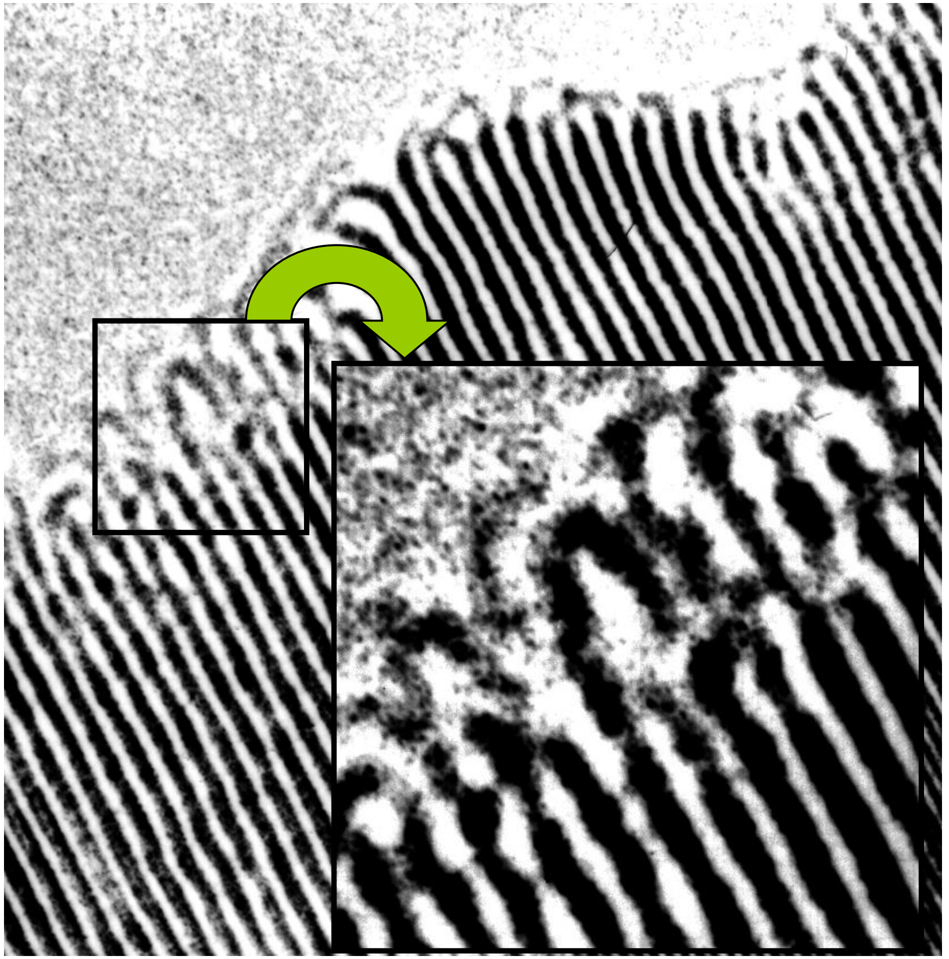
- However, complicated structure is often found.
- The morphological diversity confirmed simply by SEM observation cannot be neglected, considering possibly their different physical properties.

Various cross sections of CNFs

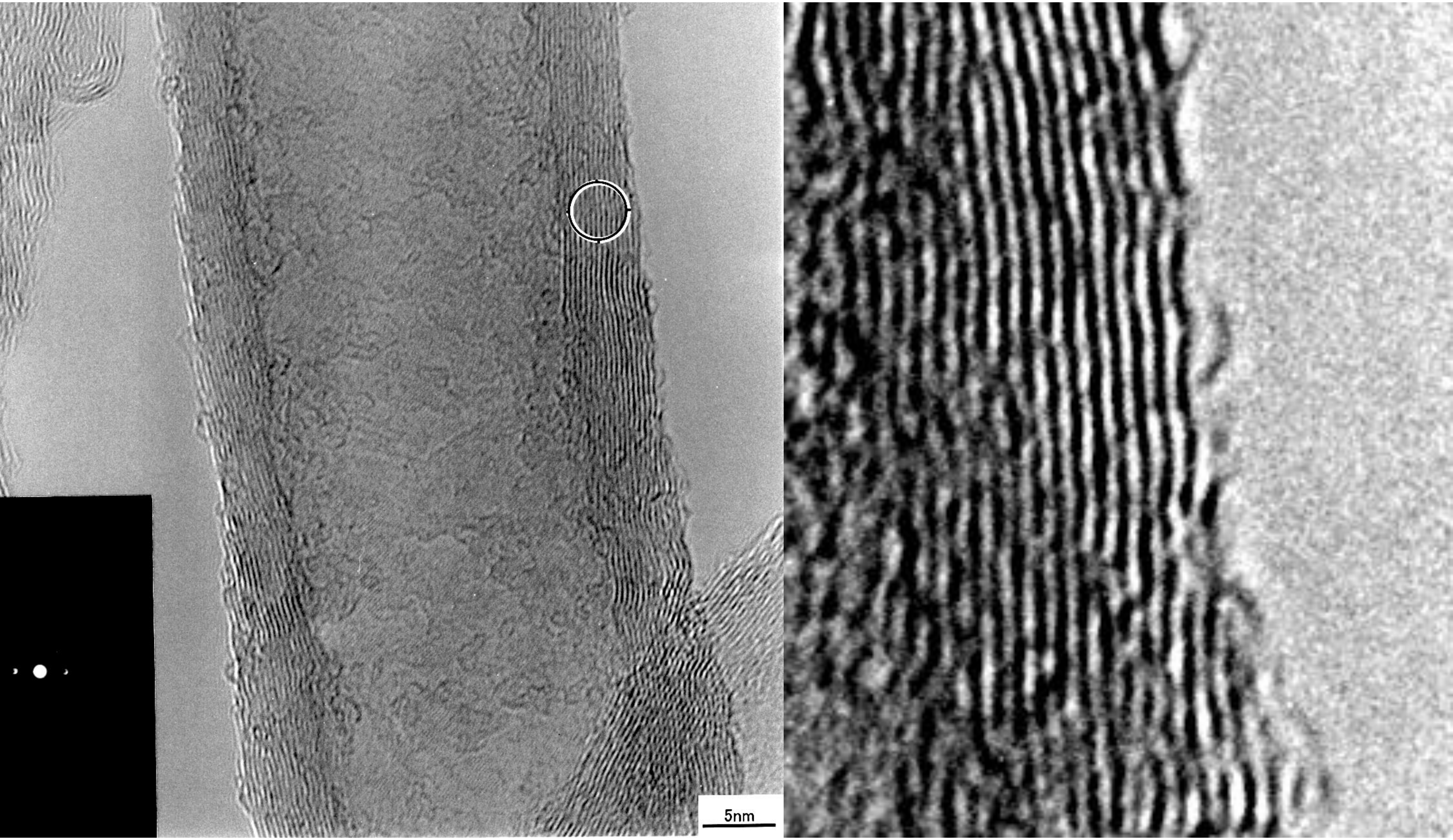


Surface of Platelet CNF

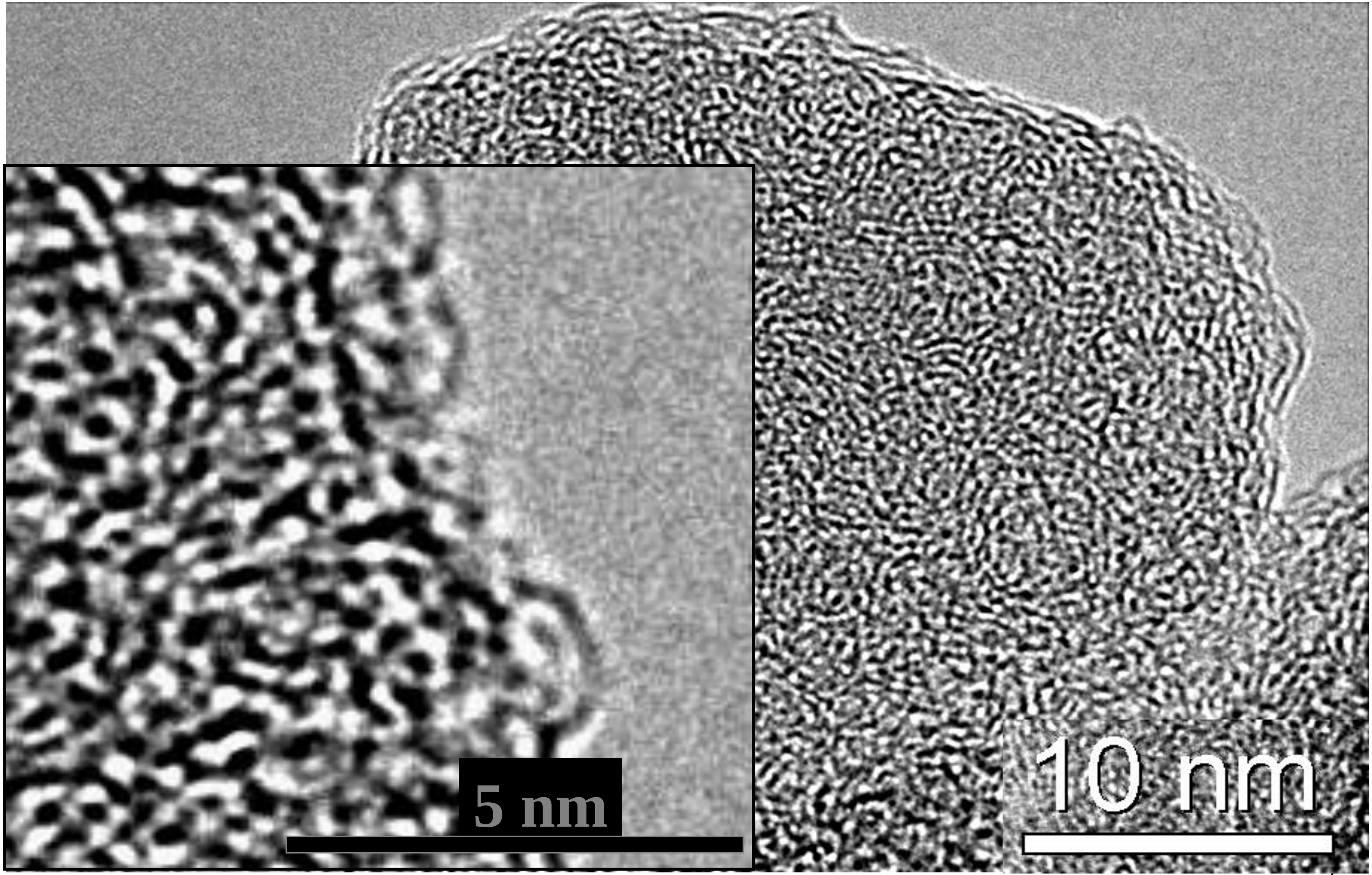




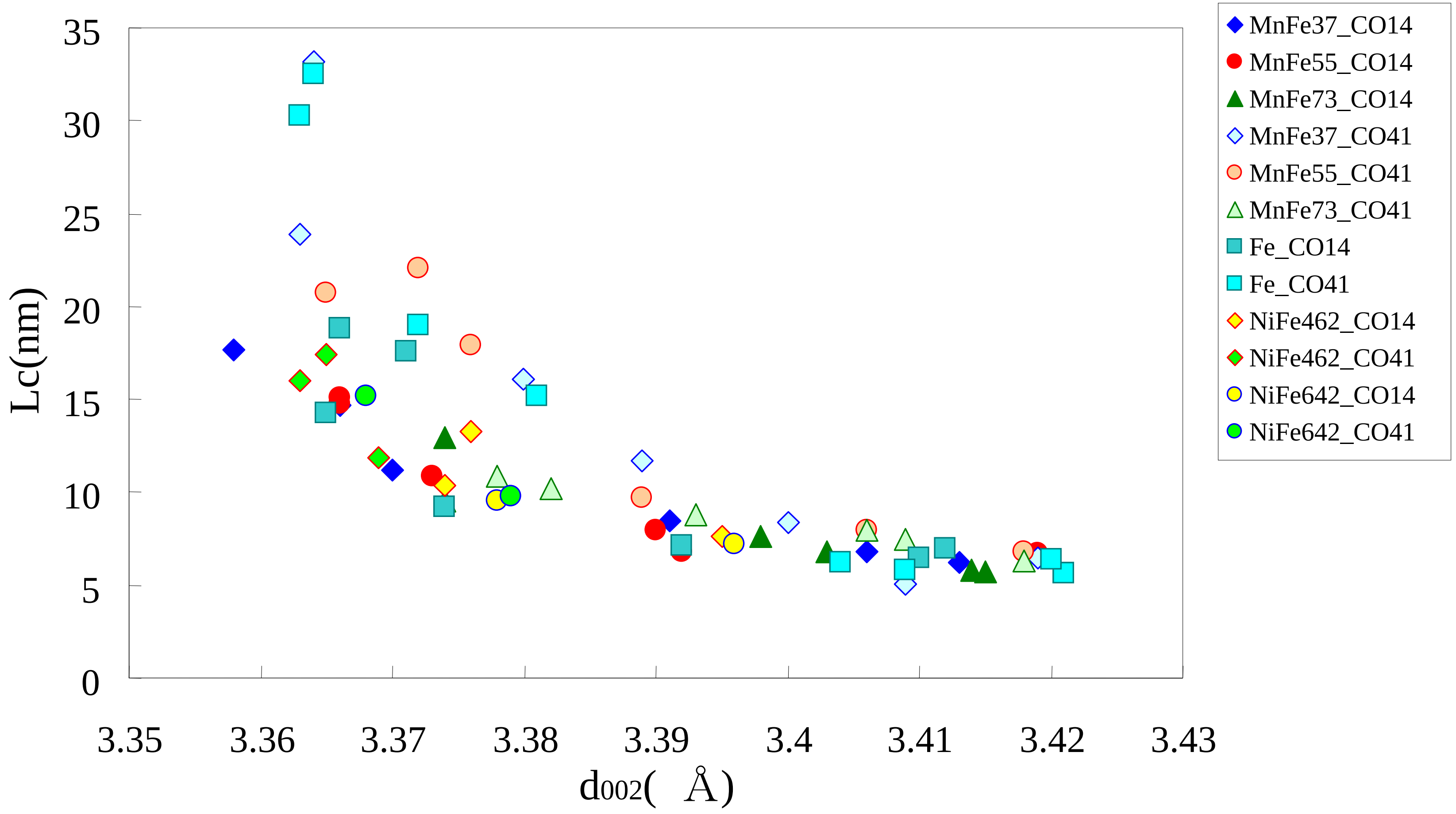
Surface of Platelet CNT



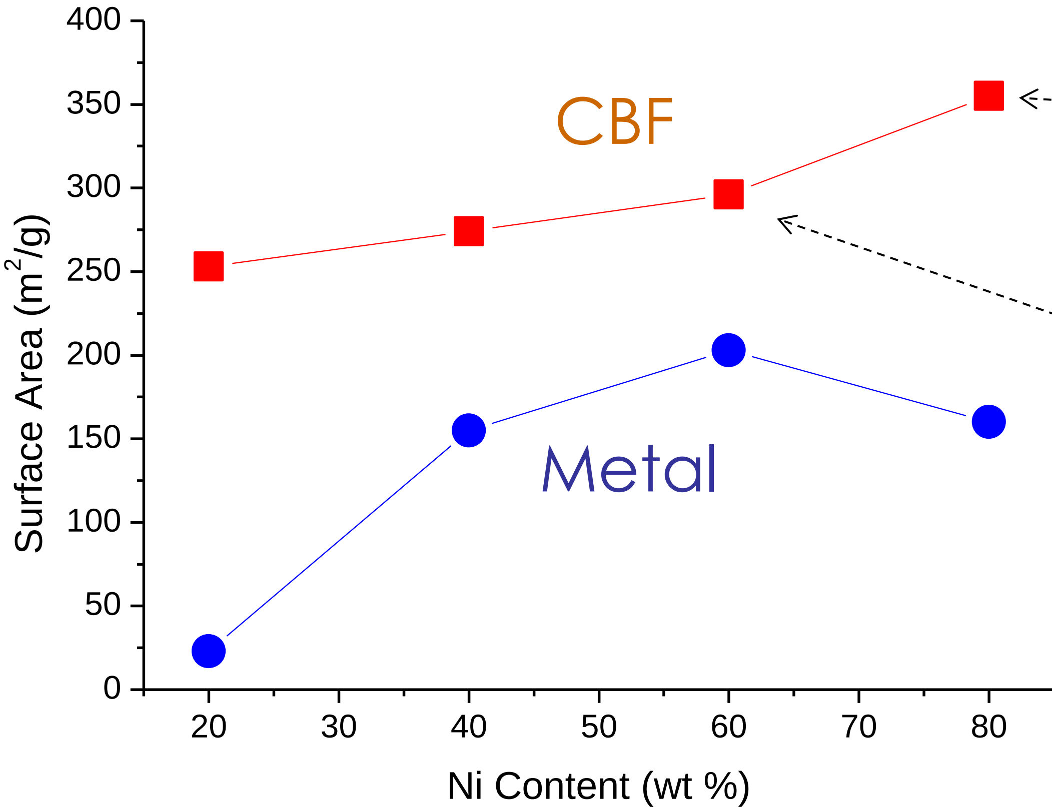
Surface of carbon blacks

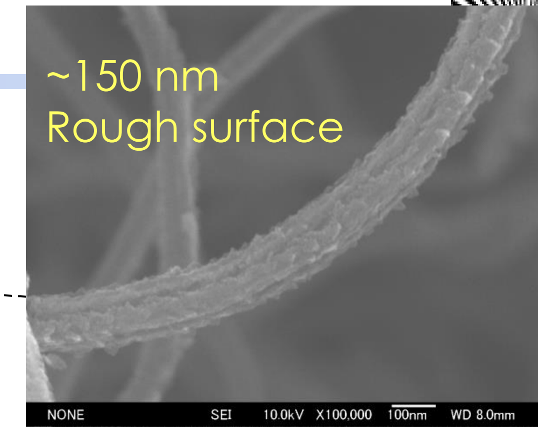


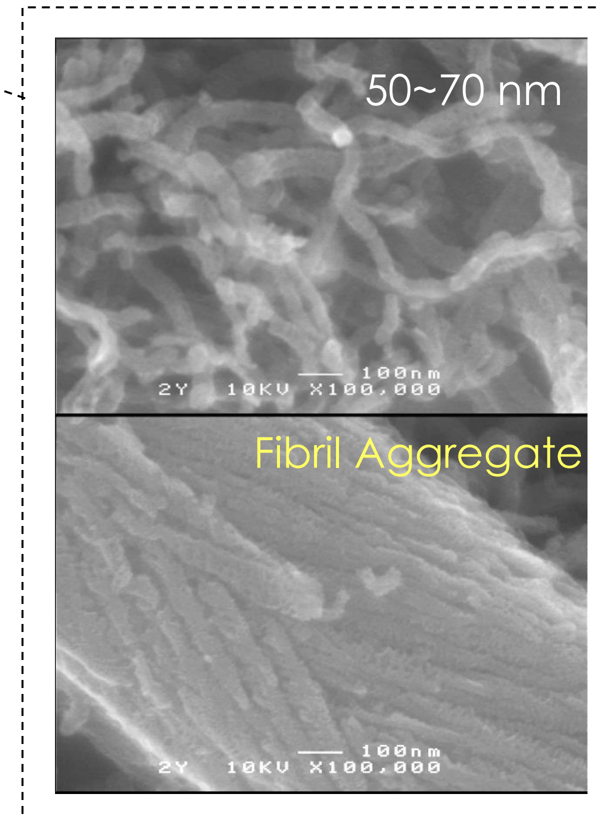
Control of Graphitic Properties of TCNFs



Control of surface area







- CBF fibers 250 ~ 350m^2/g, Metal fibers 20 ~ 200 m^2/g
- CBF fibers shows 2~10 times higher SA than Metal fibers.
- SEM of CBF fibers with SA around 300 m^2/g: small fibrils, fibril aggregate, and rough surface one like activated one.

Some problems of CNFs

1. **Patents** : Relatively free but some application patents should be considered.
2. **Price** : ~10~200 $ /kg
   - Effective process for mass-production
3. **Dimension & Uniformity control**
   - Diameter
   - Surface control; edge / functional groups
   - Linearity
   - Crystallinity, surface area
4. **Useful skills : Purification, Dispersion**

Objective of this study

Backgrounds of Objectives:

Functional revolution of CNFs Based on the Carbon Nanotechnology

- CNFs
- CNF functional composites
- CNF supports
- CNF catalysts

- Basic study
- Selective preparation
- Modification
- Composition

Applications

Commercialization

- Fuel Cell Catalysts
- Anodic Materials for LIB
- Electrode of capacitors
- Reduction and Oxidation Catalysts for Green Chemistry
- Air Purification
- Refactory、FED, Nano-fluid

Synthesis of CNF

CNFs

CNFs related syntheses

Selective Preparation of CNFs

Standard CNFs

PCNF, HCNF, TCNF
Accordion CNF

Target optimized CNFs

Small CNF,
High SA CNF,
High Graphitic CNF
High Dispersable CNF
N-doped CNF

CNF functional composites

CNF-Si, SiO, TiSi
CNF-NG、CB
CNF-SiO_2, CNF-MgO

Metal & Metal Oxide Nano-chain

Fe_3O_4, MoO_2 nanochain
SiO_2, SiC nanofibers
Pt, PtRu, Pd, Au nanochain

Mass Production of CNF

Batch process

Pressurized Process

CNFs from Waste Gases

Structural Modifications

Mesoporous CNFs

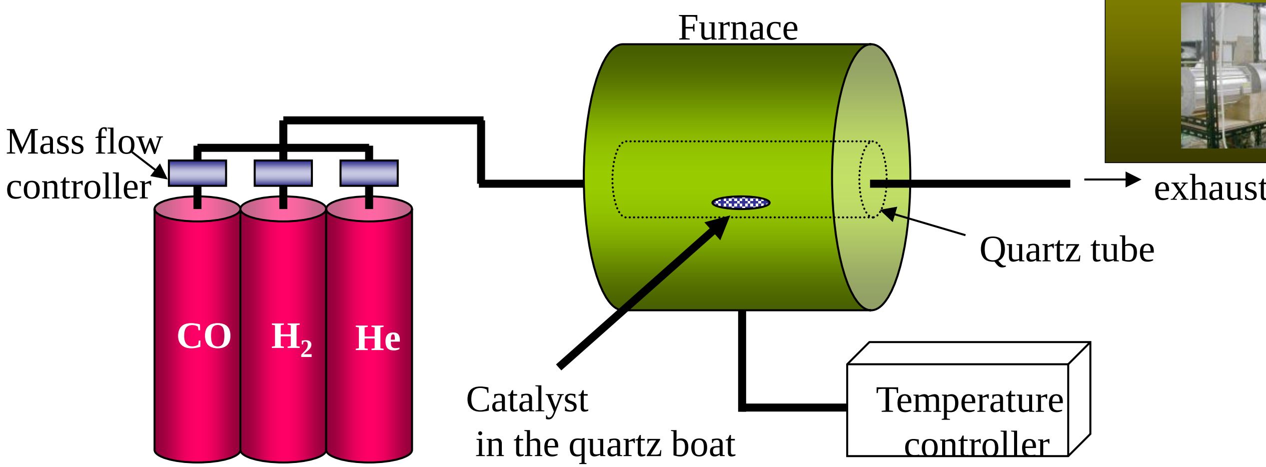
Activation

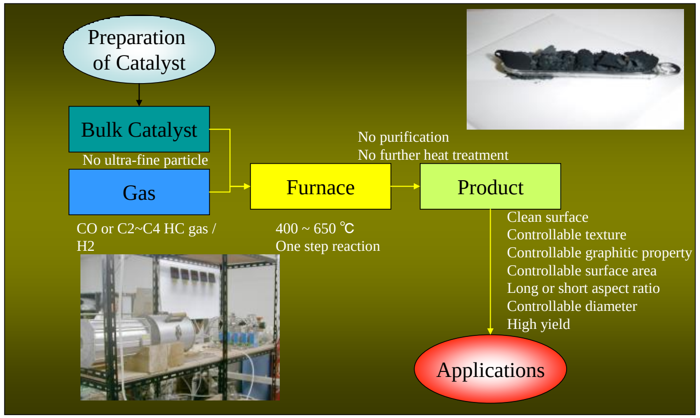
Electric oxidation

Electro-spun CNF

Indoor polutions
Dilute NOx
De-metal, De-particulation

Preparation (Fixed Bed Method)





Catalyst : Transition metals, Their alloys or supported catalyst

Catalyst preparation method : co-precipitation

1) Best, R. J. and Russell, W. W., J. Amer. Soc. 76, 838(1954)

2) Sinfelt, J. H., Carter, J. L. , and Yates, D. J. C., J. Catal. 24, 283(1972)

Reduction : H_2/He(1/9, 200sccm//4.5 cm diameter tubular furnace, 2h

Reaction : CO/H_2 (4/1 & 1/4v/v%), 200 sccm// 4.5 cm diameter tubular furnace

Reaction Time & temperature : 1 h, 540 ～ 675 ℃

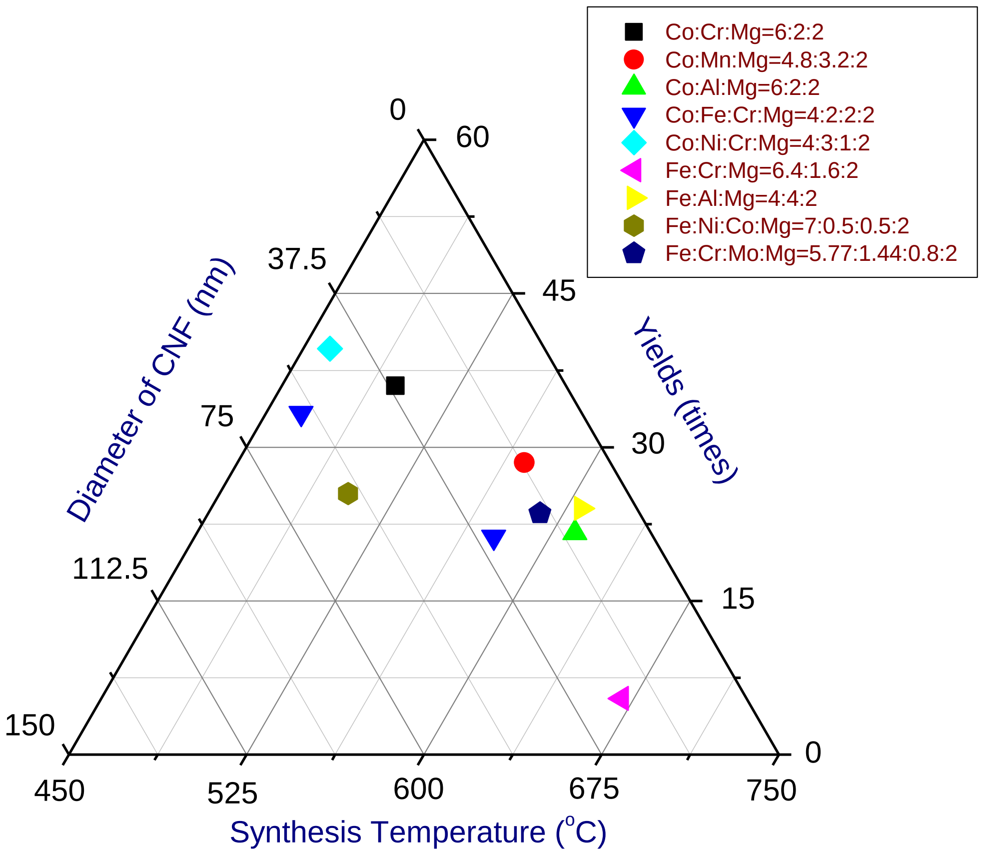
Catalysts for CNF Preparation

- Mono-metal
  - Fe, Co, Ni
  - Fe, Co, Ni / Supports
- Support: Alumina, Silica >>> MgO
- Bimetallic Catalyst
  - Fe, Co, Ni / Fe, Ni, Mn, Cu, …/Supports
- Trimetallic Catalyst
  - Fe, Co, Ni / Fe, Ni, Cu, Mn / Cr, Al, …/Supports

Functions of Second or Third Metals ?

Main Catalyst	2nd Catalyst	3rd Catalyst
Fe Fe:Mg=8:2 収率: 1.2倍	Cr Fe:Cr:Mg=6.4:1.6:2 収率：4.6倍 繊径：40nm Tubular	Mo Fe:Cr:Mo:Mg=6:1:1:2 収率：27.8倍 繊径：20nm Tubular
	Mn Fe:Mn:Mg=6:2:2 収率：1.1倍	Co Fe:Mn:Co:Mg=4:2:2:2 収率：11.6倍 繊径：50nm 不均一 CNF
	Cu Fe:Cu:Mg=6:2:2 収率：2.0倍	Co Fe:Cu:Co:Mg=6:1:1:2 収率：60.2倍 繊径：180nm Herringbone CNF
	Ni	Co Fe:Ni:Co:Mg=7:0.5:0.5:2 収率：60.2倍 繊径：120nm Tubular

Tri Metallic Catalysts



研究結果

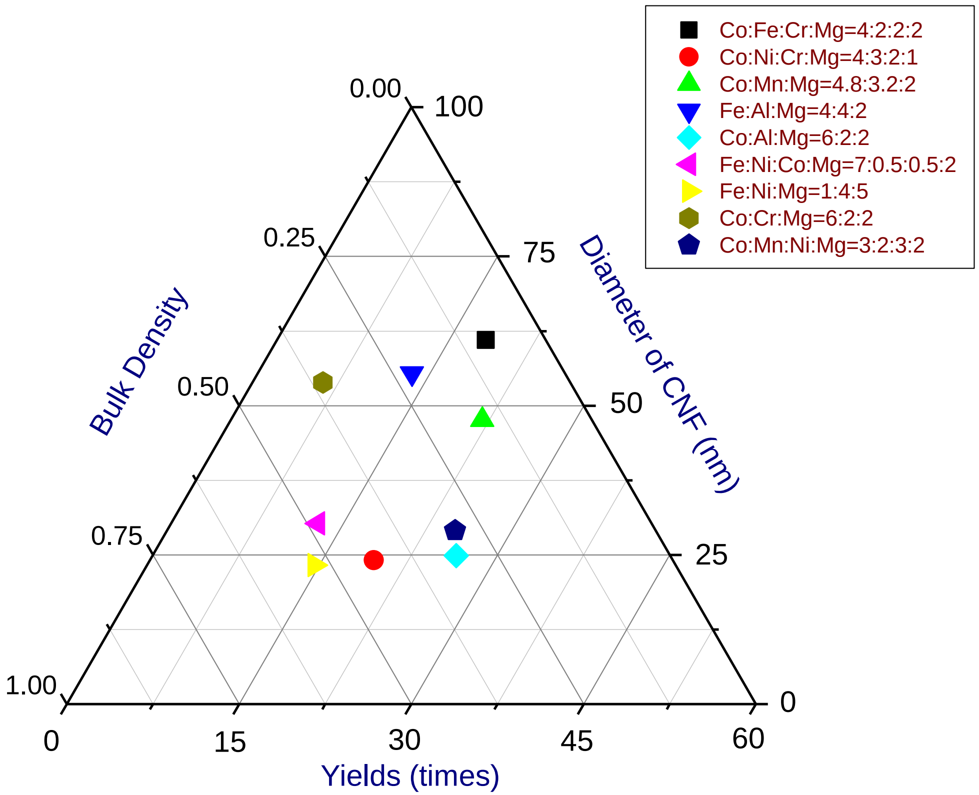
収率, 繊径, 繊維構造などに影響を与えることができる Cr, Mn, Al などの新しい補助触媒の発掘

1. Co 主触媒に対する補助触媒の効果
 − Cr 補助触媒は低い合成温度で高い触媒収率を見せて，合成温度が低くなるによって Herringbone 構造の繊維が合成される.
− Mn 及び Al 補助触媒は高い合成温度で高い触媒収率を見せて, 大部分 Tubular 構造の繊維が合成される.

2. Fe 主株触媒に対する補助触媒の効果
− Cr 及び Al 補助触媒皆合成温度が高いほど触媒収率が増加する傾向を見せて Tubular 構造の繊維が合成される.
− Cr 補助触媒の場合には触媒収率が非常に低いが一方見掛密度が非常に低い繊維が合成される.
− Cr 及び Mo 補助触媒を一緒に使う場合には 30倍以上の非常に高い触媒収率を得ることができる.

3. FeNiCoMg 触媒
− 最大繊径 120nm 程度の非常に太い Tubular 繊維を合成する触媒システム.
− Niと Coの含量がそれぞれ 0.5で等しい場合に一番高い触媒収率及び一番均一な繊維を得ることができる.

Tri Metallic Catalysts



* 모든 CNF의 합성온도는 700℃임.
(Co:Ni:Cr:Mg=4:3:1:2, Fe:Ni:Mg=1:4:5 촉매는 600℃에서 합성한 결과임)

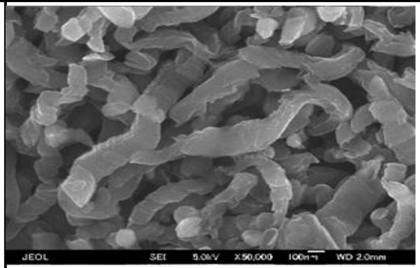
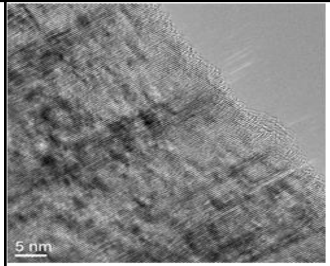
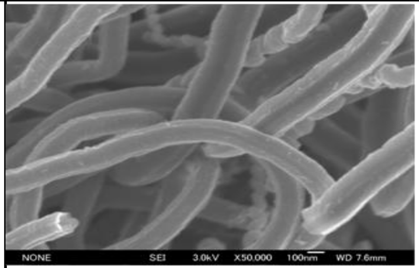
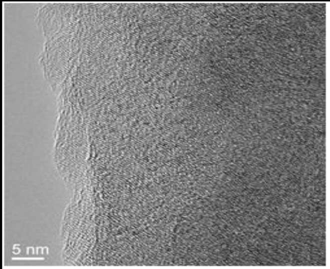
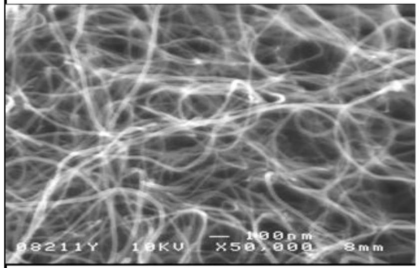
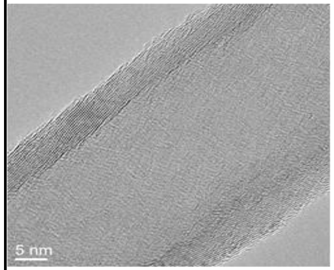
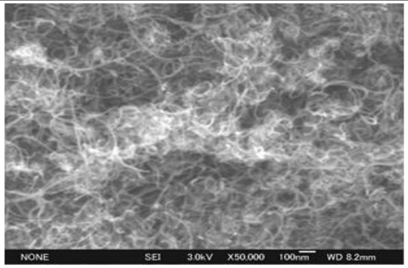
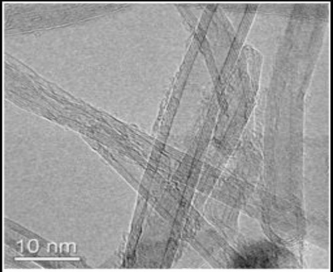
❑研究結果

経済的に有利なC3H8 ガスを利用して C2H4 ガス　より少し高い温度で CNFを合成

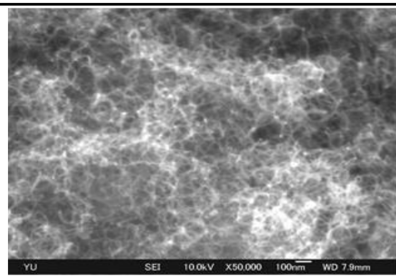
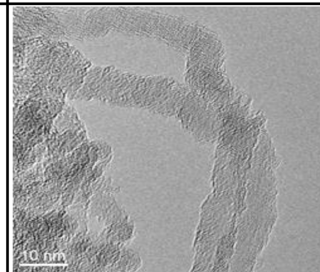
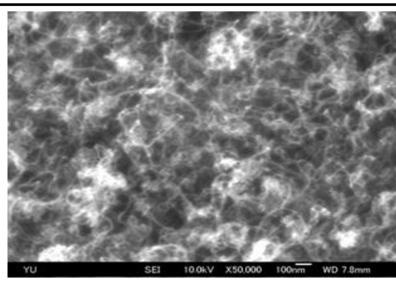
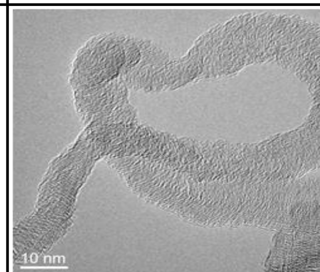
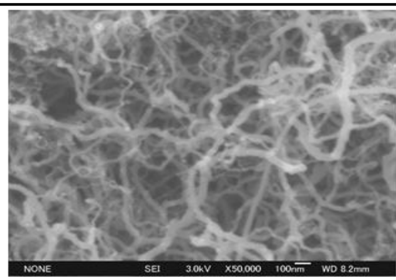
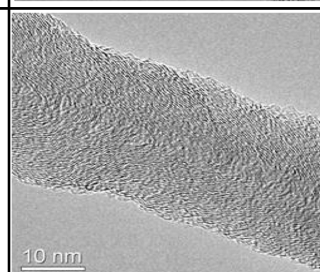
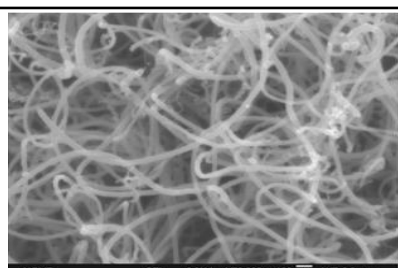
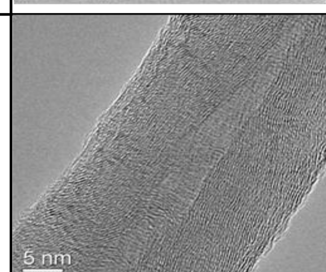
1. 主触媒に対する補助触媒の効果
- Cr 補助触媒は低い合成温度で高い触媒収率を見せて, Mn 及び Al 補助触媒は高い合成温度で高い触媒収率を見せる.
- ほとんどすべての触媒組成で Tubular 構造の繊維が合成される.

2. FeNiCoMg 触媒
- C2H4 ガスを利用して合成した場合とは全然違った素材が得られる.
- 50nm 程度の繊維も観察されたがほとんど大部分が繊維形態がカーボン固まり状であり、見掛密度も非常に高い.

Standard CNFs

Sample #	SEM	TEM	Properties	Applications	Etc.
KNF-SPR **Platelet** **Nano-rod**			Platelet high grapht. deg. 80 ~ 400 nm, SA 90 m^2/g d_{002} 3.36Å, Lc(002) 30 nm	電池材料, 触媒担体, 触媒担体 例)　高活性水素化触媒Ru/PCNF	70 g/日
KNF-SH **Herring-bone**			Herringbone high surface area 70 ~ 500 nm, SA 150 m^2/g d_{002} 3.45Å, Lc(002) 3 nm	複合材料, ガス貯蔵, 吸着剤,触媒担体, FED 例)DMFC用PtRu触媒担体	100 g/日
KNF-ST **Tubular** **高黒鉛化性**			Tubular thin walls, open tips high grapht.deg. 20 ~ 50 nm, SA 90 m^2/g d_{002} 3.37Å, Lc(002) 13 nm	複合材料, 吸着剤, 触媒担体, 触媒	20 g/日
KNF-FM **Tubular** **小繊径**			tubular, hollow 5~15 nm, 4 -7 walls	複合材料、触媒担体、FED	20 g/日

CNF (Small & Middle Diameters)

Sample #	SEM	TEM	Properties	Applications	Product
KNF-CM 小繊径 高分散			**Herringbone,** **hollow** **7 ~ 20 nm**	複合材料、吸着剤、 触媒担体、FED	**20-30 g/日**
KNF-CC 小繊径			**Herringbone** **7 ~ 15 nm**	複合材料、吸着剤、 触媒担体、FED	**15-20 g/日**
KNF-NM 中繊径			**Herringbone** **10~60 nm (30~40)**	複合材料、吸着剤、 触媒担体	**50-70 g/日**
KNF-NF 中繊径 直線性			**Herringbone** **20 ~ 50 nm** **Straightness**	複合材料、吸着剤、 触媒担体	**50-70g/日**

Highly graphitic CNFs

- CNF of similar graphitic properties with Natural Graphite
- CNT usually shows low graphitic properties
- Conductive materials or supports for heterogeneous catalysts

GPCNF-N

PCNF, HCNF

↓ 黒鉛化

GPCNF

↓ 硝酸処理

G-PCNF-N

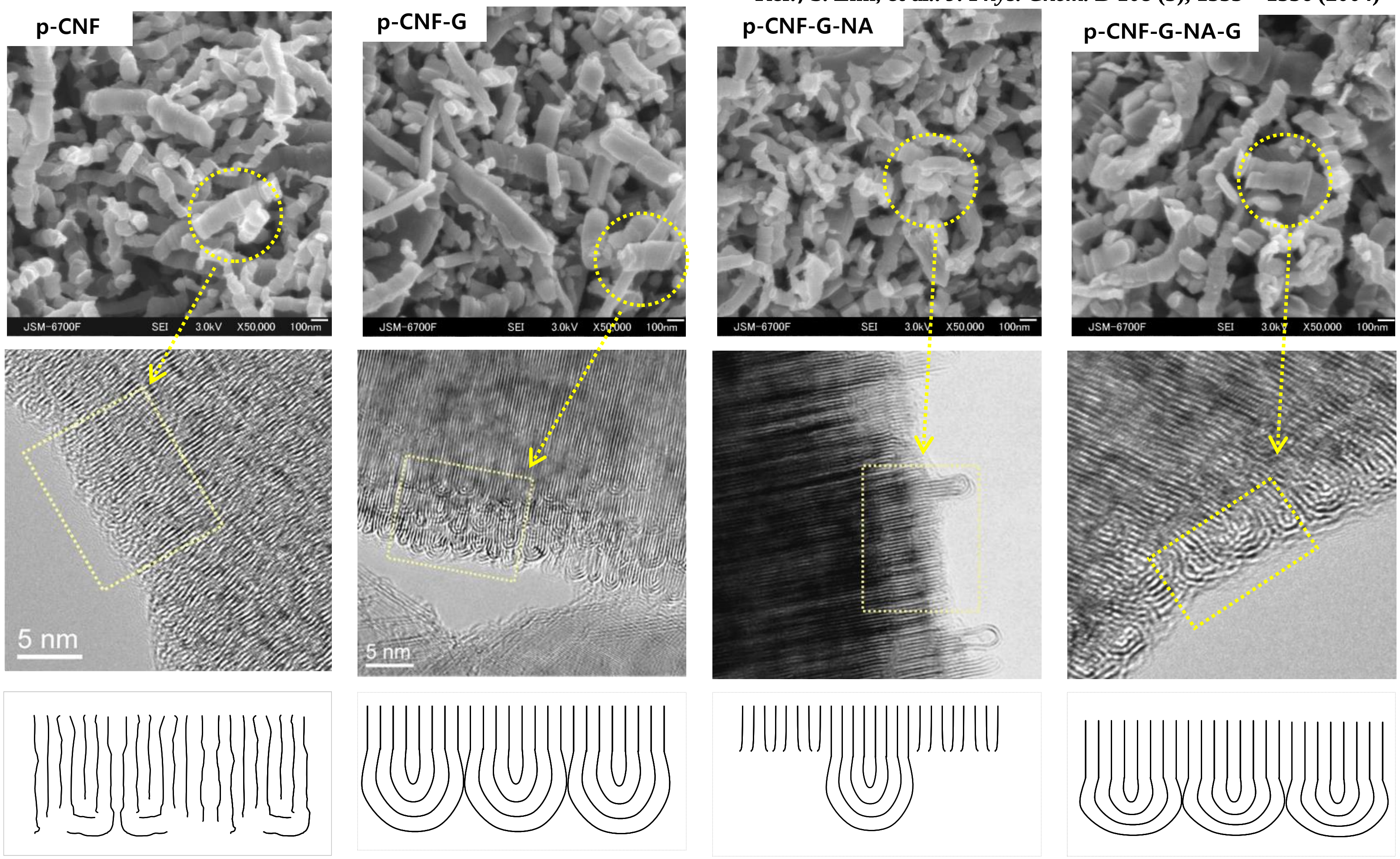
↓ B黒鉛化

BA-GGPCNF-N

	Preparation conditions	d_{002} (nm)	Lc(002) (nm)
PCNF	Fe catalyst, 620, CO/H2 : 4/1	0.3365	72
G-PCNF	2800℃ heat treatment of PCNF	0.3364	83
G-PCNF-N	30% HNO3 treatment of GPCNF for 50℃, 8hs	0.3362	152
GG-PCNF-N	2800℃ heat treatment of GPCNFN	0.3362	106
BA-G-PCNF	Boric acid added heat treatment of PCNF	0.3359	115
BA-GG-PCNF-N	30% HNO3 treatment of GPCNF for 50℃, 8hs Boric acid added heat treatment	0.3357	377
BC-G-PCNF	Boron carbide added heat treatment of PCNF	0.3354	178
BC-GG-PCNF-N	30% HNO3 treatment of GPCNF for 50℃, 8hs Boron carbide added heat treatment	0.3354	167

Surfaces of PCNF

Ref.) S. Lim, et al.. *J. Phys. Chem. B* 108 (5), 1533 – 1536 (2004)

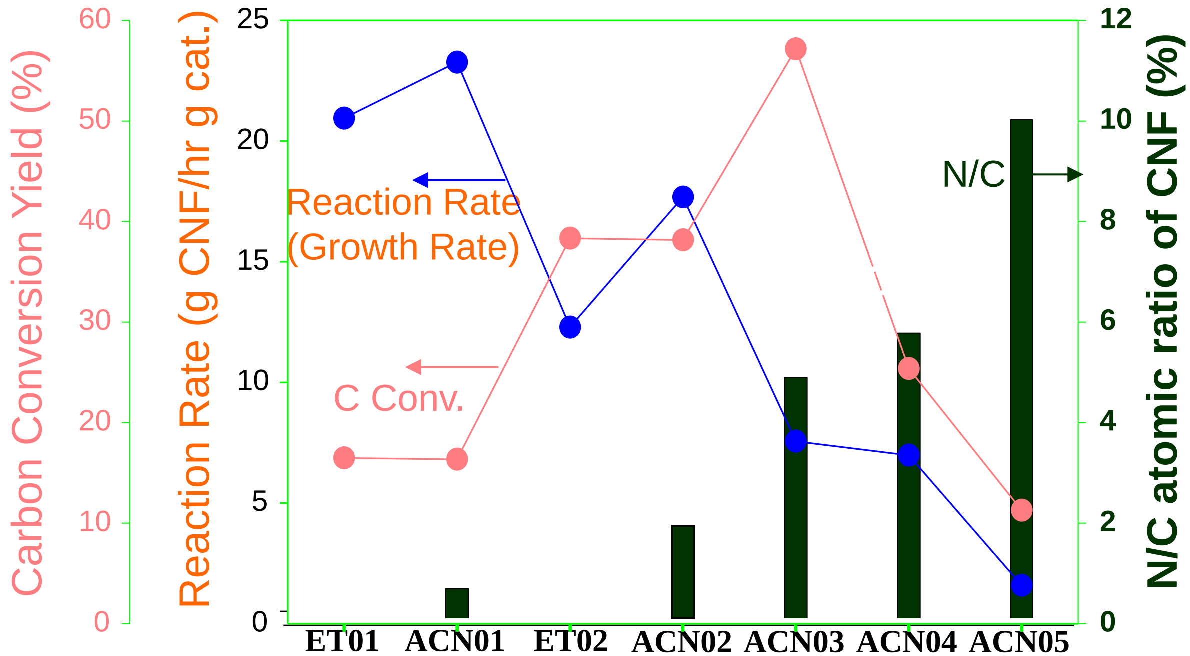


According to the graphitization degree,
we found some difference at edge plane by TEM analysis

N-doped CNFs

N-Source
: Acetonitrile

Reaction Temp.
530°C



Ethylene	ml/m (*g*)	**160**	**160**	**40**	**40**	**0**	**0**	**0**	Total 200 ml/m
Hydrogen		**40**	**40**	**40**	**40**	**40**	**40**	**0**	
He		**0**	**0**	**120**	**120**	**160**	**160**	**200**	
Acetonitrile (*liq.*)	μl/m	**0**	**35**	**0**	**35**	**35**	**70**	**35**	
Input N/C	at.%	0	4.6	0	14.5	50	50	50	

Preparation of N-doped CNFs

A. Direct Synthesis of Carbon Nanofibers with Nitrogen (the method of this study)

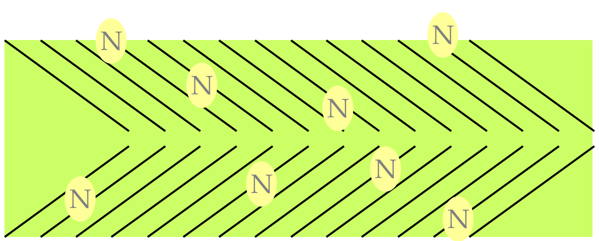
B. Deposition of Nitrogen Components on Carbon Nanofibers (Post-synthesis)

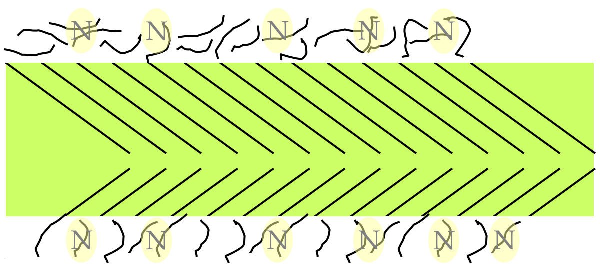
- Using Carbon Sources Containing Corresponding Heteroatoms
- Mixing General Carbon Sources with a Nitrogen Source (NH3)

Expected features

Route A	Route B
• One step synthesis	• Two step synthesis
• Graphitic structure	• Amorphous region at the surface (probably unstable)
• N both in-plane and at the surface (edge)	• N selectively at the surface (edge)

Direct Synthesis





Coating

Post-Doping

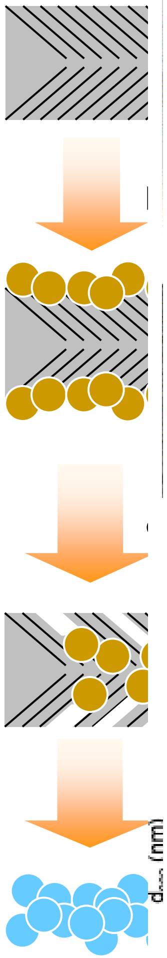
Nano-Chains

Synthesis of Magnetite Nanoparticle-Chain

Ref.) S.Y. Lim, et al. *Carbon 2006: International Conference on Carbon, Robert Gordon College, Scotland (2006)*

- Syn

Ca



Metal

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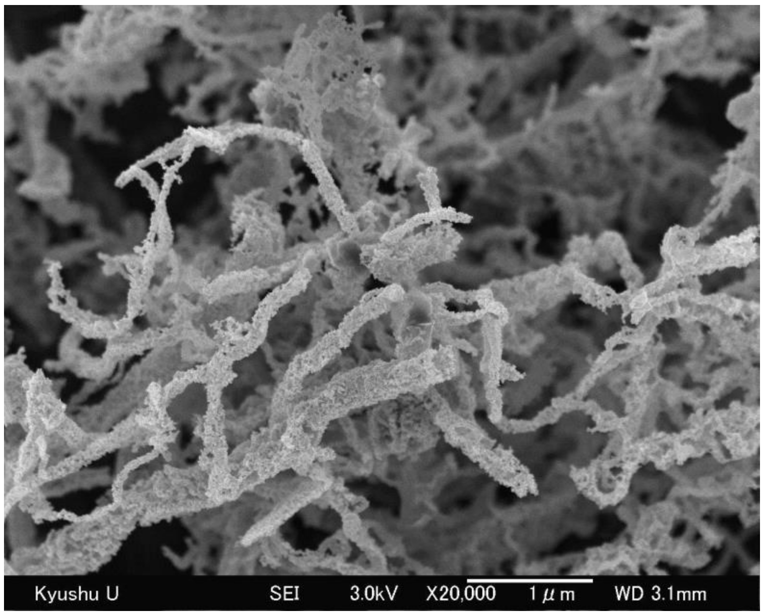
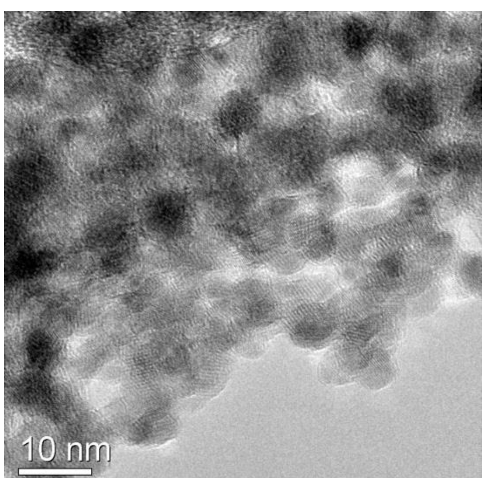
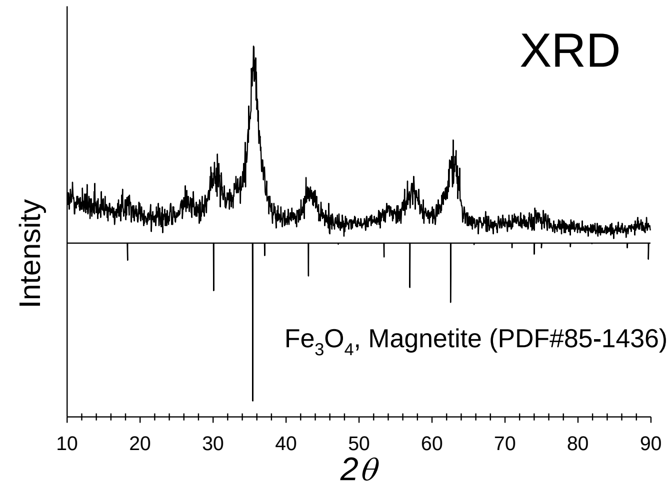
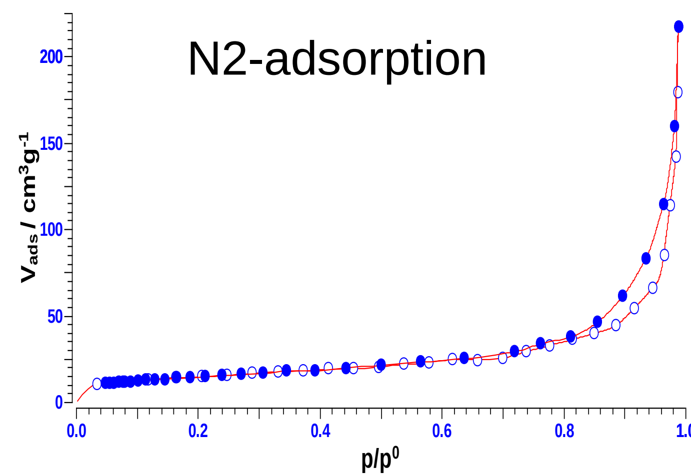




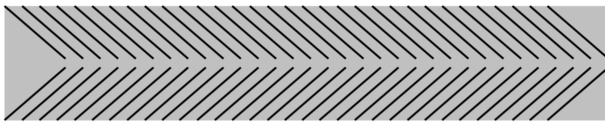


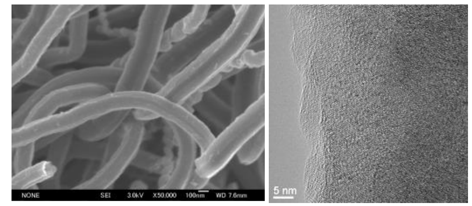


Schematic Procedure of SiO2 NF

- Synthesis of SiOx Nano-fibers Using CNF as a template

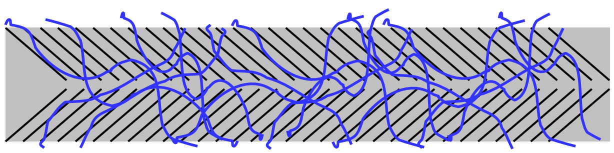
Carbon Nano-fiber

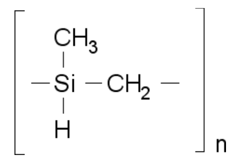




- CNF: Herringbone
- 150 nm dia.
- Some coiled

Coating with Polysilane



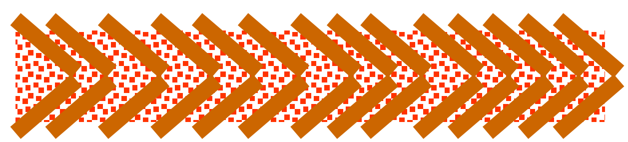


Polycarbomethylsilane (Aldrich)
- average Mw ~800, electronic grade
- mp 79-84 °C
- density 1.1 g/mL at 25 °C(lit.)
- Sol. in Toluene, partly sol. in acetone

Oxidation under Prescribed Conditions

Metal Oxide Nano-tubes

or



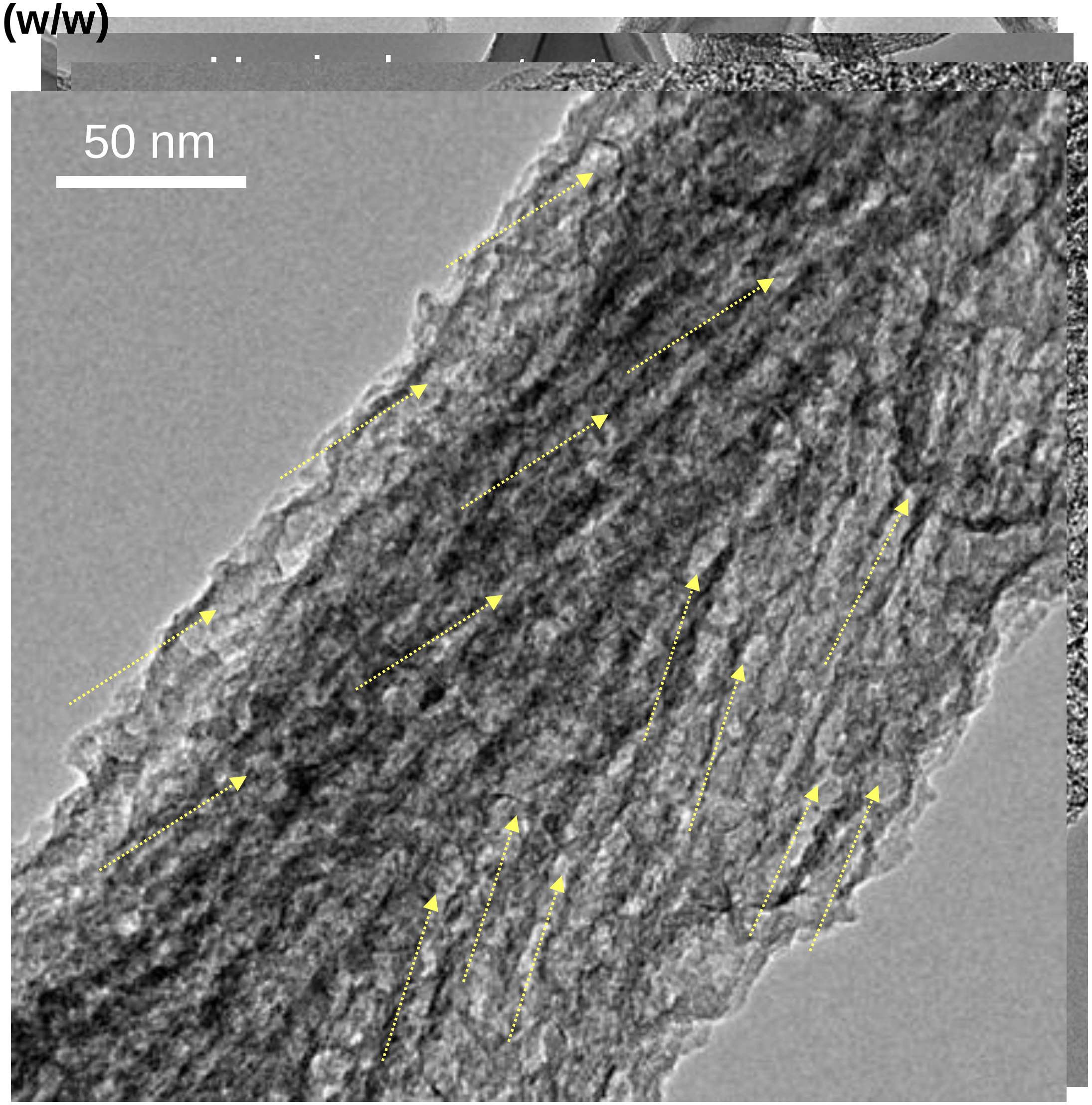
Metal Oxide Nano-fibers

Highly-porous Nano-fibers

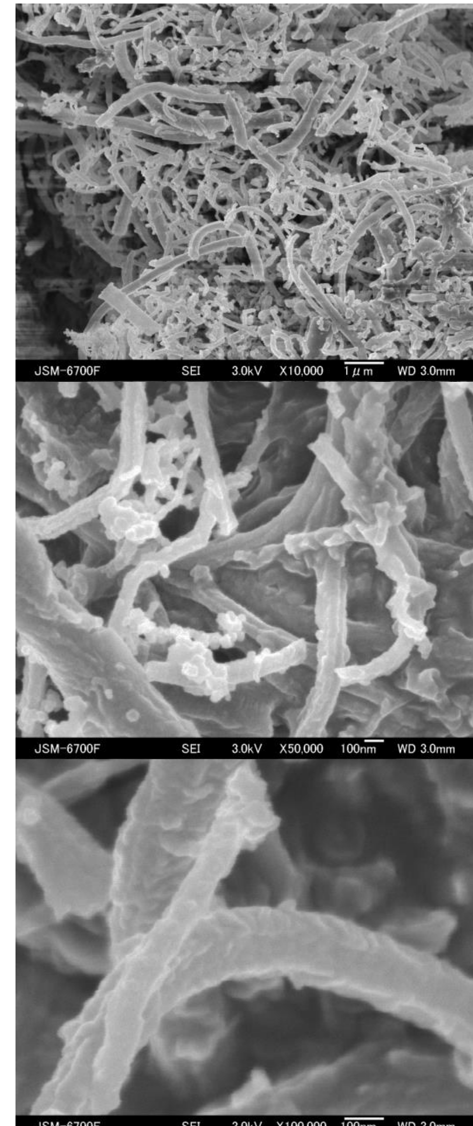
TEM & SEM of SiOx NFs

- **PS in Toluene**
  * completely soluble
- **PS/HCNF 1/5 (w/w)**
- **450ºC in Air**

TEM of SiOx-NF

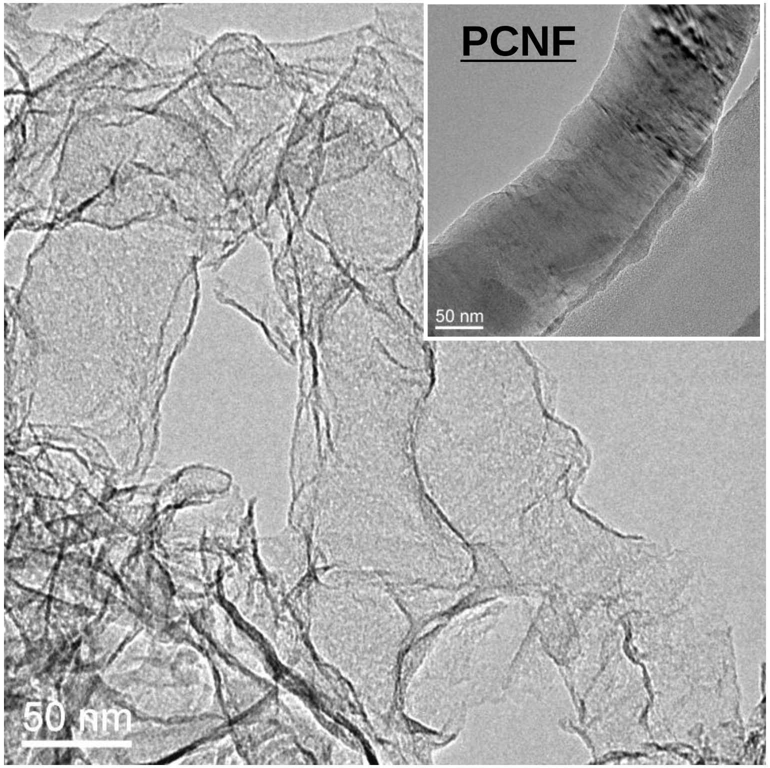


SEM of SiOx-NF

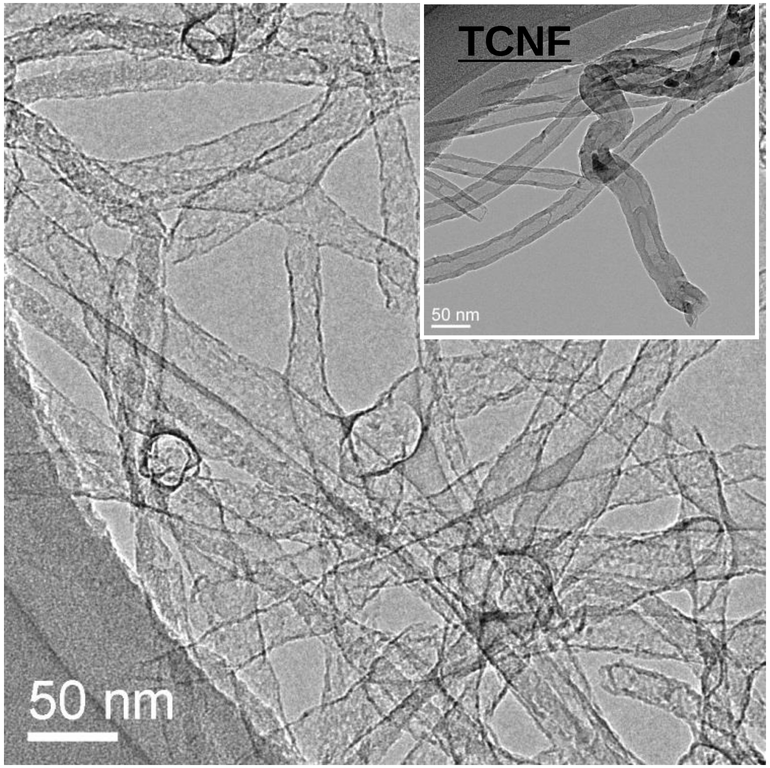


Various SiOx NFs

TEM of SiOx-NF using PCNF



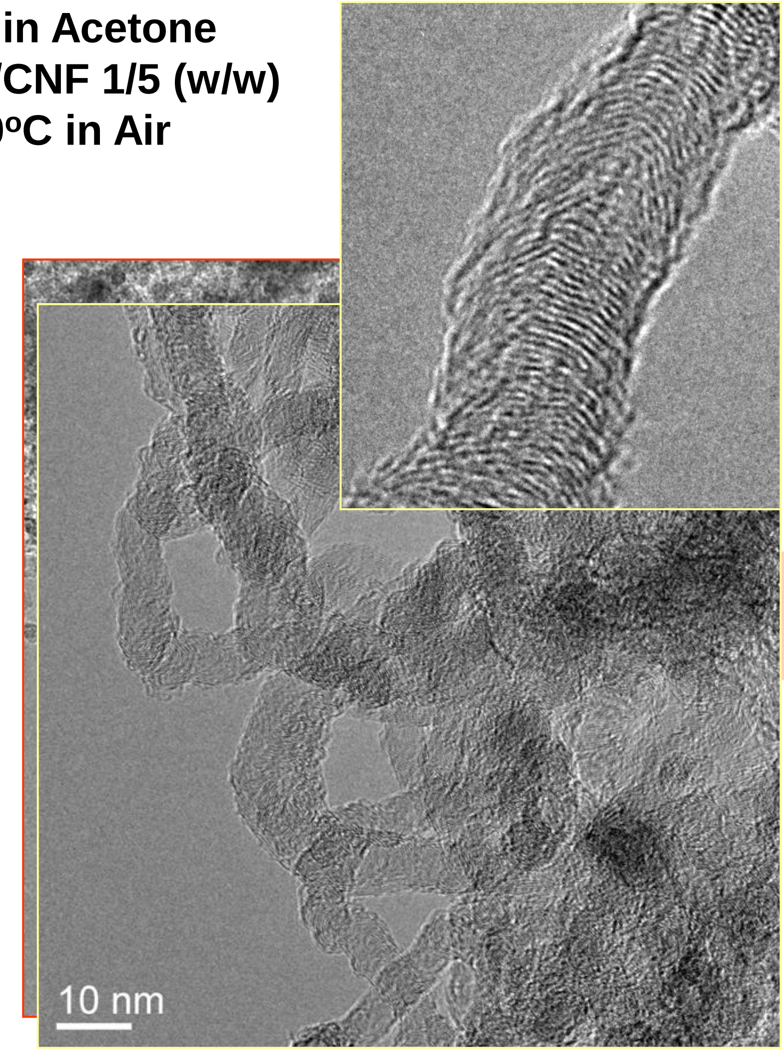
TEM of SiOx-NF using TCNF



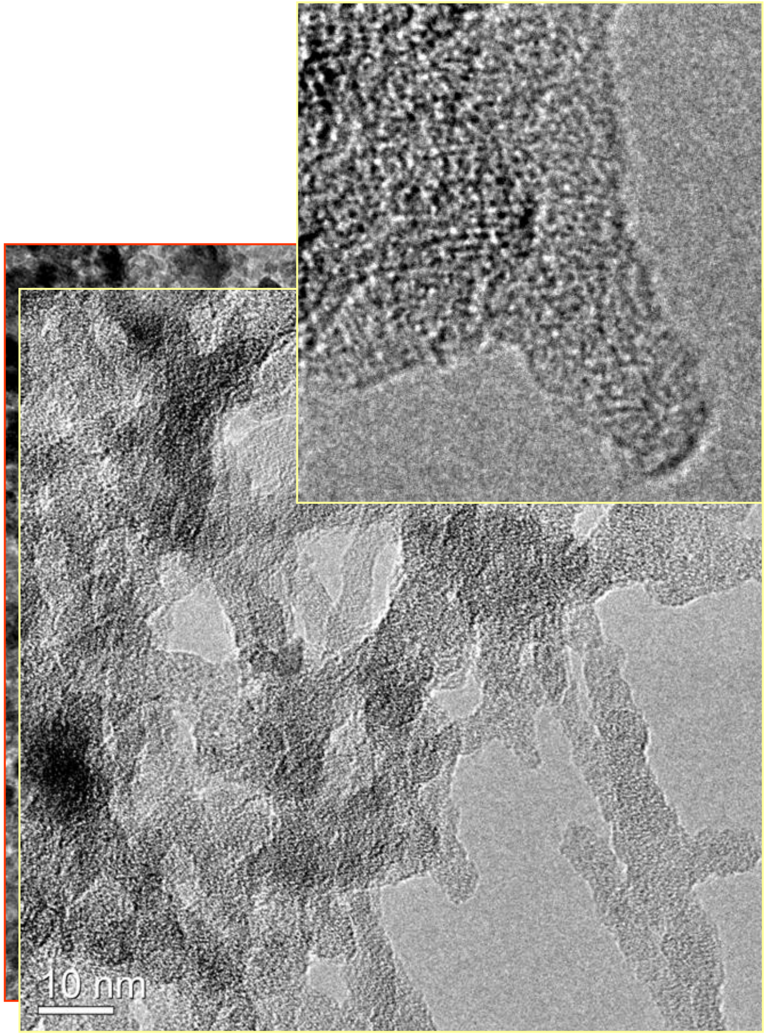
SiOx NF Using Thin CNF

• Thin CNF (~20 nm dia.)

- PS in Acetone
- PS/CNF 1/5 (w/w)
- 450°C in Air



Thin CNF

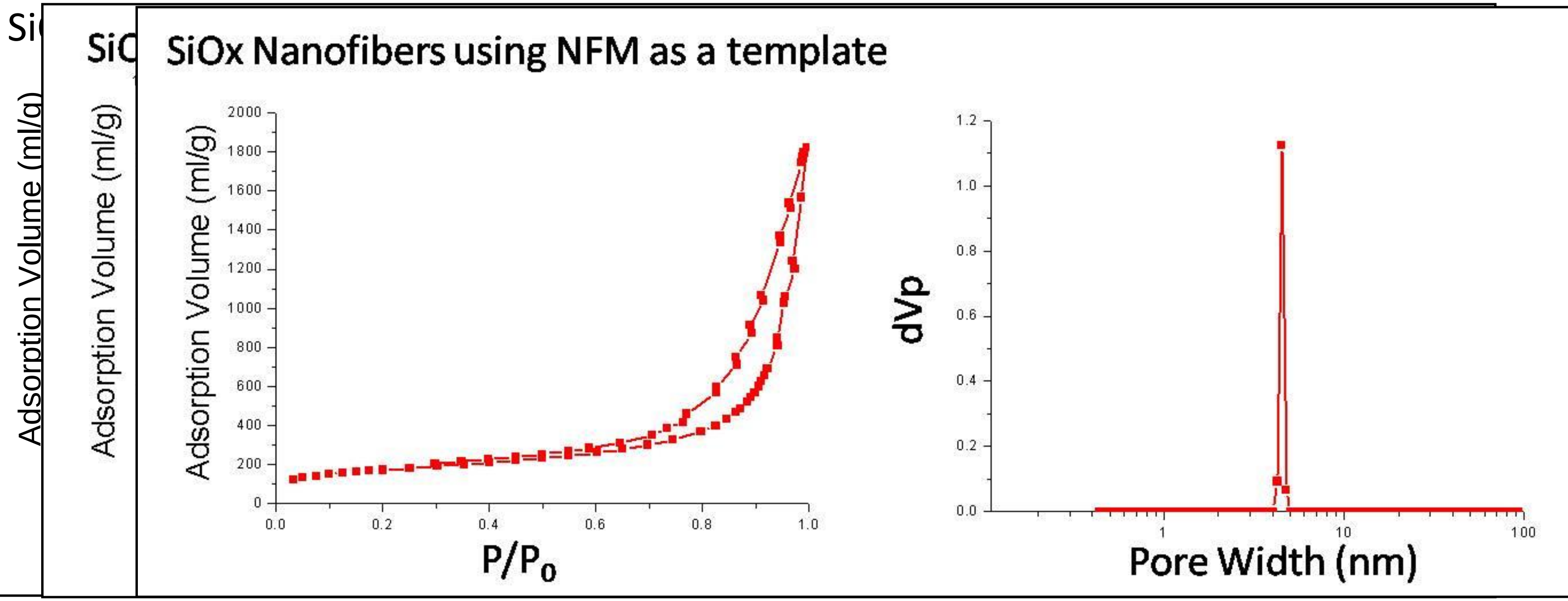


Corresponding SiOx-NF

SA and PSD of SiOx NFs

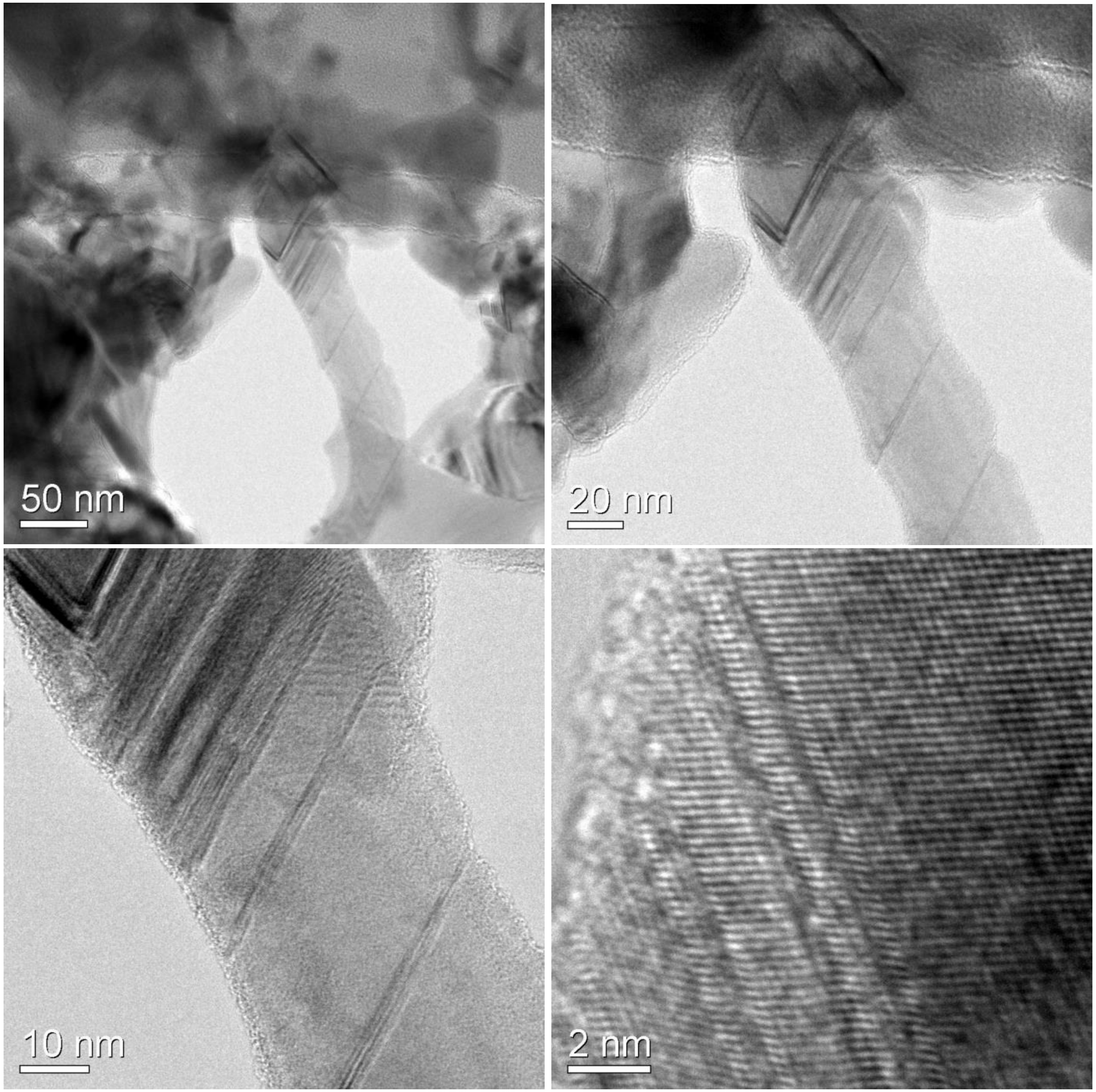
Surface Area and **Pore Size Distribution** depending on the synthesis **template**

- PS in Toluene
- PS/CNF 1/5 (w/w)

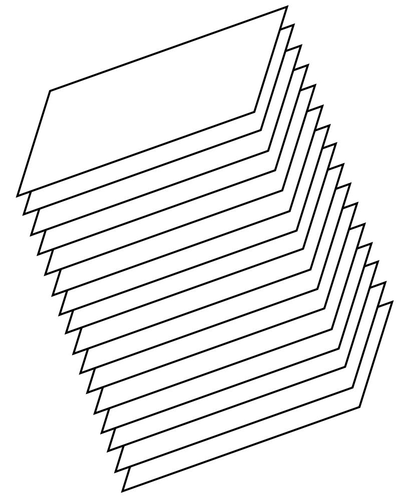


Name of template	Synthesis Conditions (in Air 200 ml/min)	Surface Area (m^2/g)	Pore Volume (ml/g)	Average Pore Size (nm)
PCNF	700°C-4h	538	2.40	17.8
TCNF	700°C-2h	289	1.10	15.2
NFM	500°C-4h	619	2.58	16.7
HCNF	500°C-2h	889	1.90	8.6

β-SiC NF



Structure model of platelet nano SiC



Layer spacing of platelet SiC:
0.225nm observed under TEM

0.253nm from XRD data according to Bragg equation

Nano functional composites

Functional Material

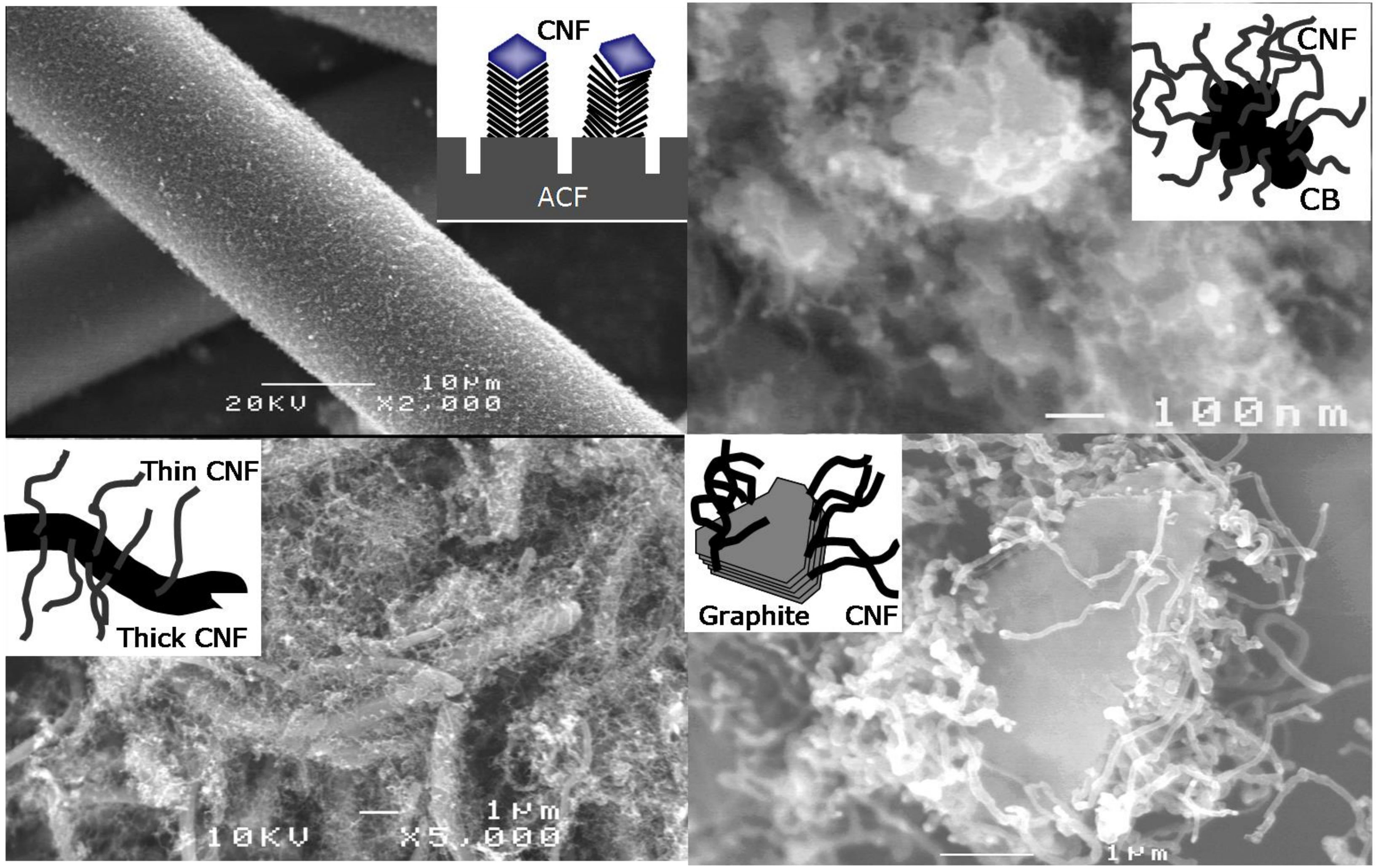
- **Adsorption**
- **Support**
- **Electrode**
- **Filler**
- **etc.**

CNF
複合化

Improvement of Functions by the composition with CNFs

Function improvement
Function Hybridization
Function Creation

Various CNF composites



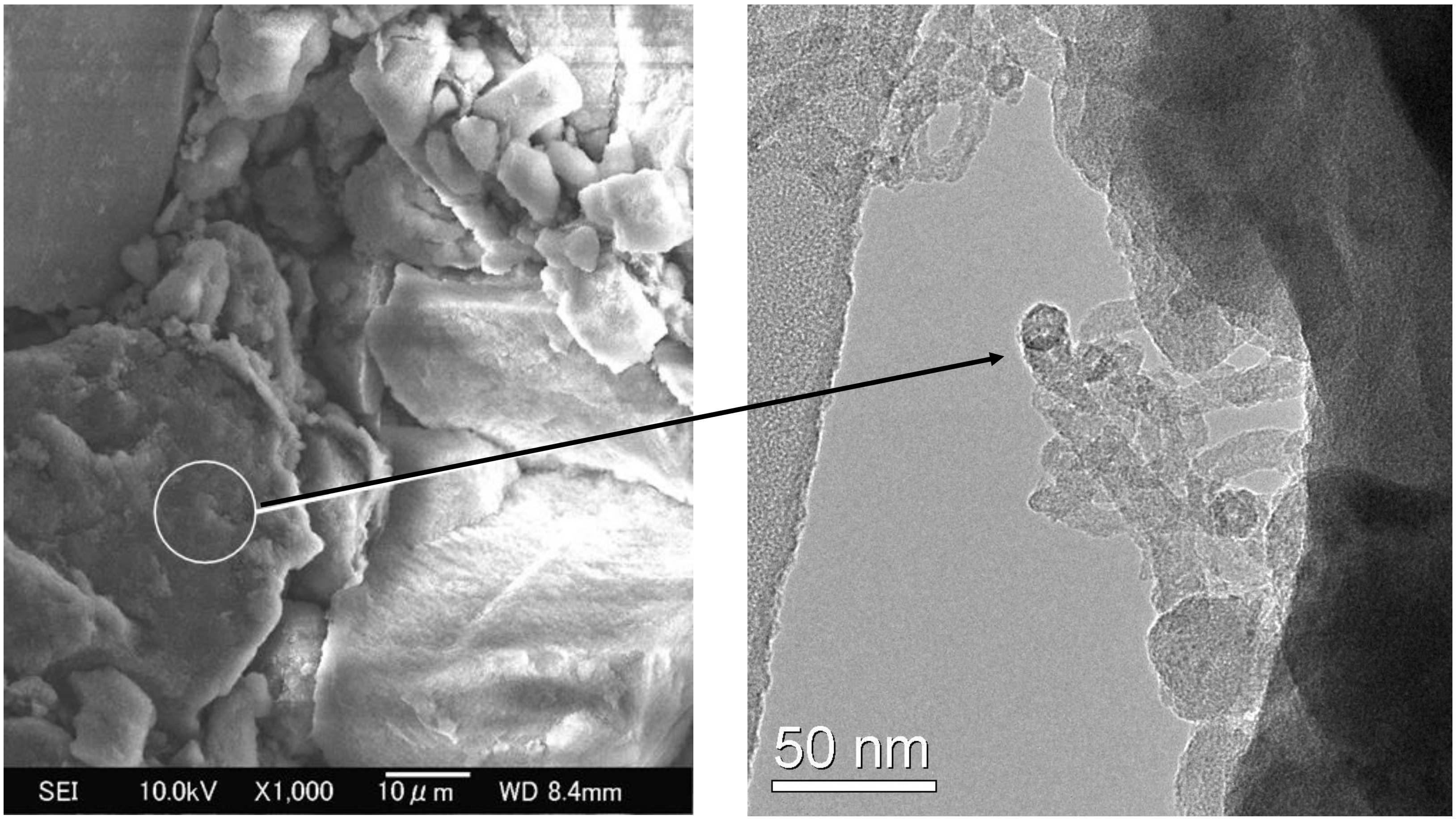
Magnifying the functions of basic materials：Silica,Alumina,Si,TiO_2, Magnetites

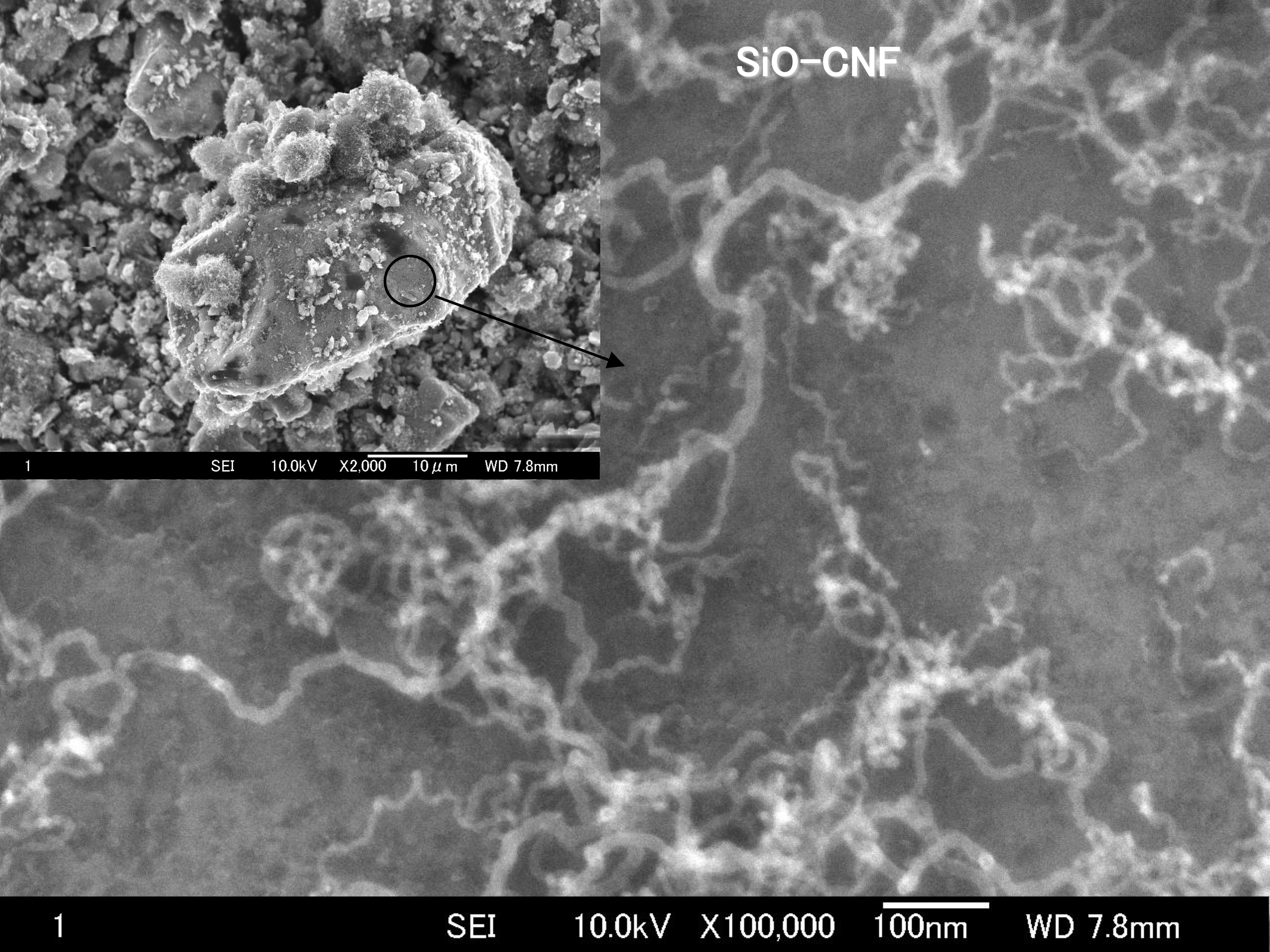
Silica – CNF Composites

Additive to Tire

Bad compatibility to rubber

- **CNF-silica composite to solve – Improvement of compatibility**




SiO-CNF
1
SEI
10.0kV
X2,000
10 μm
WD 7.8mm
1
SEI
10.0kV
X100,000
100nm
WD 7.8mm

Mass Production of CNFs

Horizon type
Capacity：several grams

Capacity：H-, P-CNF 100g/1batch
T-CNF 20g/1batch

Scale up
Vertical type

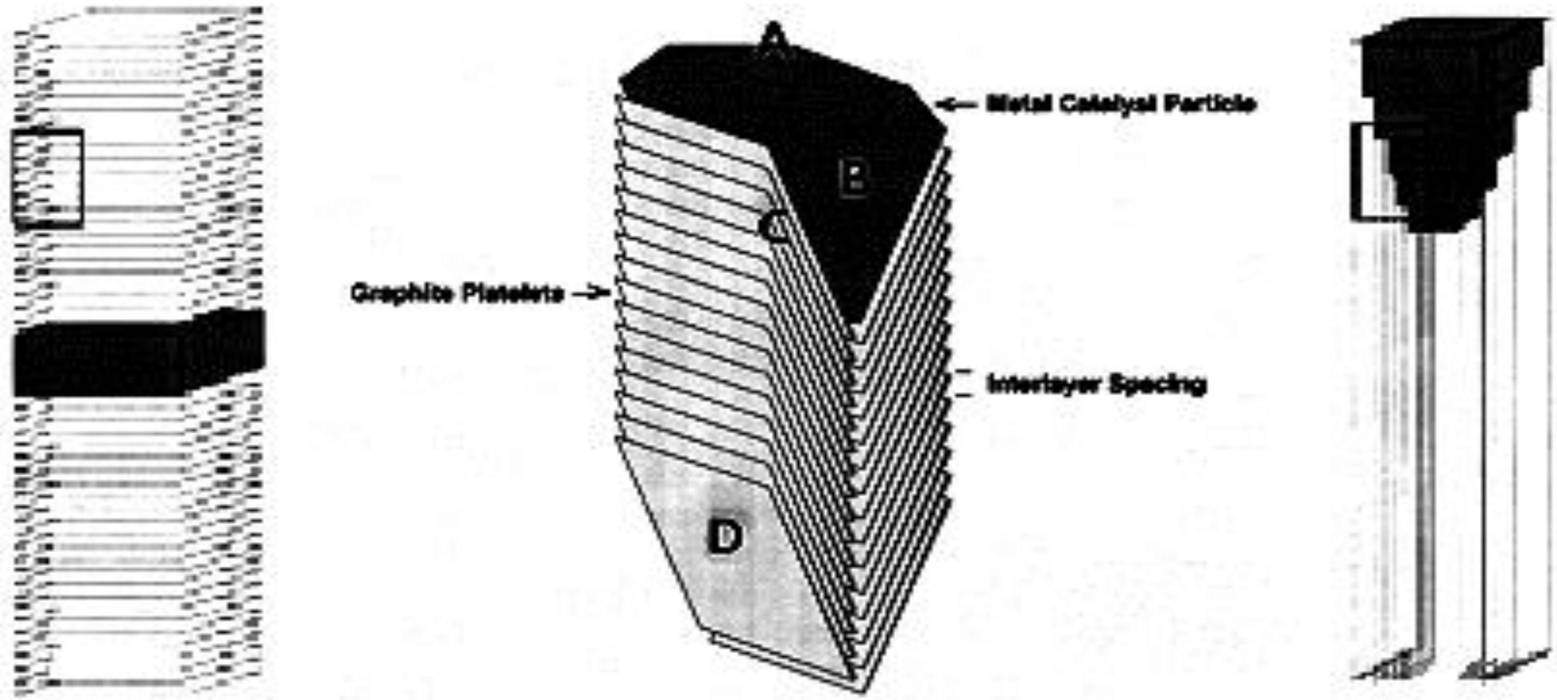
Capacity: 500g/day

Scale up
Vertical type
Pressure

Structure of CNF

Old structural models of CNFs

（Rodriguez, N.M. 1993. *J. Mater. Res*. 8: 3233）



Platelet　炭素ナノ繊維　　Herringbone　炭素ナノ繊維　　Tubular　炭素ナノ繊維

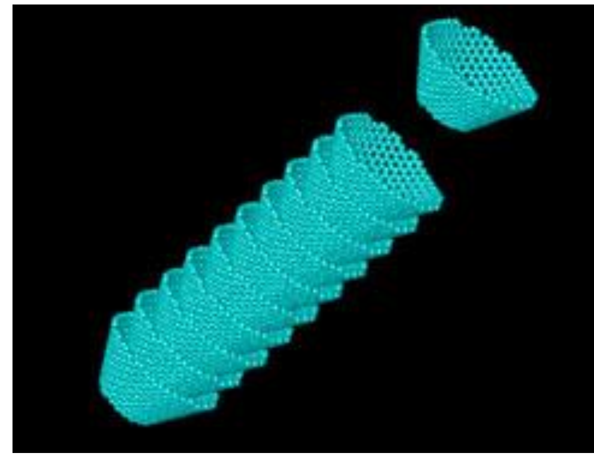
Graphitic cones in palladium catalysed carbon nanofibres：分子 → ナノ繊維

Chemical Physics Letters, Volume 343, Issues 3-4, 3 August 2001, Pages 241-250

H. Terrones, T. Hayashi, M. Muñoz-Navia, M. Terrones, Y. A. Kim, N. Grobert, R. Kamalakaran, J. Dorantes-Dávila, R. Escudero, M. S. Dresselhaus and M. Endo

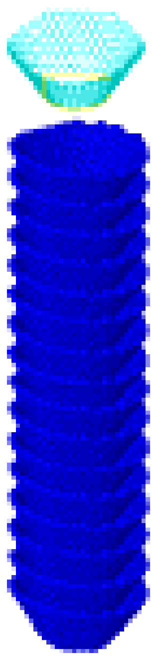
カルベール®（カーボンナノチューブ）

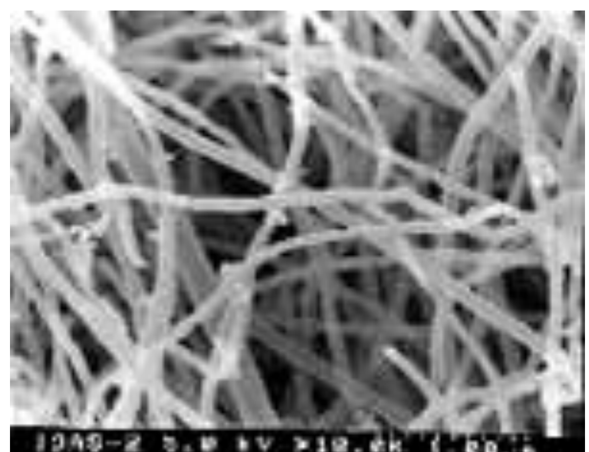
Carbere®（Carbon Nano Tube）

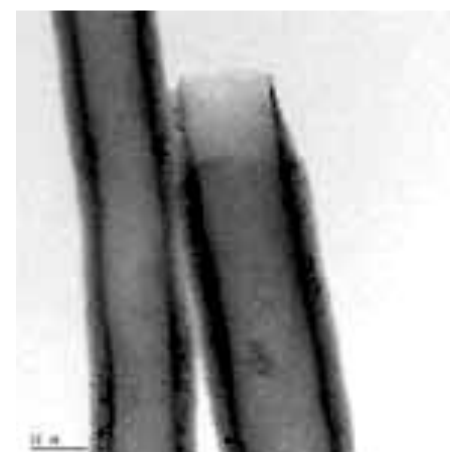


■カルベール®とは

カルベールは超微粒子の金属触媒を核として炭化水素を気相成長させる事によって得られるカーボンナノチューブです。



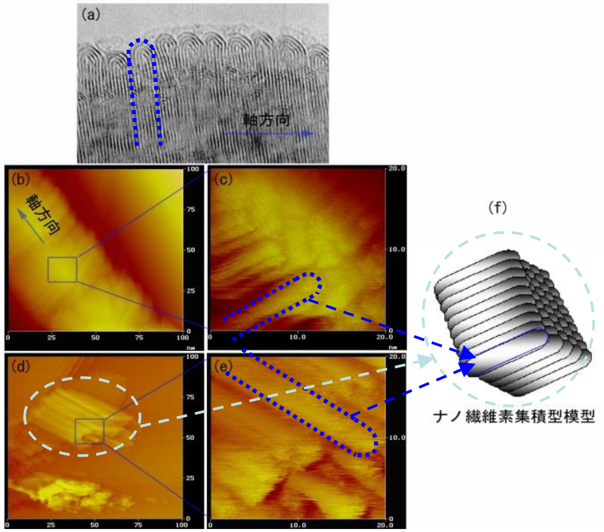




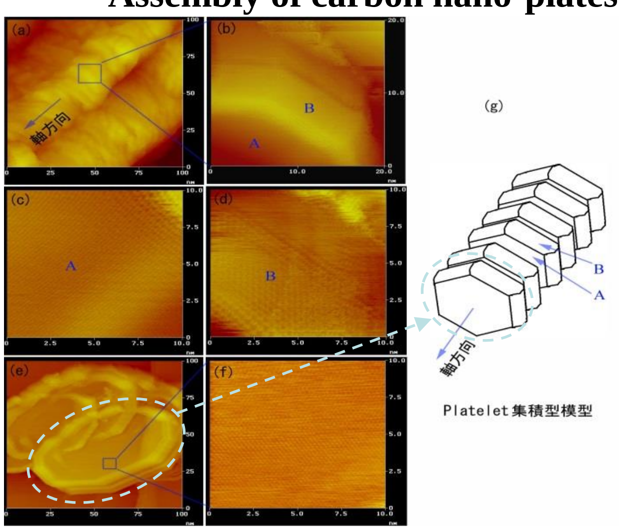
http://www.gsi.co.jp/seihin/hightech/carbere.html

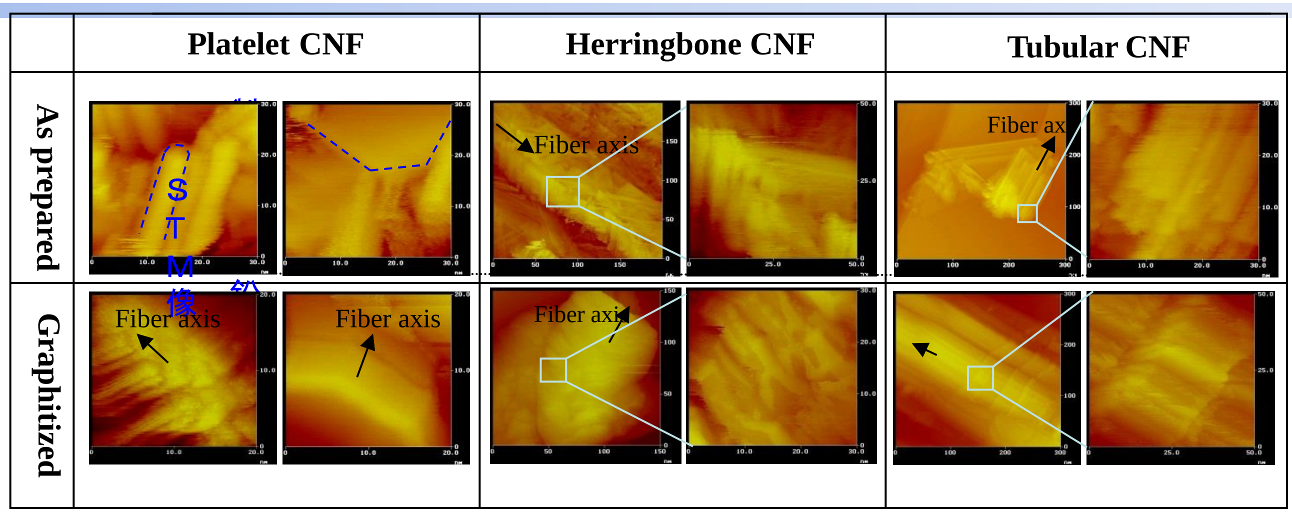
Primary Structures of Various CNFs

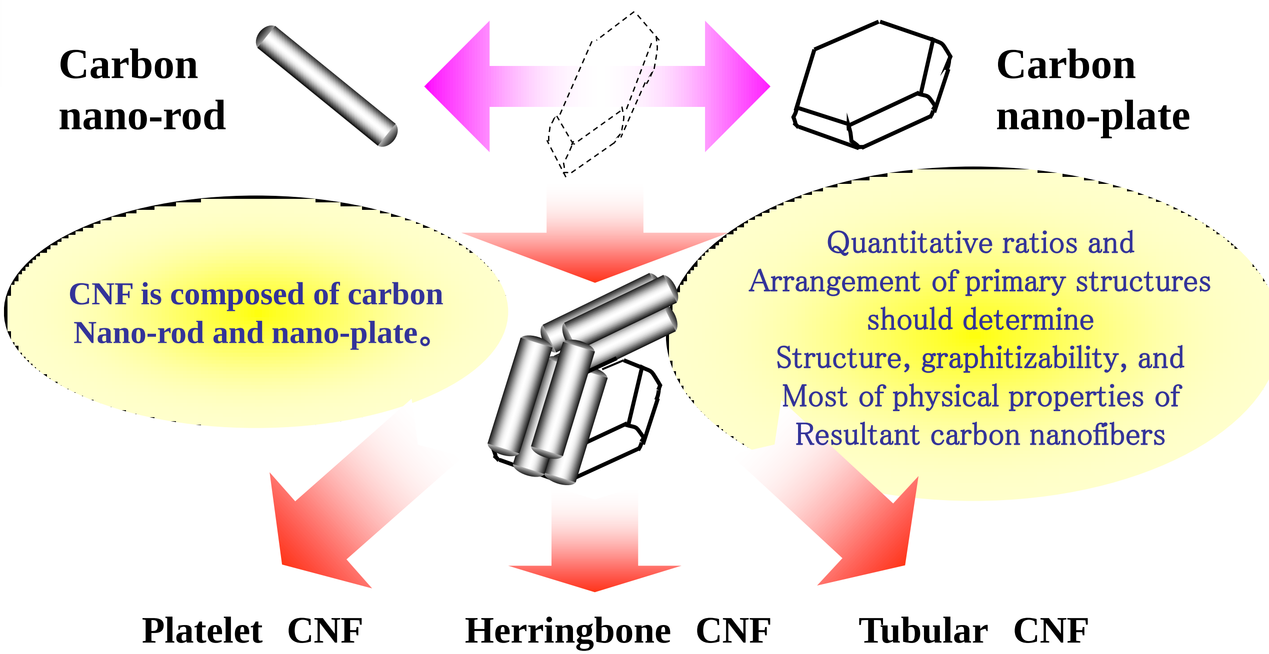
Assembly of carbon nano-rods



Assembly of carbon nano-plates







⇨ **Various structures and surfaces of CNFs are determined by the arrangements of primary structural units**

SEM of PCNF, stabilized PCNF and PACNF

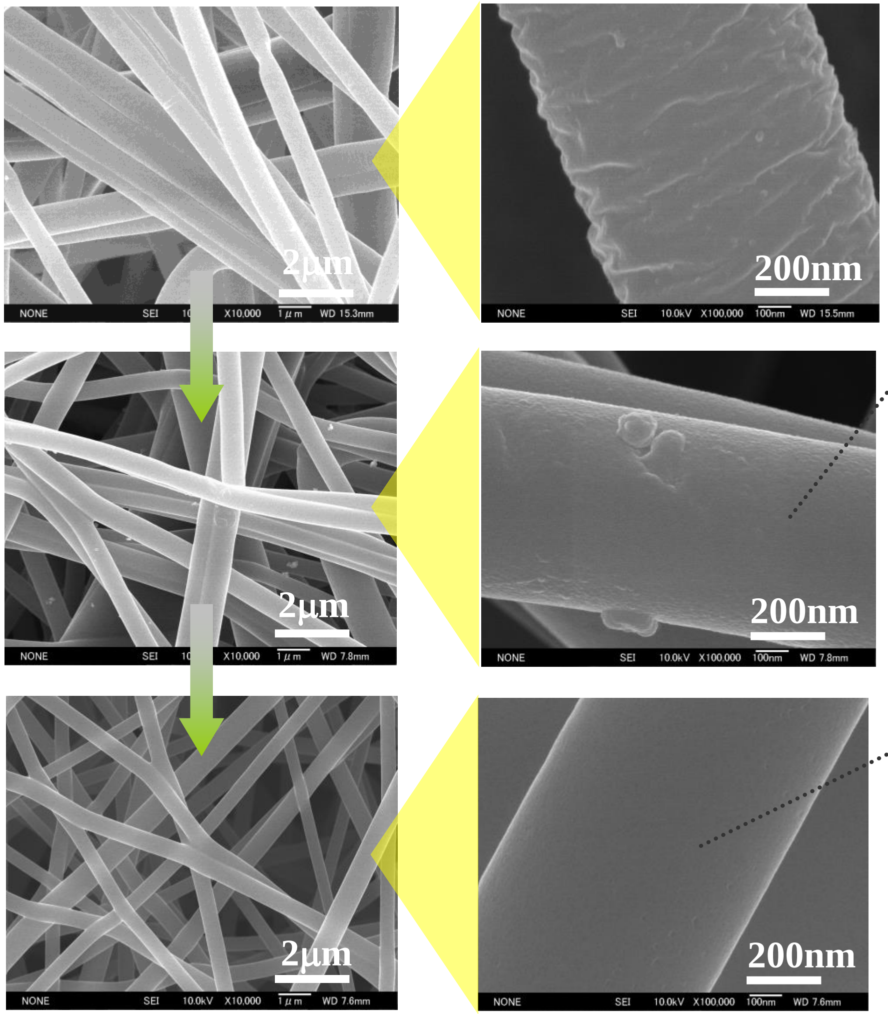
PCNF
(starting material)

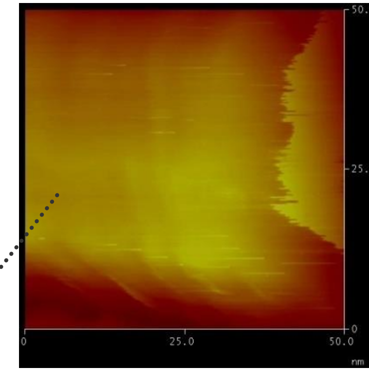
270°C
(0.5°C / min)

Stabilized PCNF

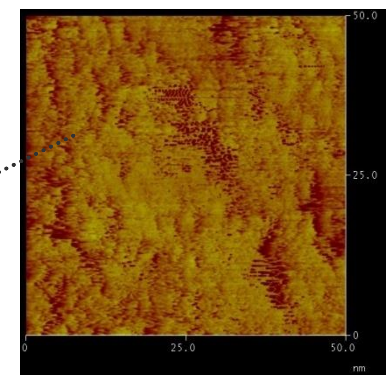
600°C in He
or
steam activation

PACNF





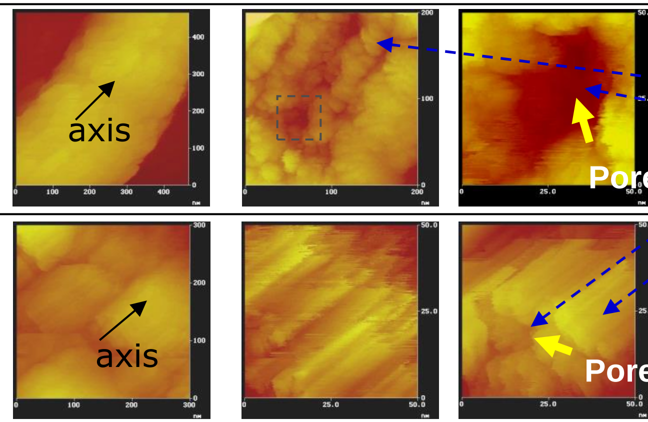
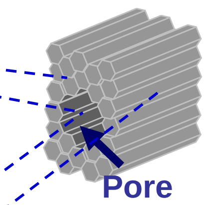
Assembly of
1.8nm~3.6nm thin film



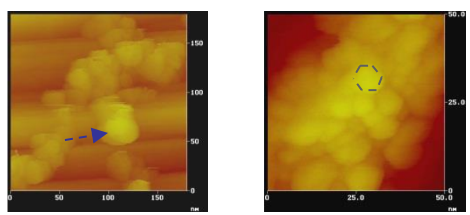
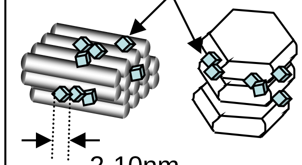
Nano particle
assembly structure

Mesoporous CNFs

CNFの高触媒機能化
（ナノ構造単位を利用した機能化処理）

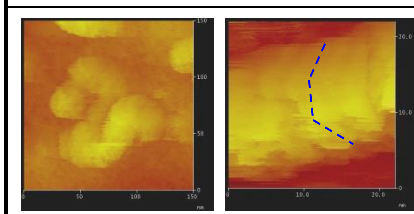
全体像 → 拡大像	モデル
	 Nano-Rod単位素の選択的ガス化によりメゾポーラスが生成される。

CNFへのPt-Ru触媒担持

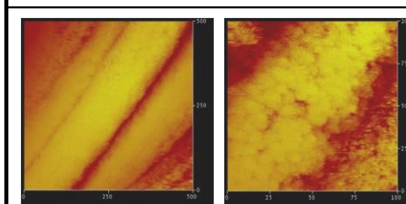
5%触媒 → 60%触媒	モデル
	 最初にヘキサゴン面のエッヂ部分や境界などの欠陥に析出して、徐々に全表面を覆う。

新しいチャレンジ
（新CNF構造の発見、新合成方法の開発）

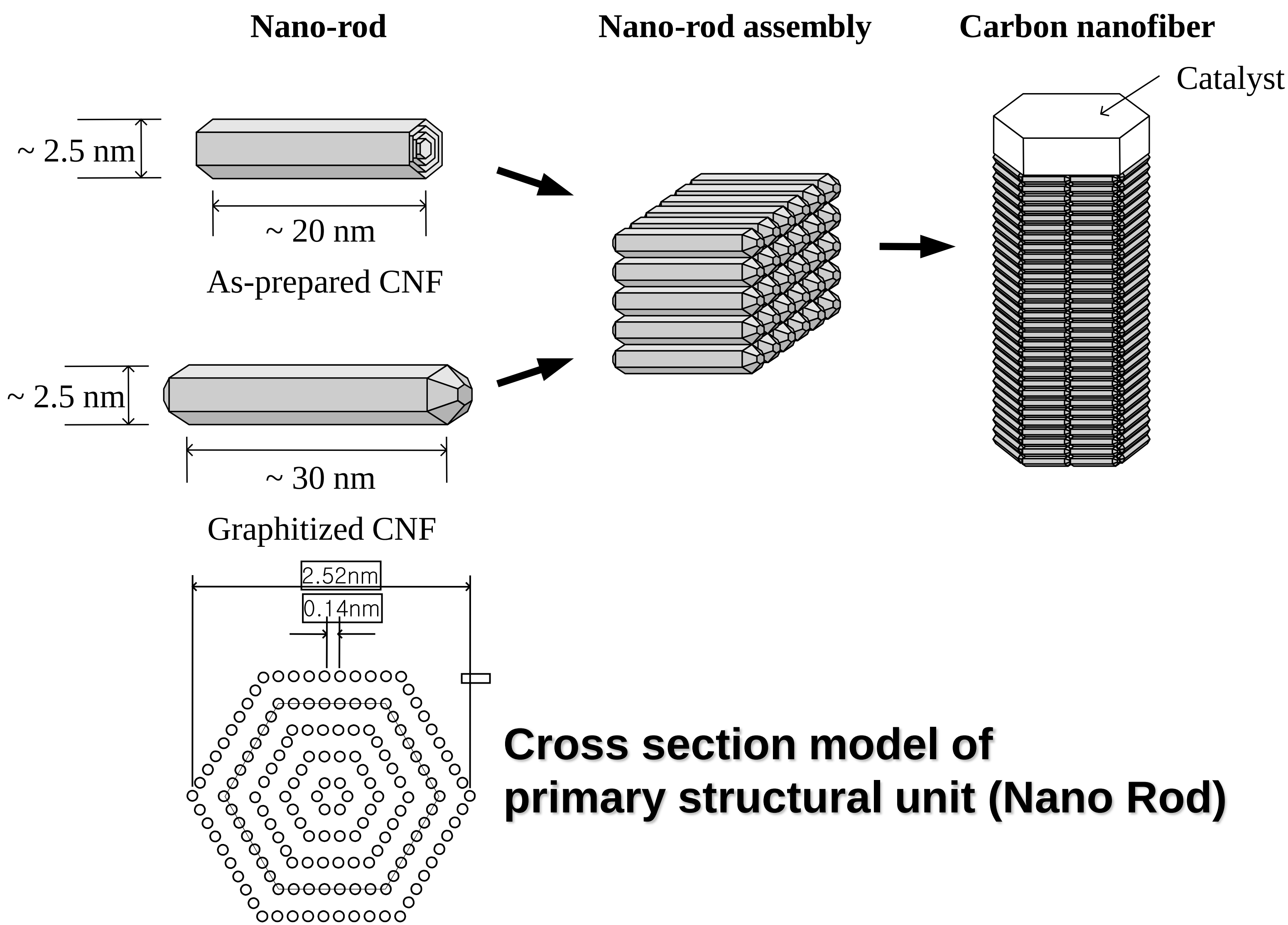
ACF上に成長させたCNF構造

全体像 → 拡大像	解析
	ACF の 表 面 積に関係なく主に「Nano-Plate」集積型の構造を構築。

新チャレンジPAN系CNF構造

全体像 → 拡大像	解析
	生成直後は不電導性膜を持つが、炭素化によって電導性のナノ粒子構造になる。

Structural Model of TCNF

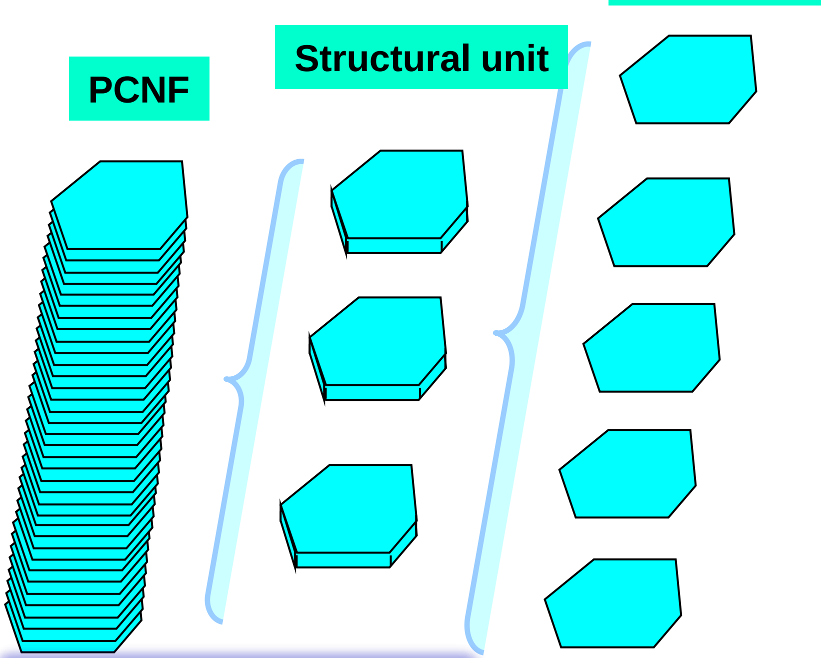


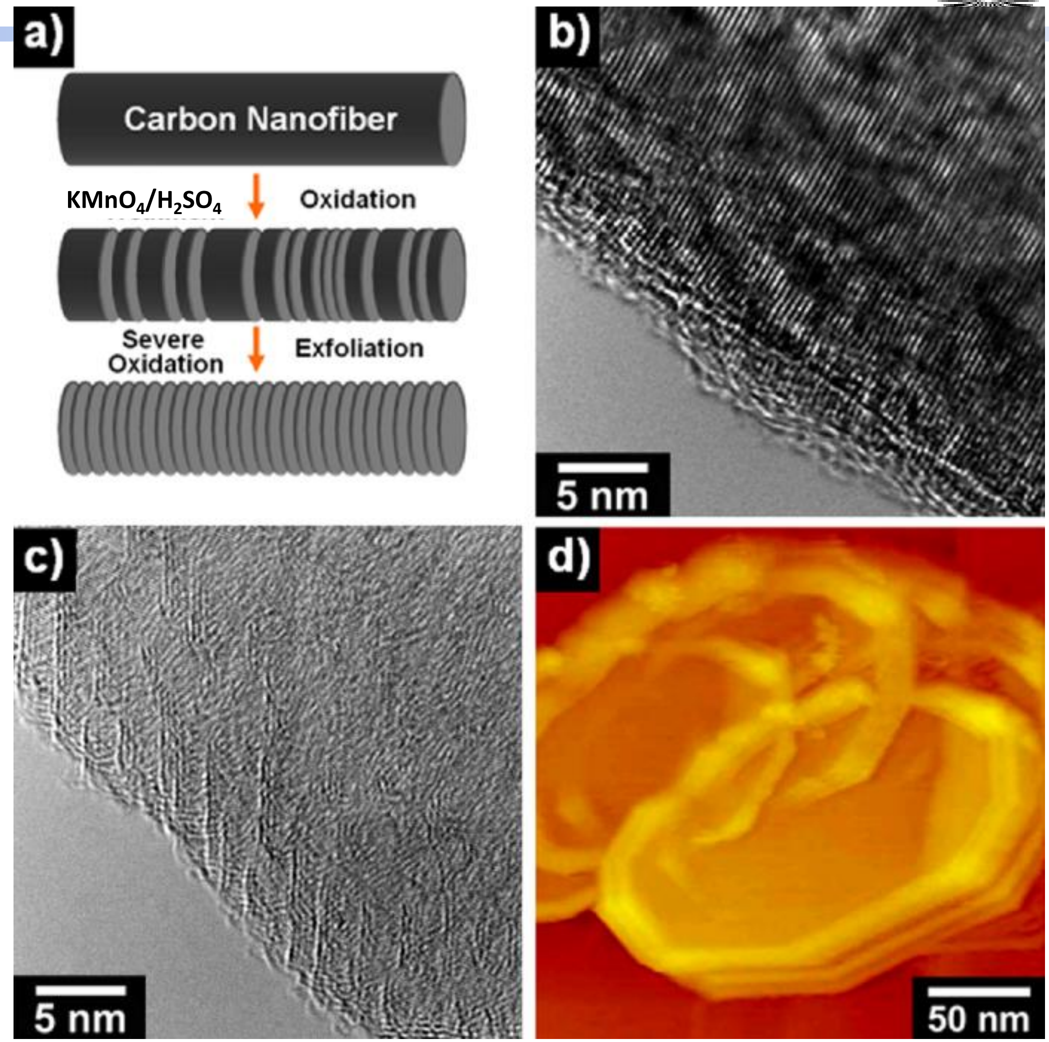
Cross section model of primary structural unit (Nano Rod)

Separation of structural unit (Nano-platelet)

Introduction

The relationship between
PCNFs and graphene



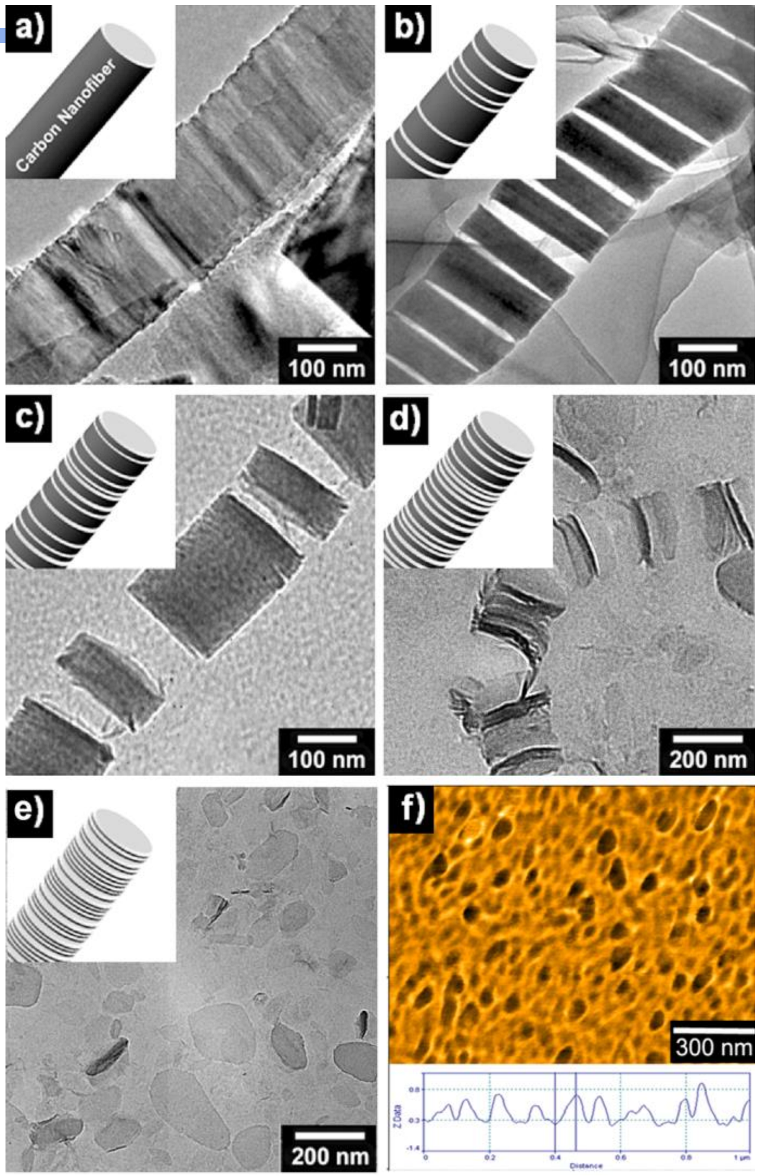


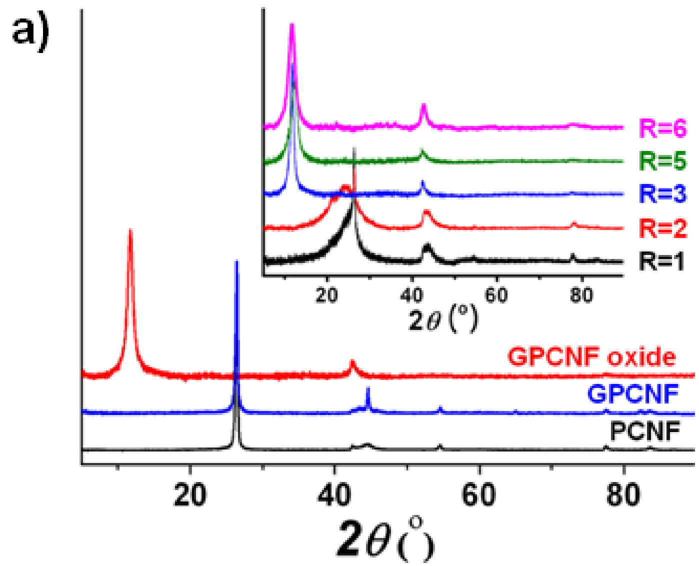
Objective

Using oxidation and exfoliation methods to transversely isolate structural unit of PCNFs for further understanding of CNFs' structure.

***ACS Nano*, 2011, *5* (8), pp 6254–6261**

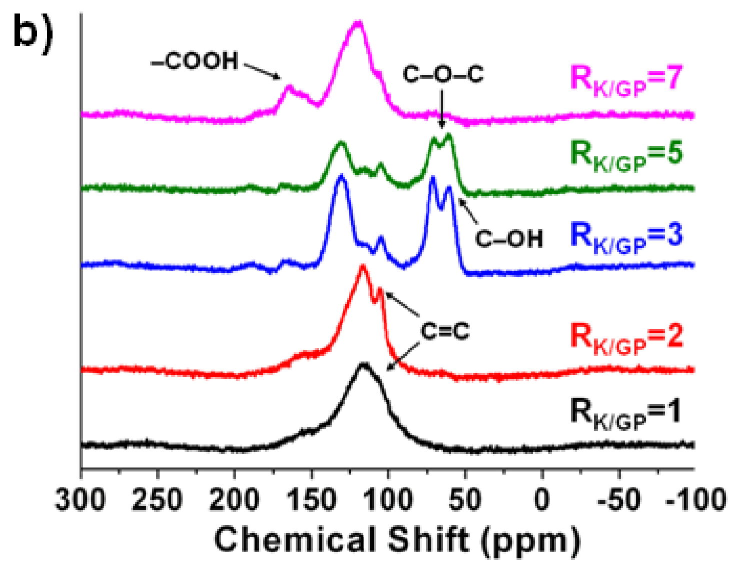
Separation of structural units from GPCNFs





(1)

Through the simple ultrasonic exfoliation, the disc-type structure units and graphene layers are isolated step by step.

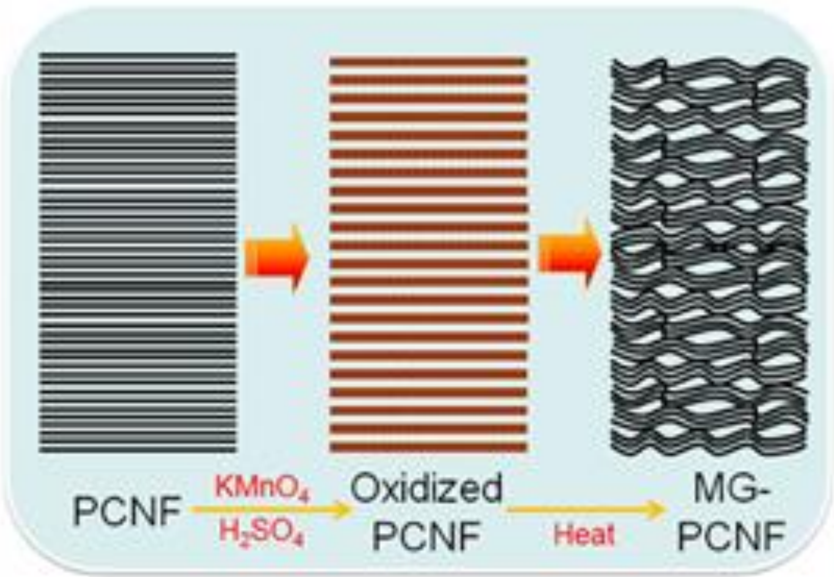


(2)

Oxidized structural units and graphene discs have graphite oxide like structure.

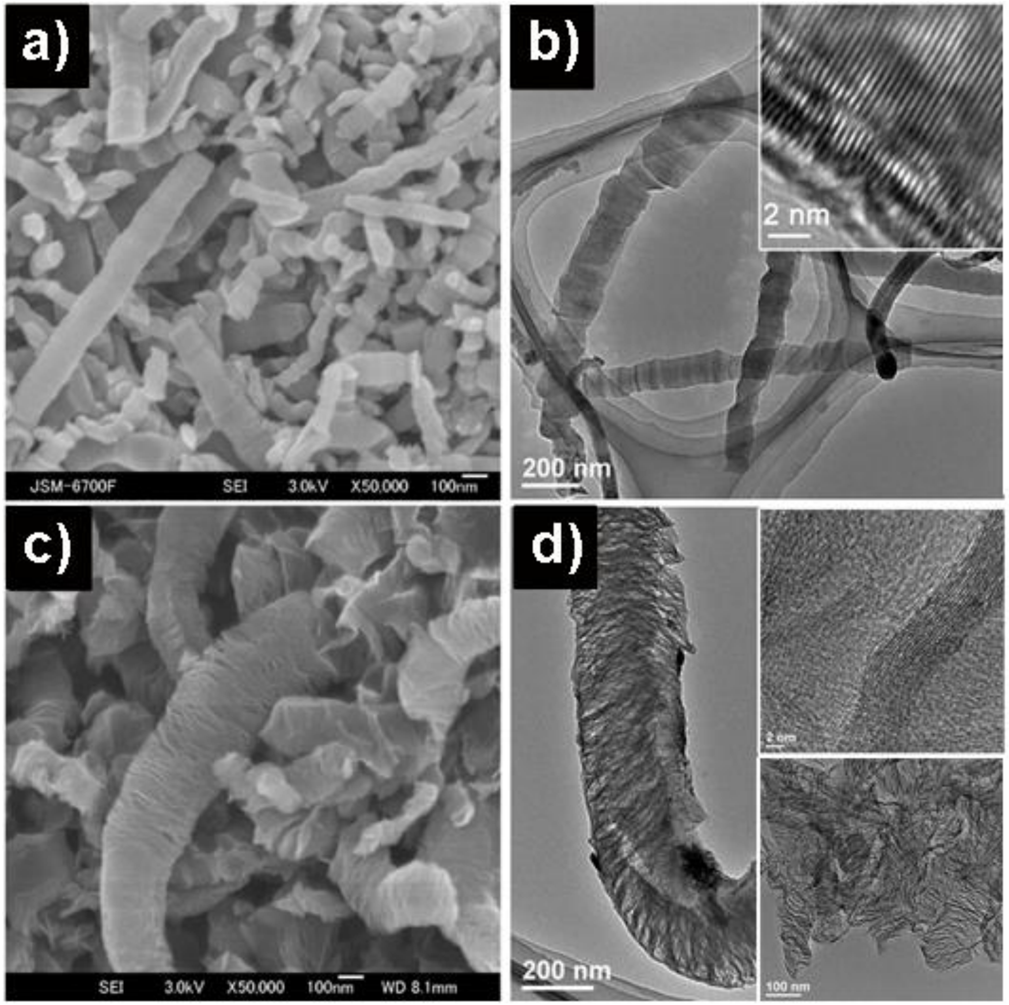
Development and control of mesopores in PCNFs

Introduction



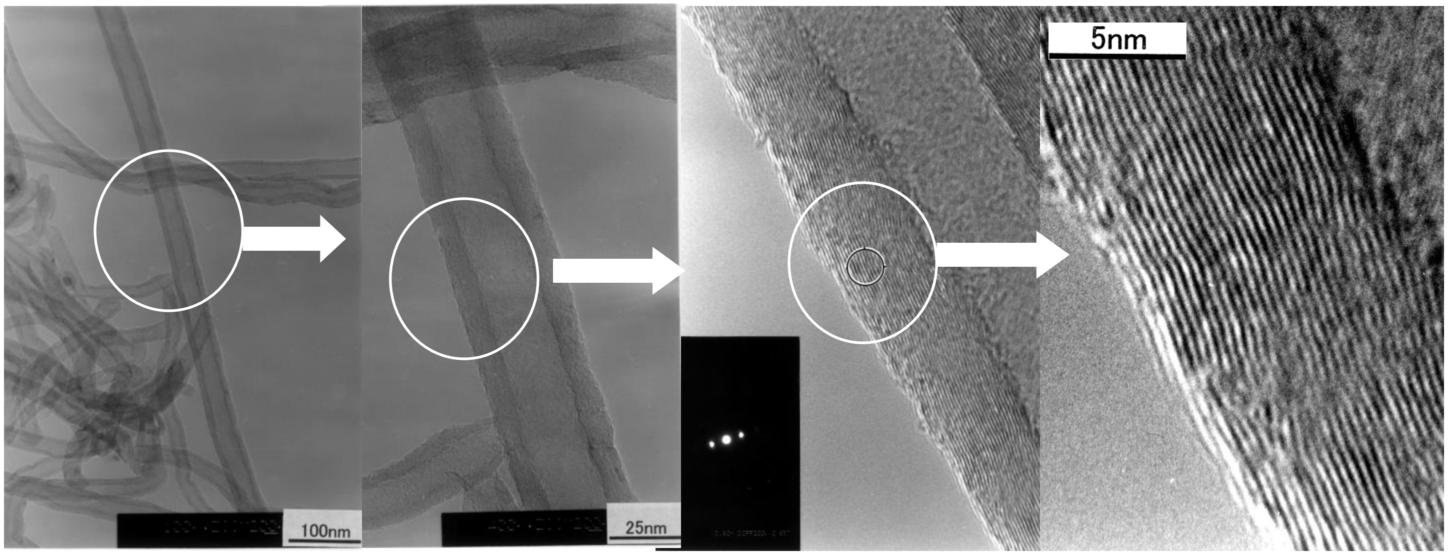
Objective

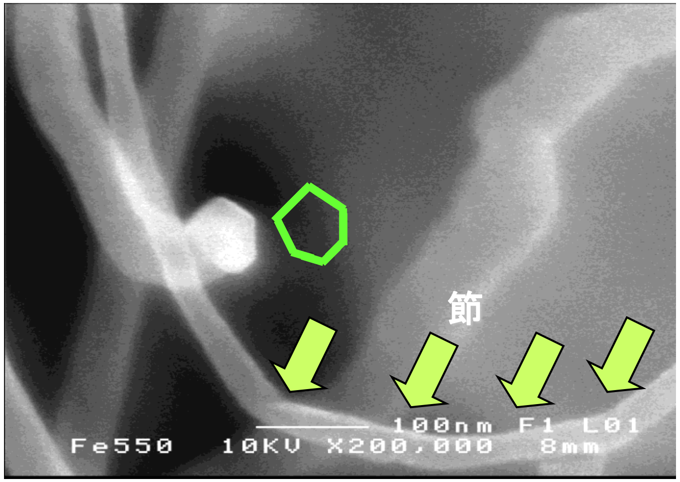
Developing a general method based on the oxidation and heat expansion to
introduce the mesoporous channels into CNFs.



Chemistry of Materials, in press (2011)

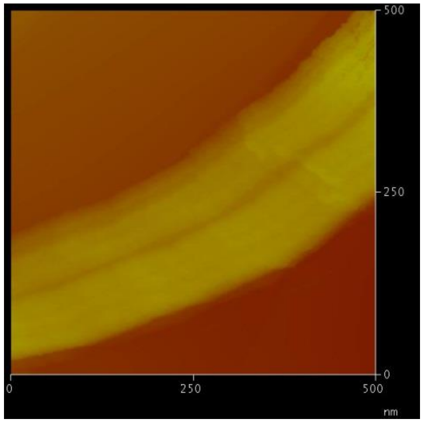
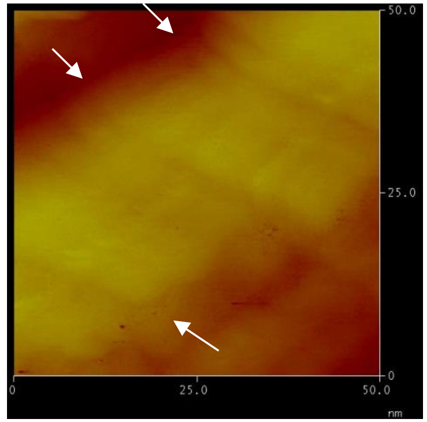
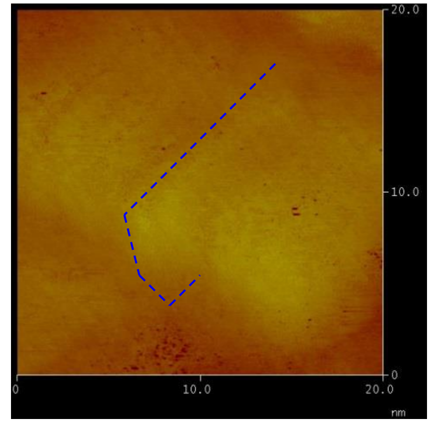
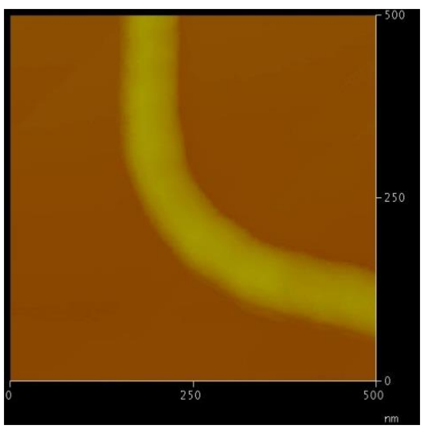
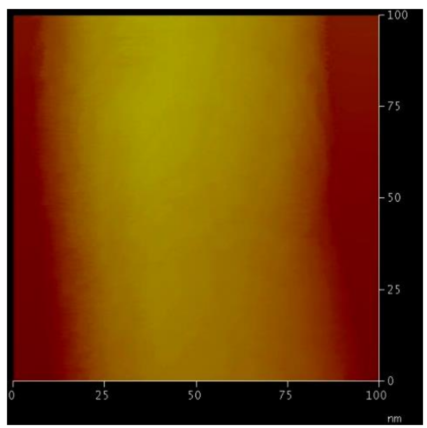
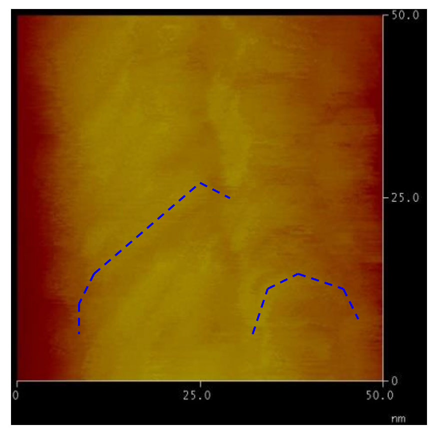
Structural Defects of TCNFs



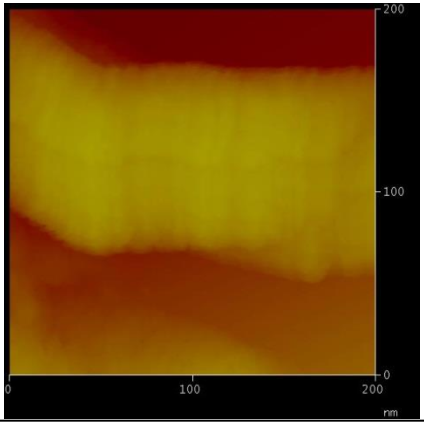
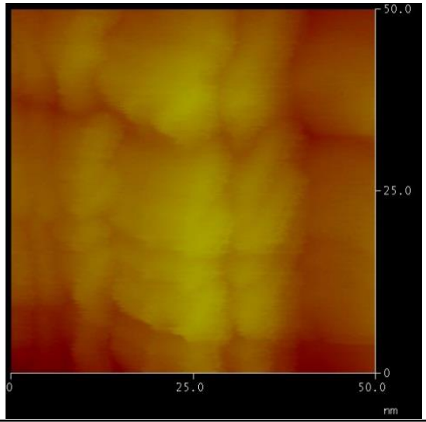
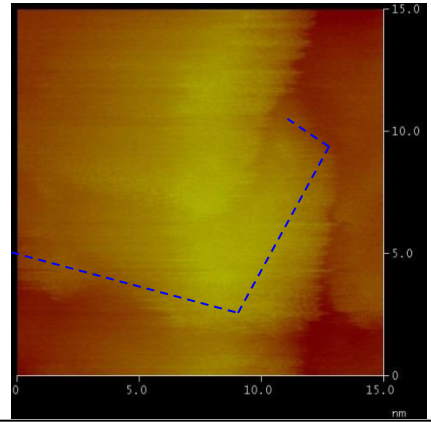
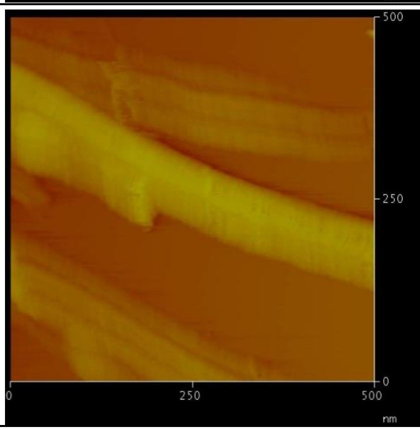
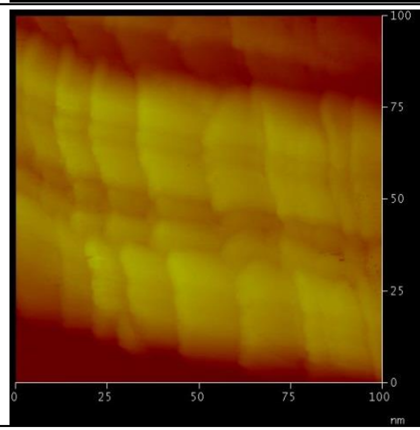
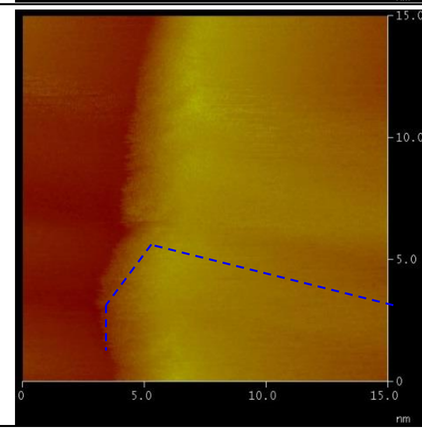
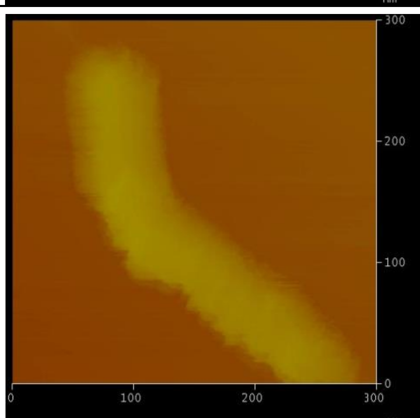
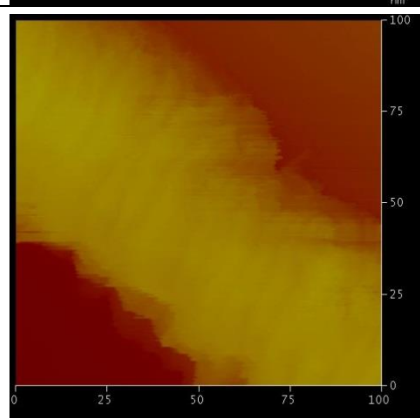
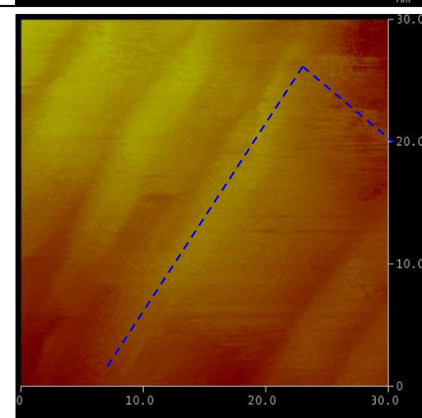


Heat treatment	d_{002}(Å)	Lc_{002}(nm)	La_{110}(nm)
As-prepared	3.369	9.5	6.5
Graphitic temp. 2000℃	3.387	13.7	6.7
Graphitic temp. 2800℃	3.375	16.2	6.9

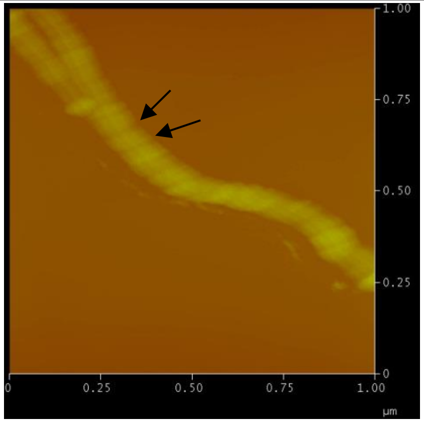
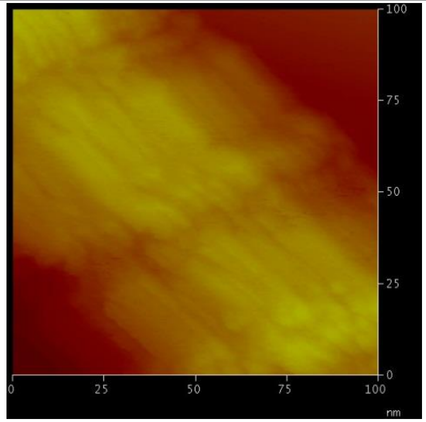
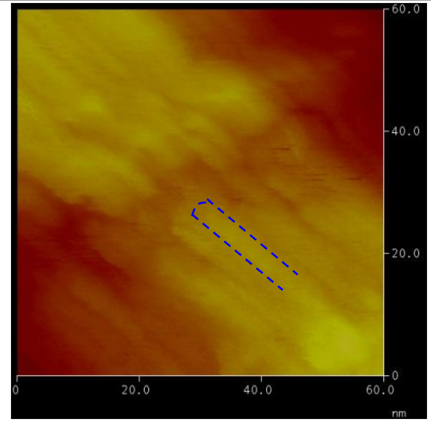
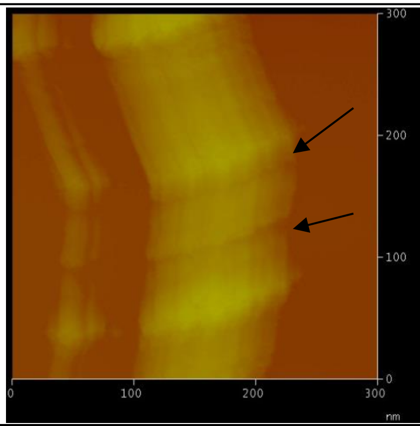
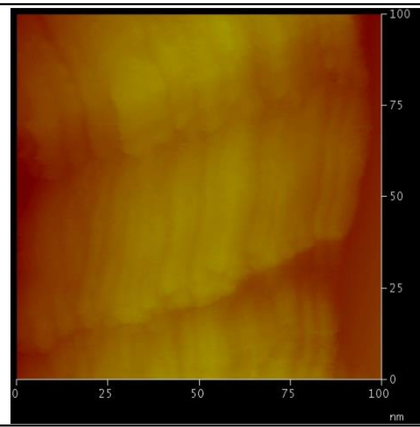
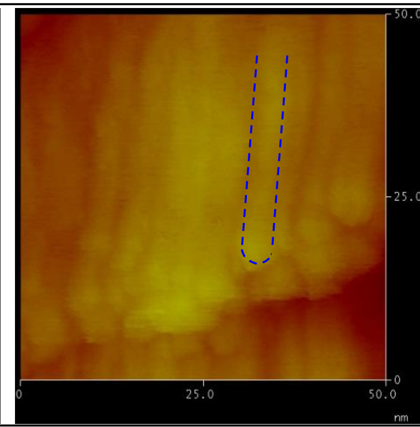
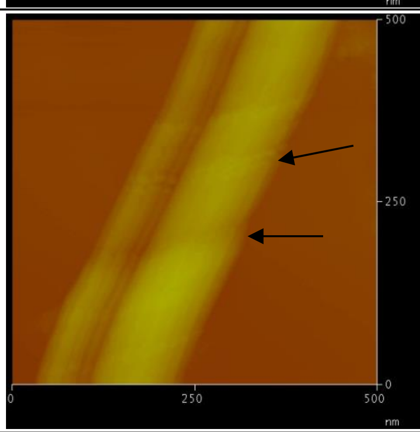
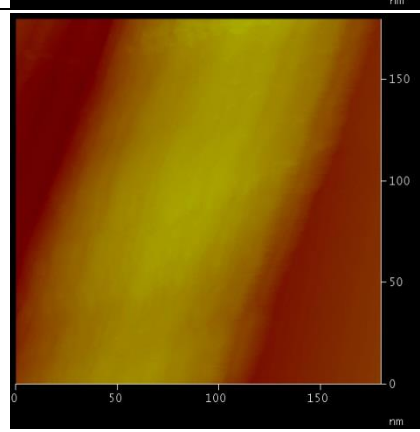
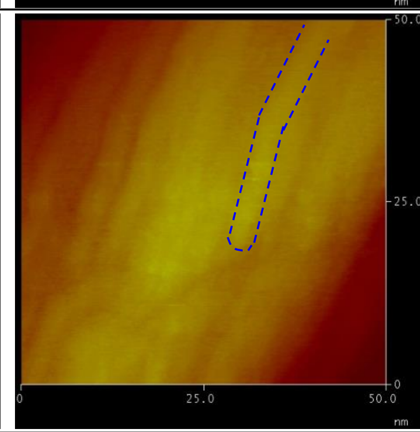
KNF-ST

	Large scale →		Small scale	説明
典型1				ナノプレットが軸と平行に並んだ構造
典型2				ナノプレットがヘリングボンCNFのように軸と角度を持って並んだ構造

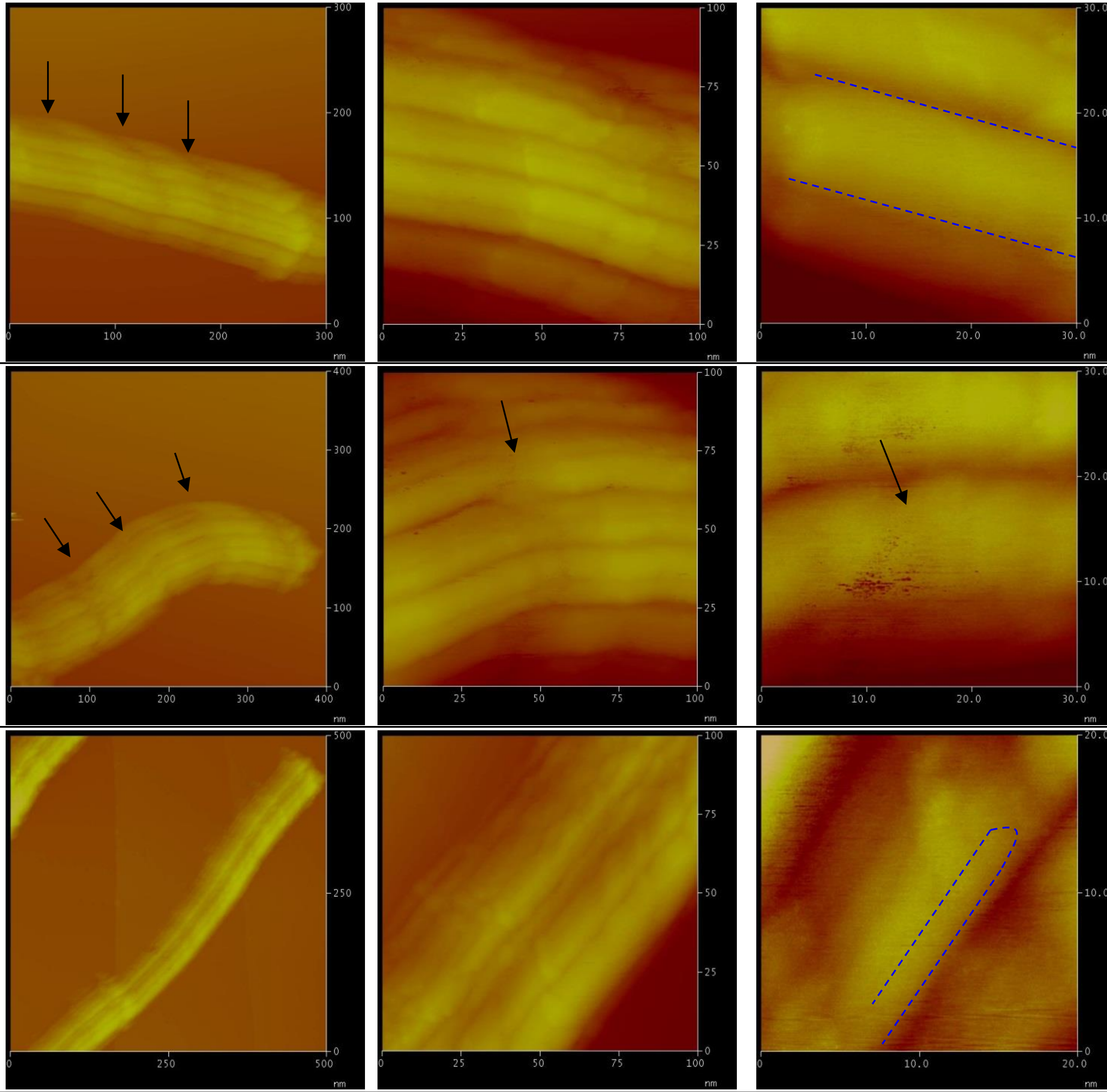
KNF-ST2000

	Large scale →		Small scale	説明
典型1				ナノプレットが軸と殆ど平行に並んだ構造
				
典型2				ナノプレットがヘリングボンCNFのように軸と角度を持って並んだ構造

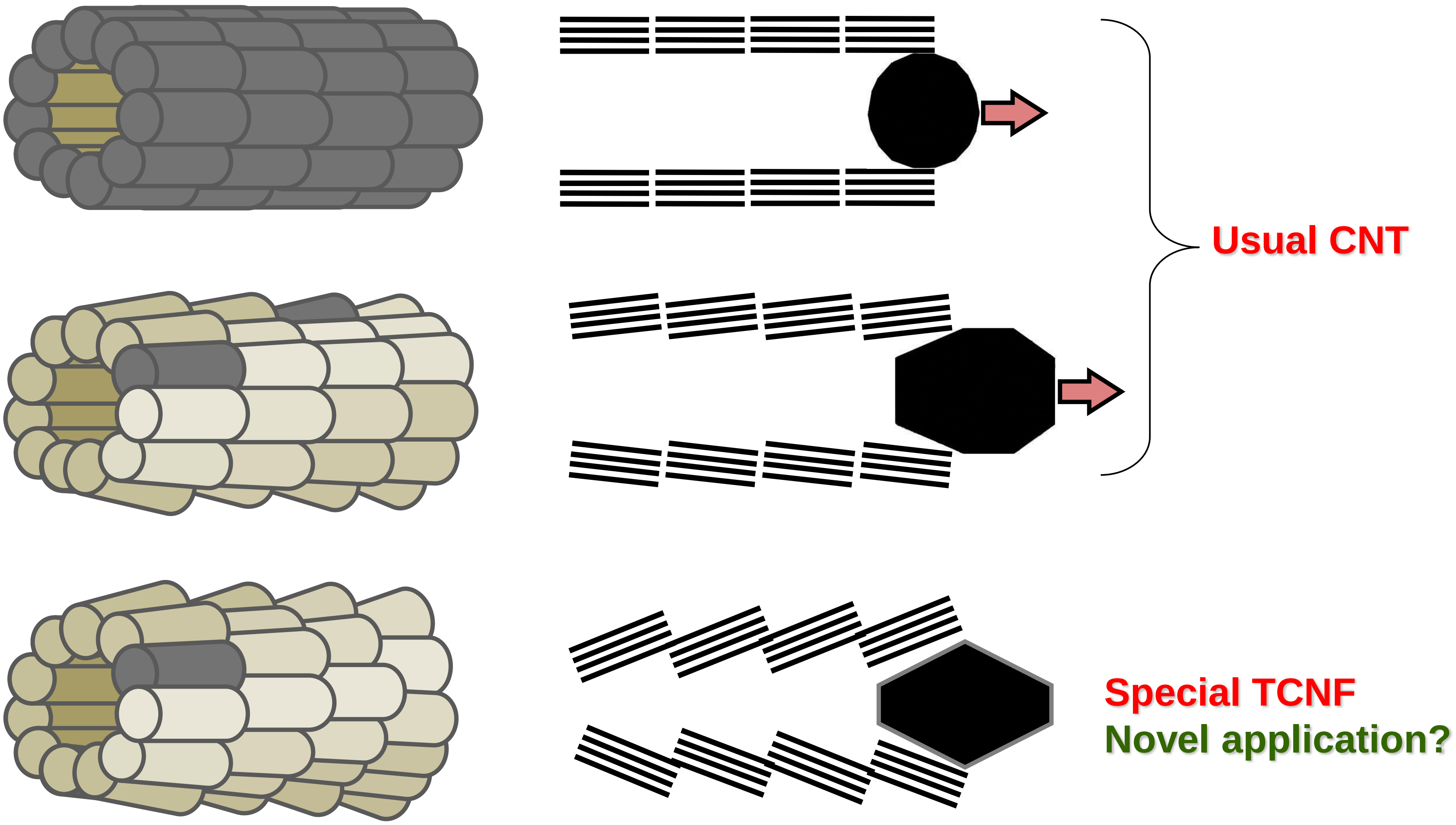
KNF-KH2

<table>
<tr><th></th><th colspan="3">Large scale → Small scale</th><th>説明</th></tr>
<tr><td rowspan="2">典型1</td><td></td><td></td><td></td><td rowspan="2">KHF-KH1と類似で、全体的に非直線状で、ナノロッドが軸と平行に並んだ構造</td></tr>
<tr><td></td><td></td><td></td></tr>
<tr><td>典型2</td><td></td><td></td><td></td><td>全体的に直線状で、ナノロッドが軸と平行に並んだ構造</td></tr>
</table>

KNF-JT

	Large scale → Small scale	説明
典型1		ナノチューブのbundleのようだが、ナノロッドが軸と平行に並んだ構造だとも理解できるかも？ 矢印はロッドの繋ぎ部分だが、正にNature論文でTEMで観察した周期的成長の痕跡

Schematic Models of TCNF



Applications of CNFs

- Energy saving devices (Battery and Capacitor)
- Nano-fluid
- Supports for heterogeneous catalysts

  Fuel Cell, Green Chemistry
- Air cleaning
- Catalyst
- FED, FEBL
- Composites

Carbons in Lithium Ion Batteries

Roles of Carbon for Anode of Li-ion Batteries

- Anodic Electrode to Hold Reduced Li-ion

  Intercalation → Graphite

  Surface Electron Transfer into Sealed Void → Hard or Low Temperature Calcined Carbon

- Electron Conductive Material

  Anodic Carbon and Cathodes Material

- Expansion Moderator

  Holding and Release of Ion Is Accompanied with Volumetric Charge

  Larger Capacity per Volume → Larger Expansion

Carbon Electrode for Li-ion Battery

- **Graphite electrode is currently established.**
  - Low cost with cheaper natural graphite
  - Limited capacity less than 372 mAh/g
  - Limited power density

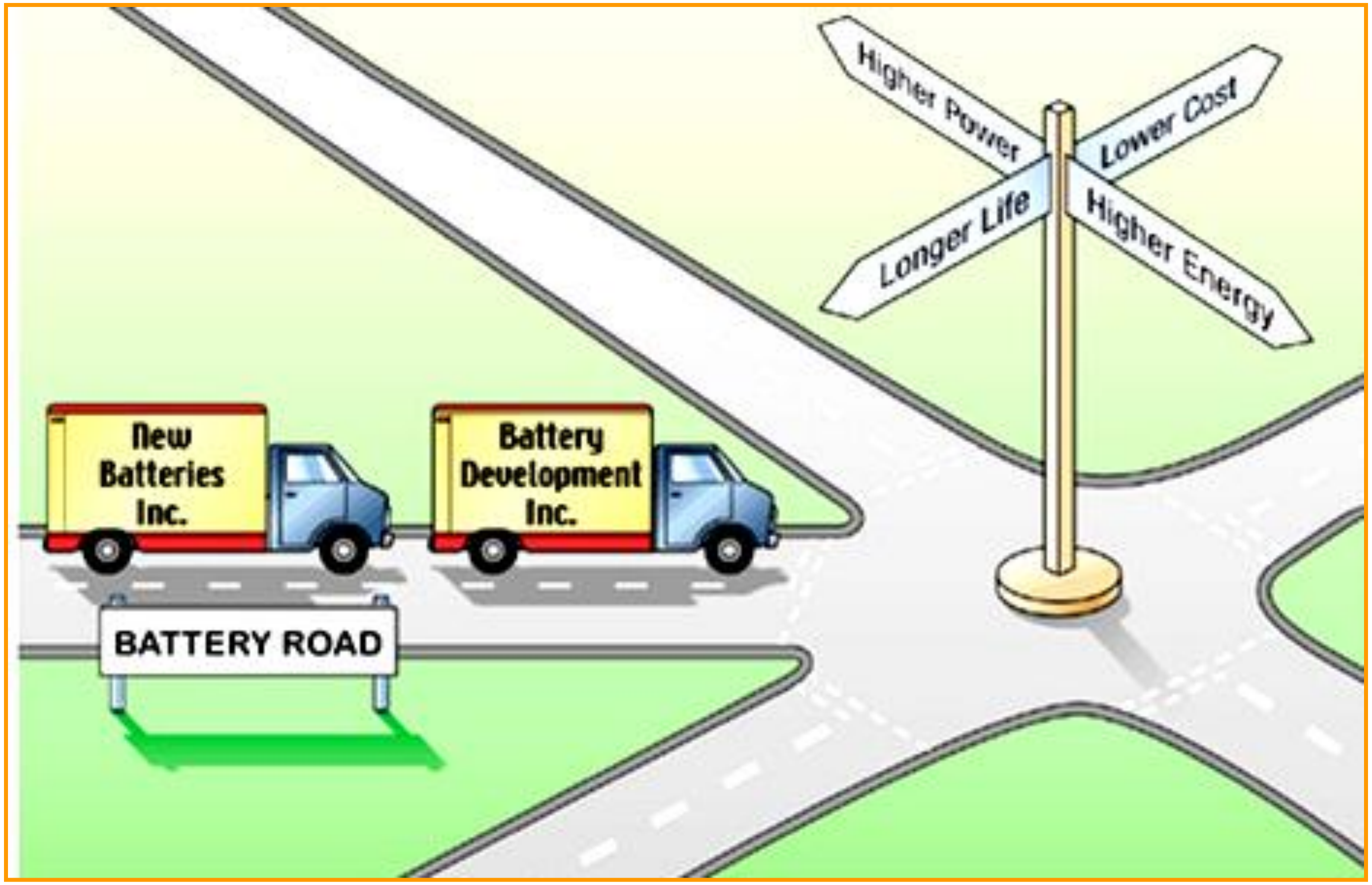
Larger power density for hybrid vehicle
➔ Glassy carbon with small crystalline unit (Low Cond.)
Thinner carbon nanofiber

Larger capacity
➔ Glassy carbon with large inner surface
Si or Sn family (Large volumetric change at Ch/Disc)
⇨ **Functional nano-composites**

Electrode Materials for Lithium Secondary Battery

<u>Different materials for different applications</u>

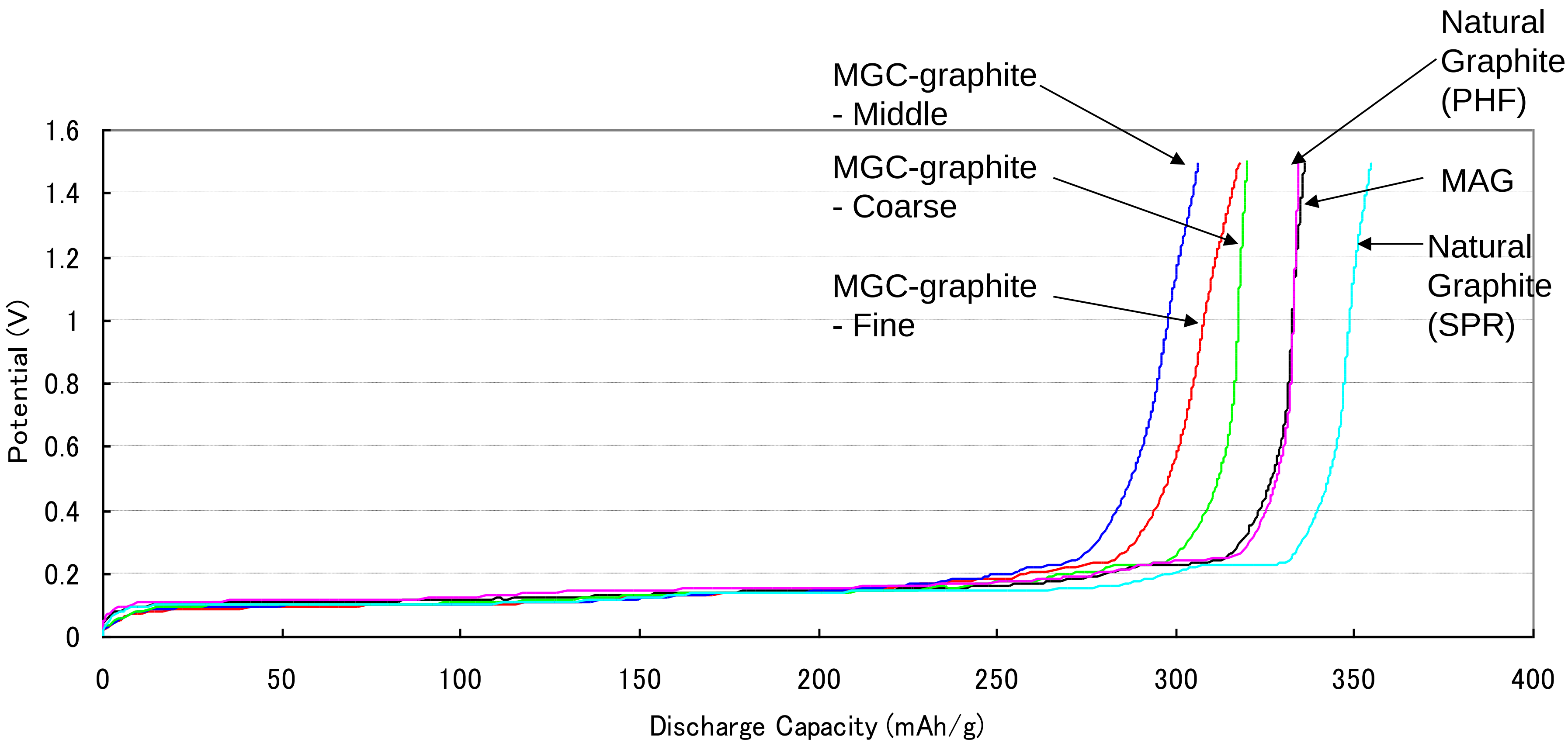
A spectacularly reactive cathode
Nature Materials **2,** 705–706 (2003)



Characteristics of Basic Raw Materials

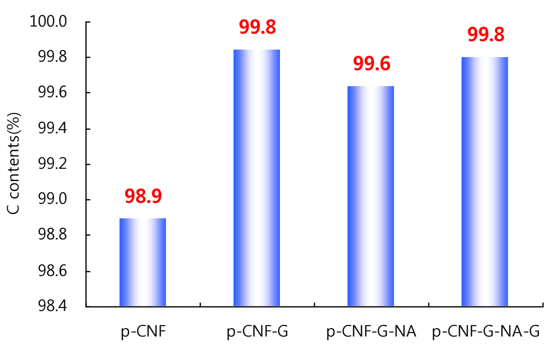
	Graphite	Si	Sn	CNF		
				Platelet	Tubular	Herring-bone
Capacity (mAh/g)	350	4000	900	290 (340)	220 (280)	80 (600)
Density (g/cc)	2.24	2.33	5.77~ 7.27	2.1	2.1	2.0
Expansion ratio (time)	1.2	4	3	Less than 1.2	Less than 1.2	Less than 1.2

Typical Properties of Synthetic Graphites

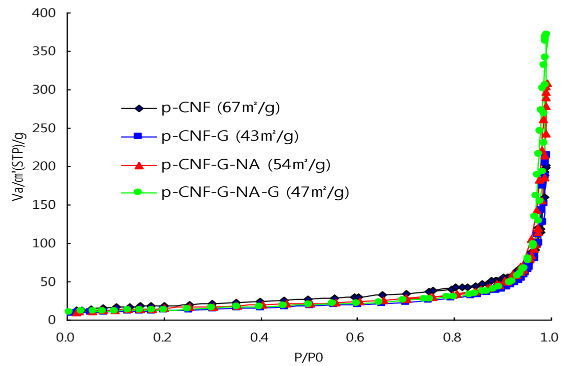


Analysis of physical properties

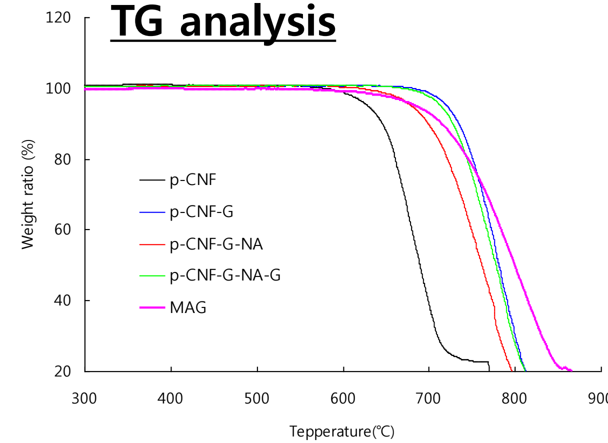
Elemental analysis



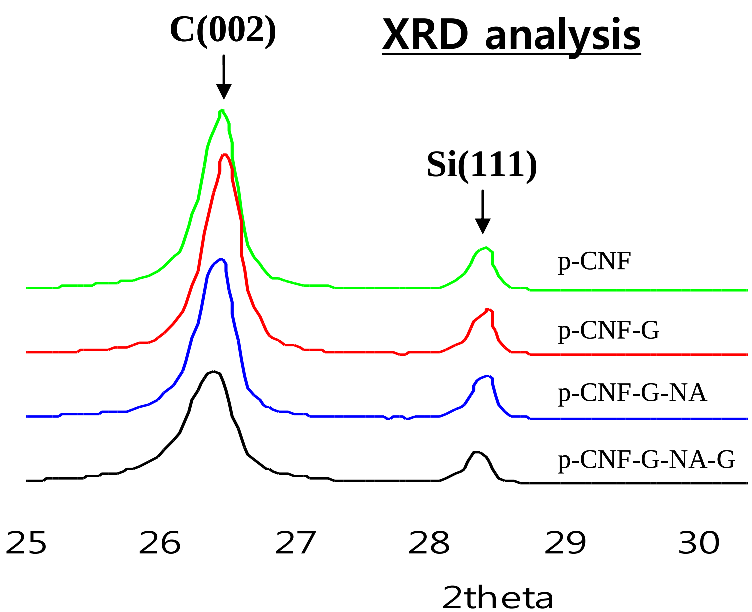
Isotherm curve



TG analysis



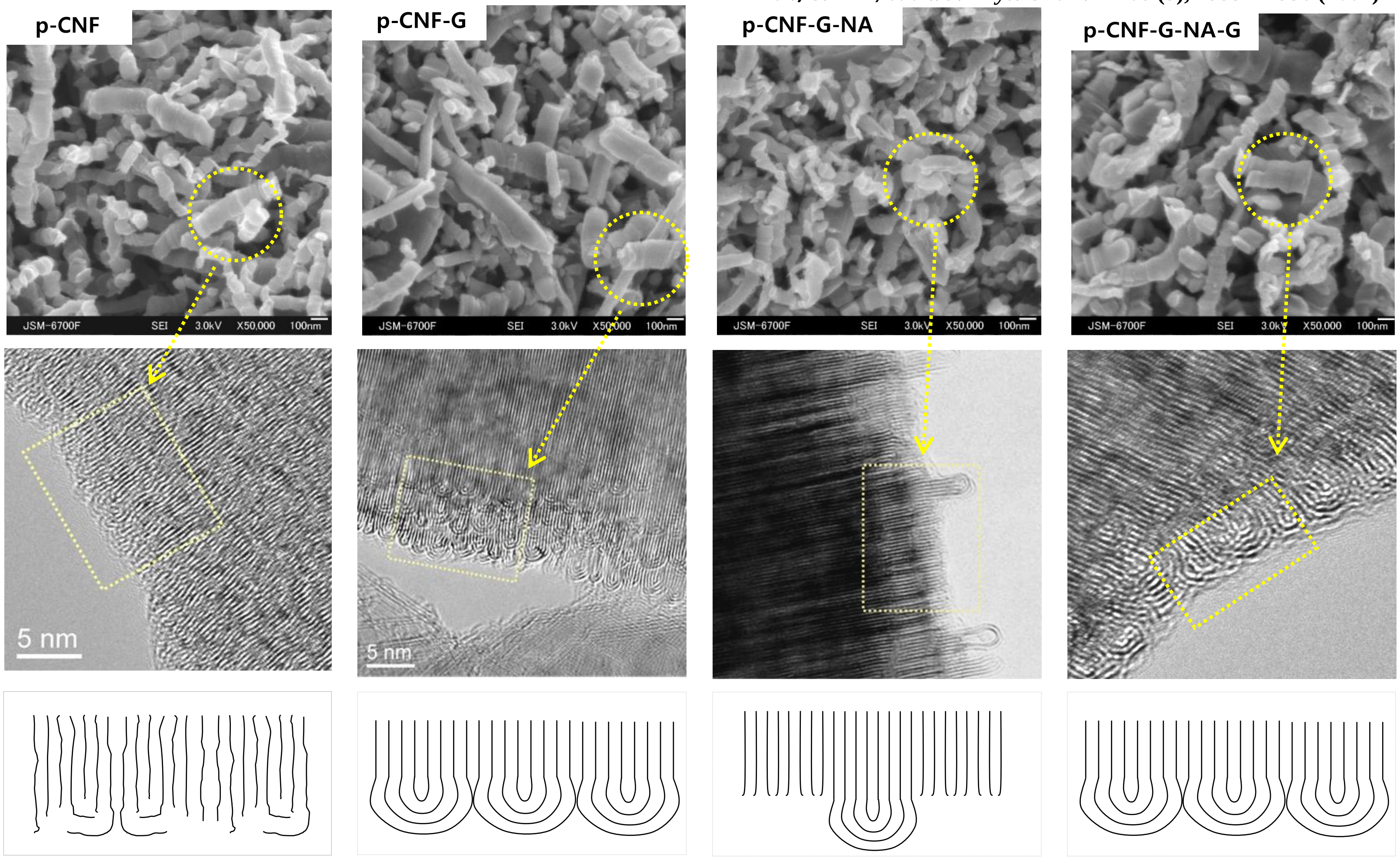
XRD analysis



	Elemental Analysis C(%)	Surface area (㎡/g)	Oxidation starting Temp.(℃)	XRD Analysis	
				D_{002} (Å)	Lc_{002} (nm)
p-CNF	98.9	67	582	3.363	29
p-CNF-G	99.8	43	680	3.365	59
p-CNF-G-NA	99.6	54	628	3.360	>100
p-CNF-G-NA-G	99.8	47	674	3.362	>100
MAG	99.8	< 4	580	3.354	99

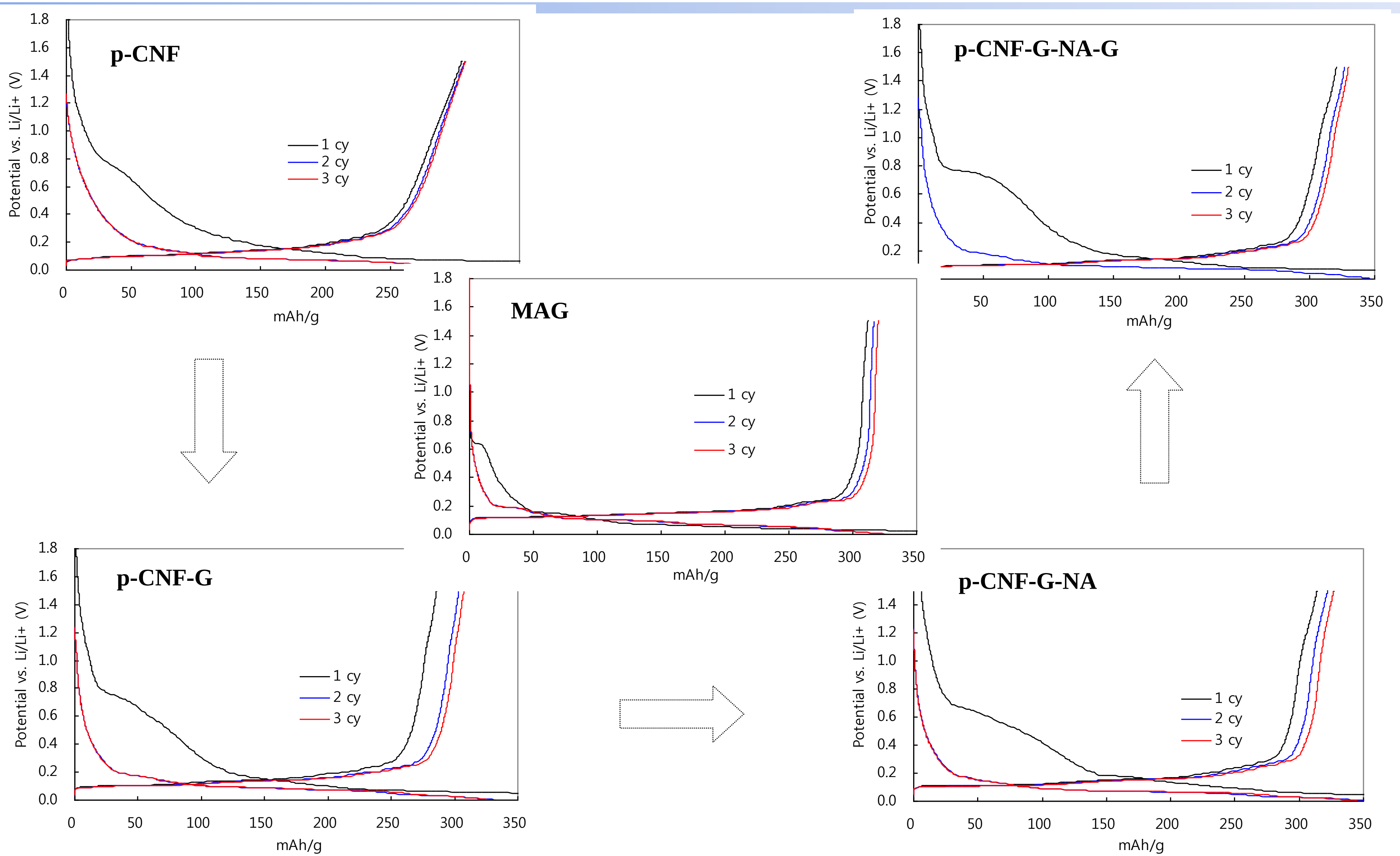
Analysis of SEM & TEM Image

Ref.) S. Lim, et al.. *J. Phys. Chem. B* 108 (5), 1533 – 1536 (2004)

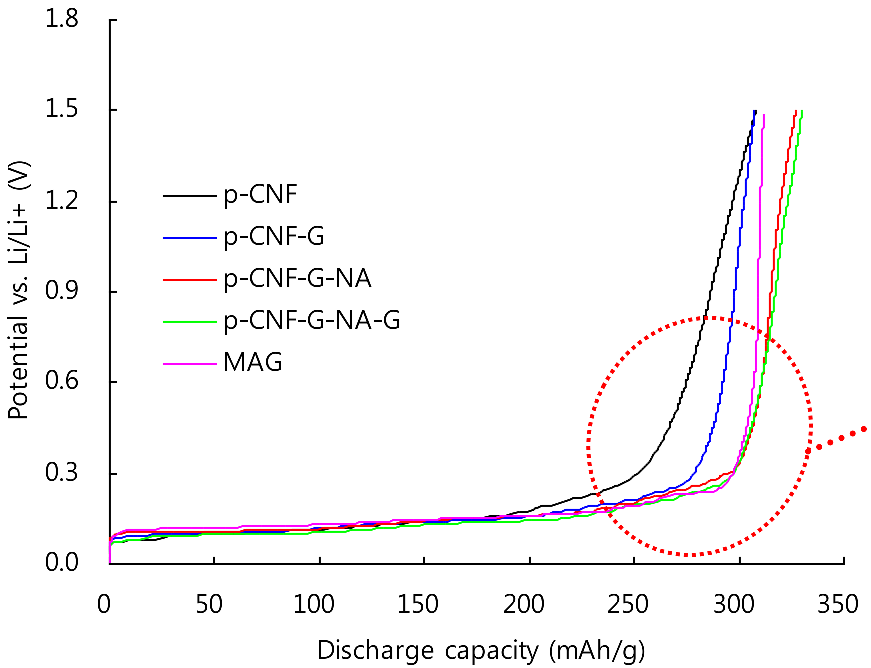


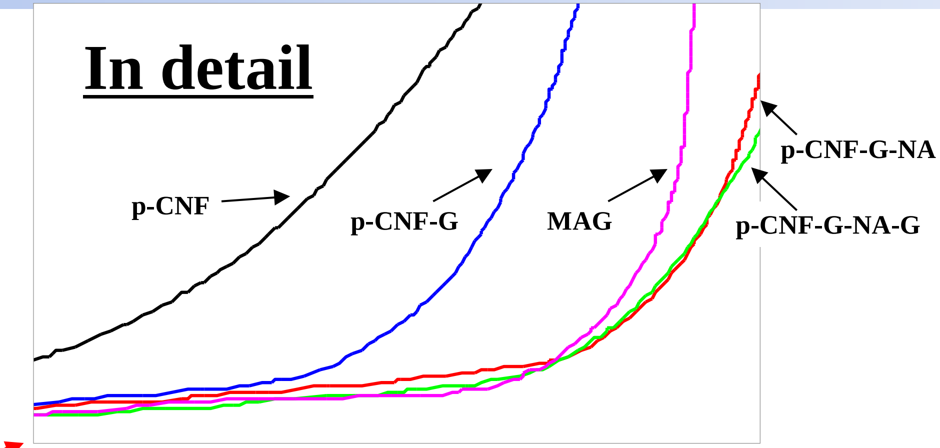
According to the graphitization degree, we found some difference at edge plane by TEM analysis

Electrochemical properties



Electrochemical properties



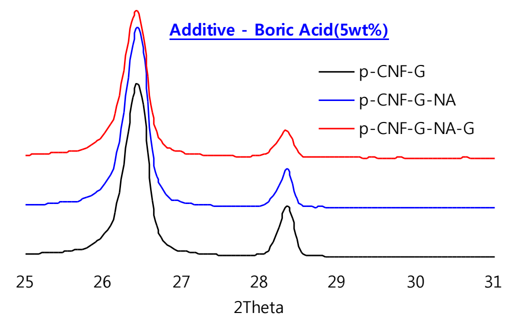


- **Discharge capacity depends on graphitization degree .**
- **p-CNF-G-NA (& -G) showed good electrochemical properties.**
- **They are almost same with MAG (synthetic graphite)**

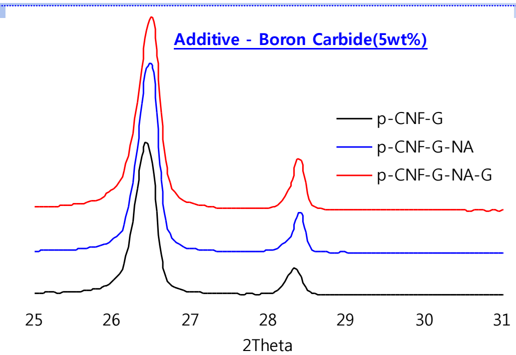
- **But, initial coulombic efficiency is low (52~60%) compared to MAG(over 80%)**

	Discharge capacity (mAh/g)			Initial coulombic efficiency(%)
	0.25V	0.5V	1.5V	
p-CNF	239	270	308	60.4
p-CNF-G	268	290	307	58.2
p-CNF-G-NA	274	308	327	52.5
p-CNF-G-NA-G	285	308	330	59.5
MAG	290	305	320	80.6

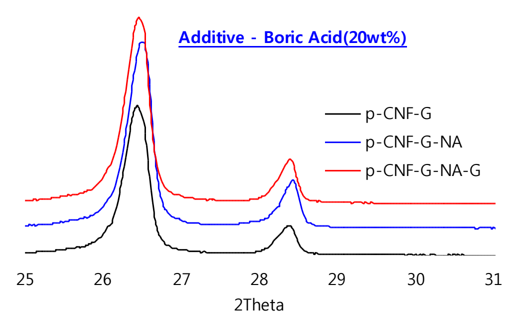
Effects of Boron Additives – XRD analysis



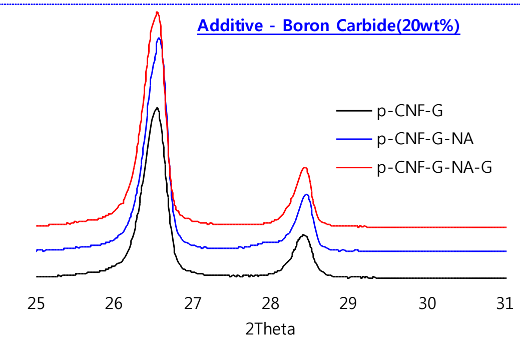
B/A (5wt%)	d002(A)	Lc002 (nm)
p-CNF-G	3.357	> 100
p-CNF-G-NA	3.356	85.4
p-CNF-G-NA-G	3.356	75.4



B/C (5wt%)	d002(A)	Lc002 (nm)
p-CNF-G	3.355	> 100
p-CNF-G-NA	3.359	82.2
p-CNF-G-NA-G	3.357	> 100



B/A (20wt%)	d002(A)	Lc002 (nm)
p-CNF-G	3.357	> 100
p-CNF-G-NA	3.361	> 100
p-CNF-G-NA-G	3.358	> 100



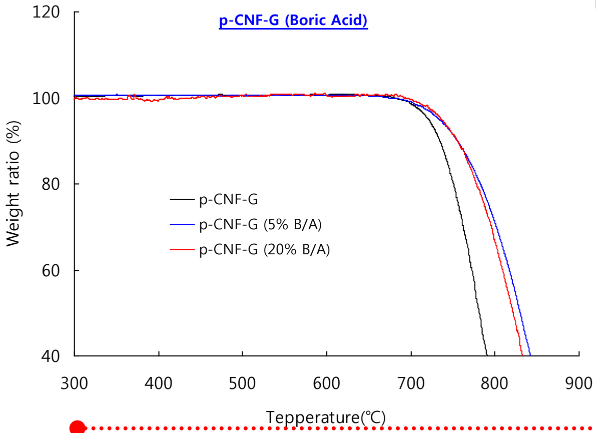
B/C (20wt%)	d002(A)	Lc002 (nm)
p-CNF-G	3.355	> 100
p-CNF-G-NA	3.355	> 100
p-CNF-G-NA-G	3.355	66.7

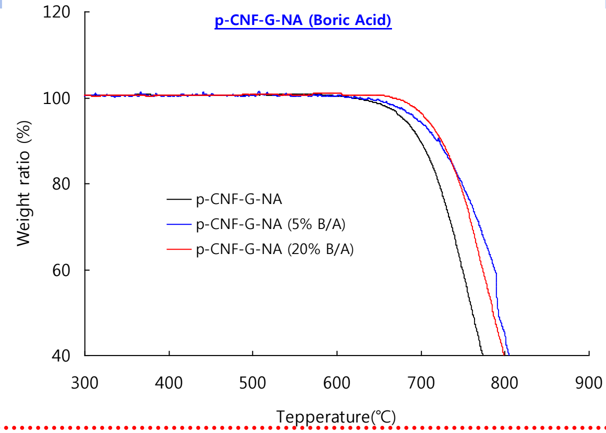
No additive	XRD Analysis	
	D_{002}(Å)	Lc_{002}(nm)
p-CNF	3.363	29
p-CNF-G	3.365	59
p-CNF-G-NA	3.360	>100
p-CNF-G-NA-G	3.362	>100

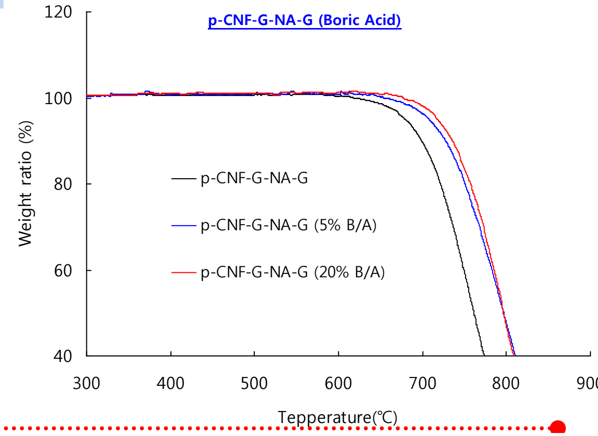
Compare to no additives,

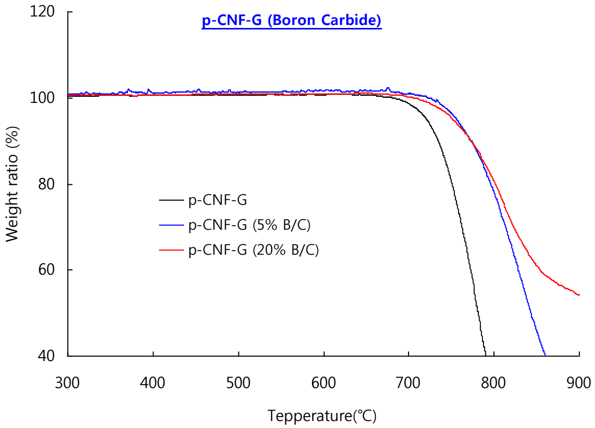
- Added elements had an effect on increasing graphitization degree.
- Graphitization degree was increased more by B/C addition.

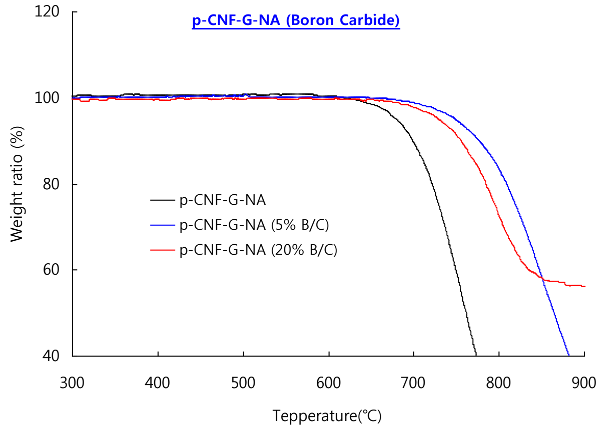
Effects of Additive – TG analysis

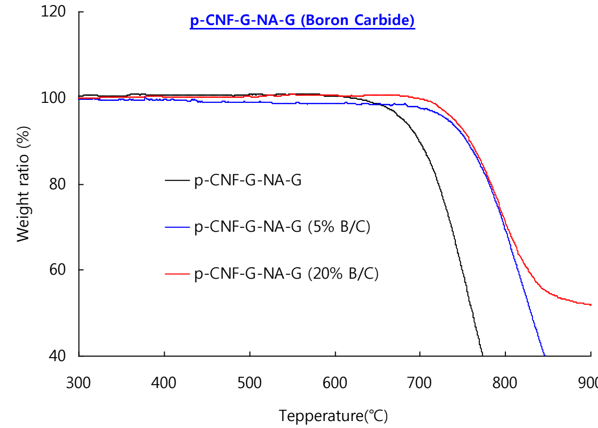








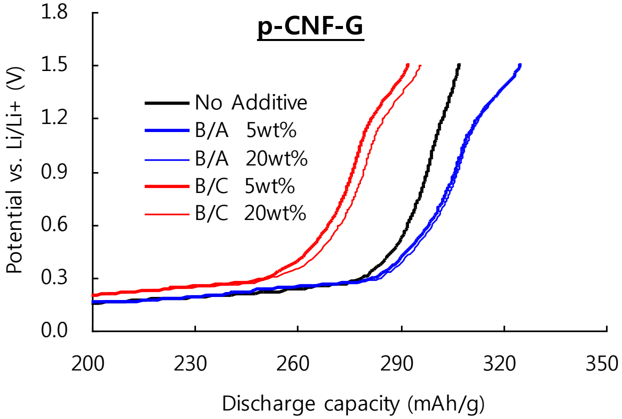


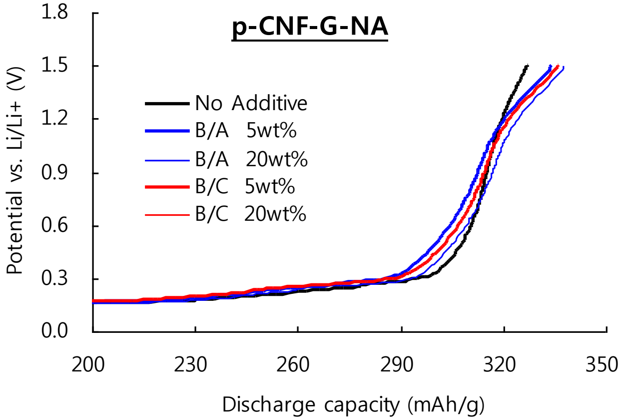


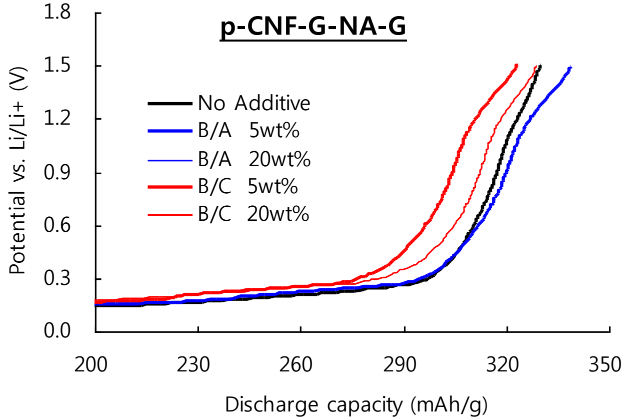
	Oxidation starting temperature (℃)		
	p-CNF-G	p-CNF-G-NA	p-CNF-G-NA-G
No additive	680	628	674
B/A (5wt%)	686	634	661
B/A (20wt%)	697	670	683

	Oxidation starting temperature (℃)		
	p-CNF-G	p-CNF-G-NA	p-CNF-G-NA-G
No additive	680	628	674
B/C (5wt%)	727	671	687
B/C (20wt%)	706	659	700

Effects of Additive – Electrochemical properties



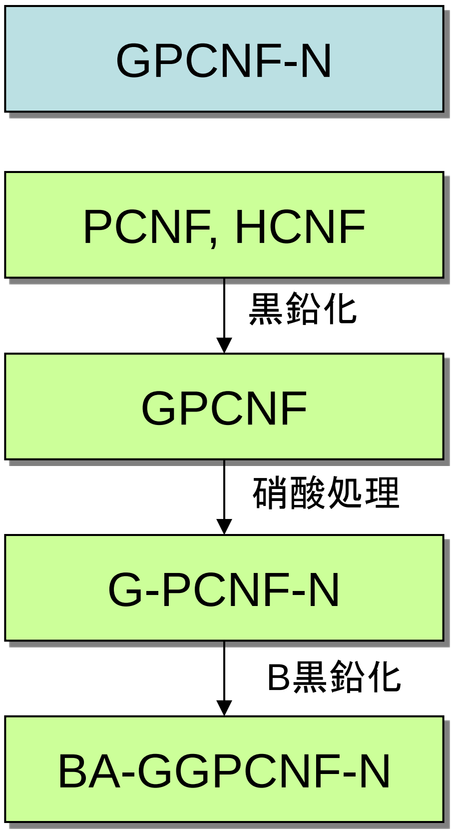




	p-CNF-G				p-CNF-G-NA				p-CNF-G-NA-G			
	Discharge capacity (mAh/g)			Coulombic efficiency (%)	Discharge capacity (mAh/g)			Coulombic efficiency (%)	Discharge capacity (mAh/g)			Coulombic efficiency (%)
	0.25V	0.5V	1.5V		0.25V	0.5V	1.5V		0.25V	0.5V	1.5V	
No additive	268	290	307	58.2	274	308	327	52.5	285	308	330	59.5
B/A (5wt%)	259	294	325	61.1	260	300	334	58.6	276	308	339	58.6
B/A (20wt%)	261	295	325	77.3	266	303	338	70.3	-	-	-	-
B/C (5wt%)	233	265	292	66.9	259	303	336	65.7	261	293	323	60.3
B/C (20wt%)	227	268	296	72.7	-	-	-	-	259	300	329	72.2

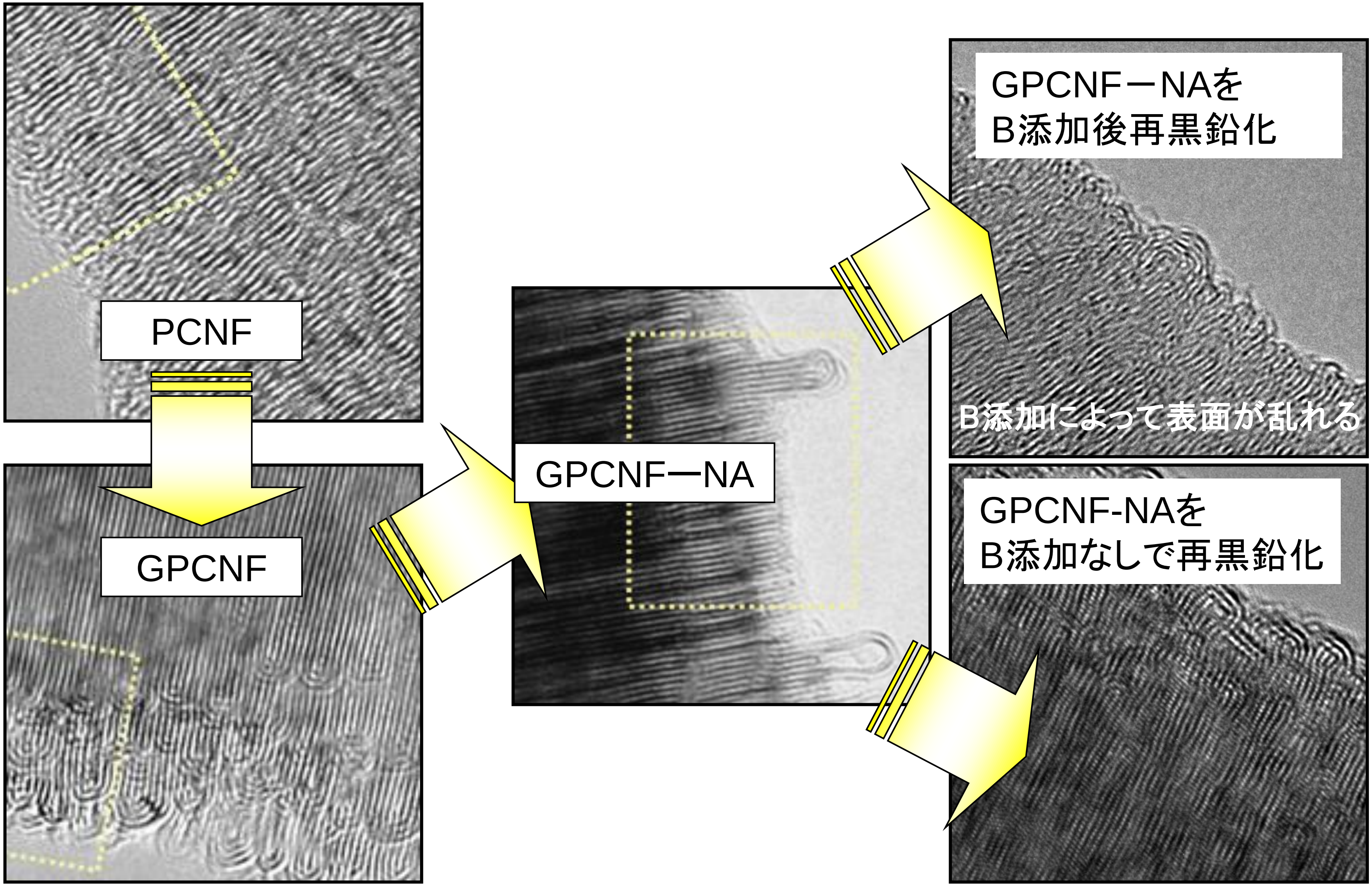
Highly graphitic CNFs

- CNF of similar graphitic properties with Natural Graphite
- CNT usually shows low graphitic properties
- Conductive materials or supports for heterogeneous catalysts

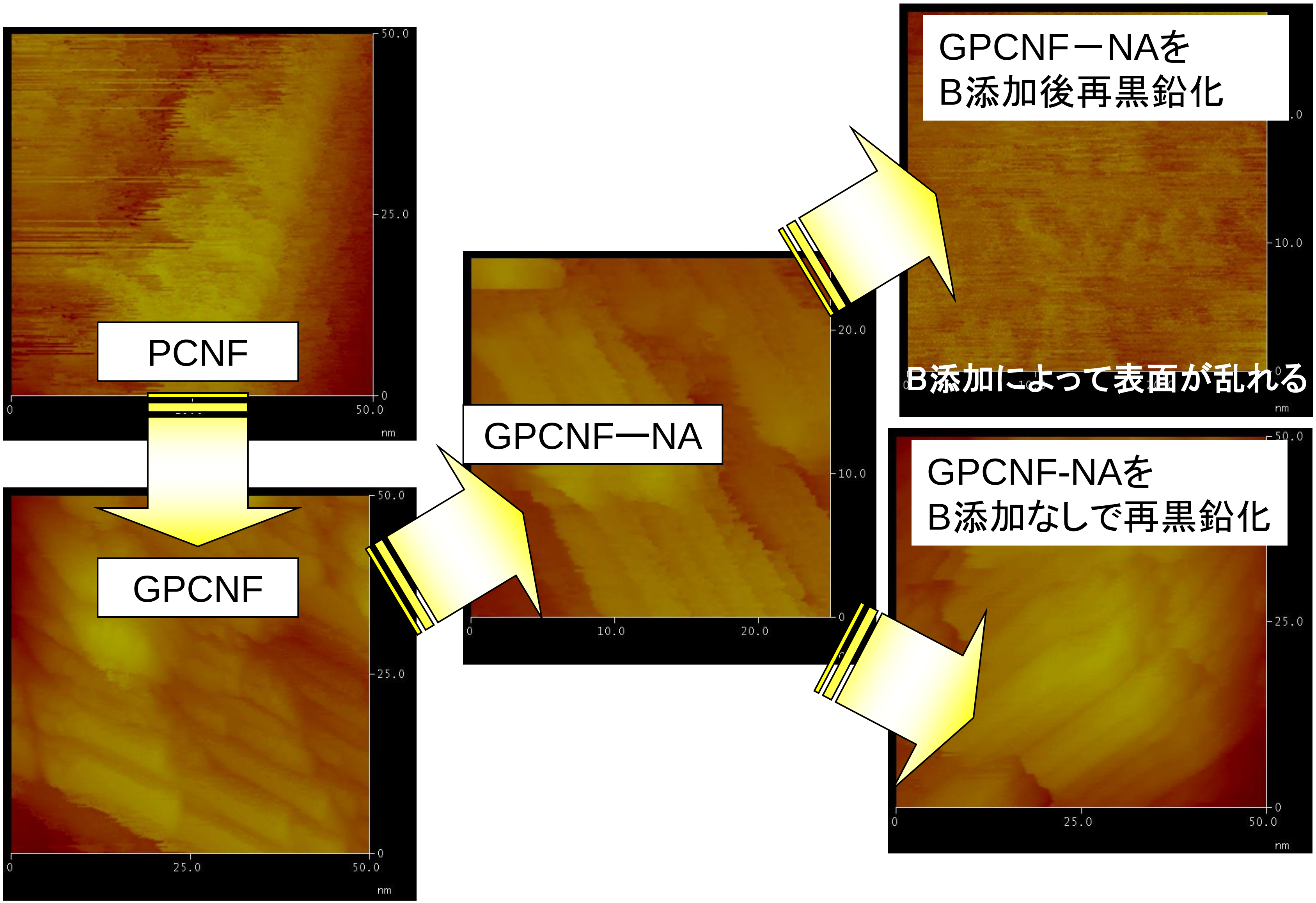


	Preparation conditions	d_{002} (nm)	Lc(002) (nm)
PCNF	Fe catalyst, 620, CO/H2 : 4/1	0.3365	72
G-PCNF	2800℃ heat treatment of PCNF	0.3364	83
G-PCNF-N	30% HNO3 treatment of GPCNF for 50℃, 8hs	0.3362	152
GG-PCNF-N	2800℃ heat treatment of GPCNFN	0.3362	106
BA-G-PCNF	Boric acid added heat treatment of PCNF	0.3359	115
BA-GG-PCNF-N	30% HNO3 treatment of GPCNF for 50℃, 8hs Boric acid added heat treatment	0.3357	377
BC-G-PCNF	Boron carbide added heat treatment of PCNF	0.3354	178
BC-GG-PCNF-N	30% HNO3 treatment of GPCNF for 50℃, 8hs Boron carbide added heat treatment	0.3354	167

TEM of GPCNF（B addition）

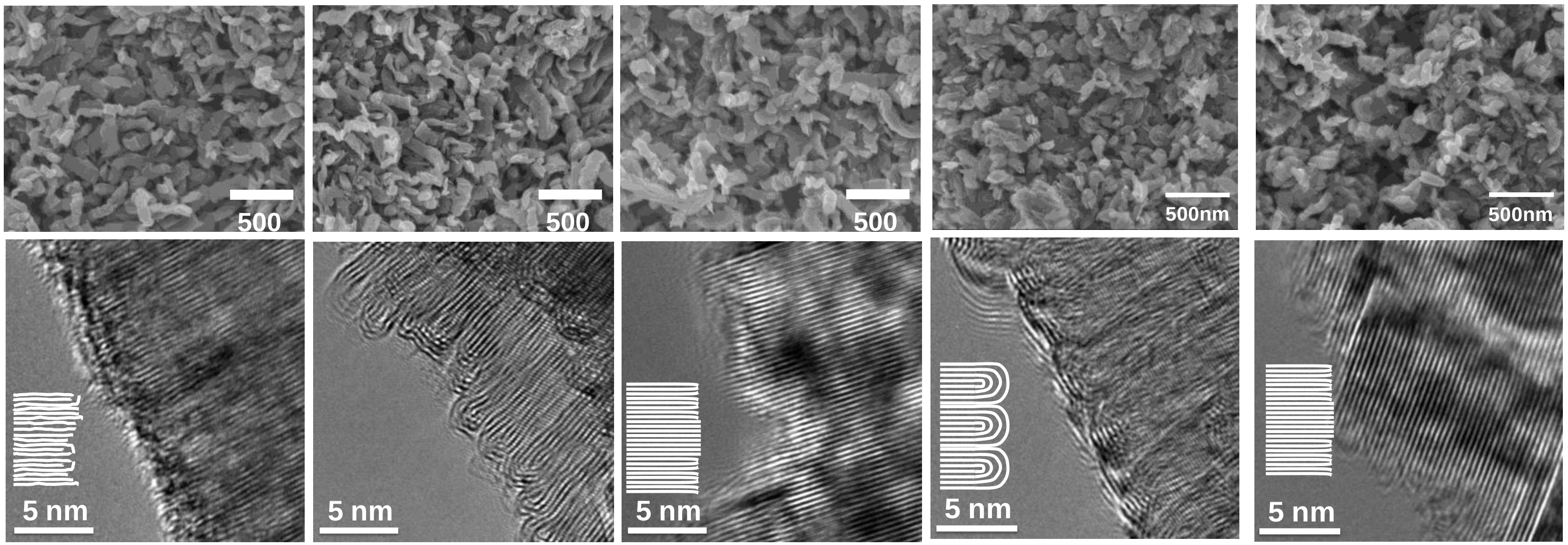


STM of GPCNF（B addition）

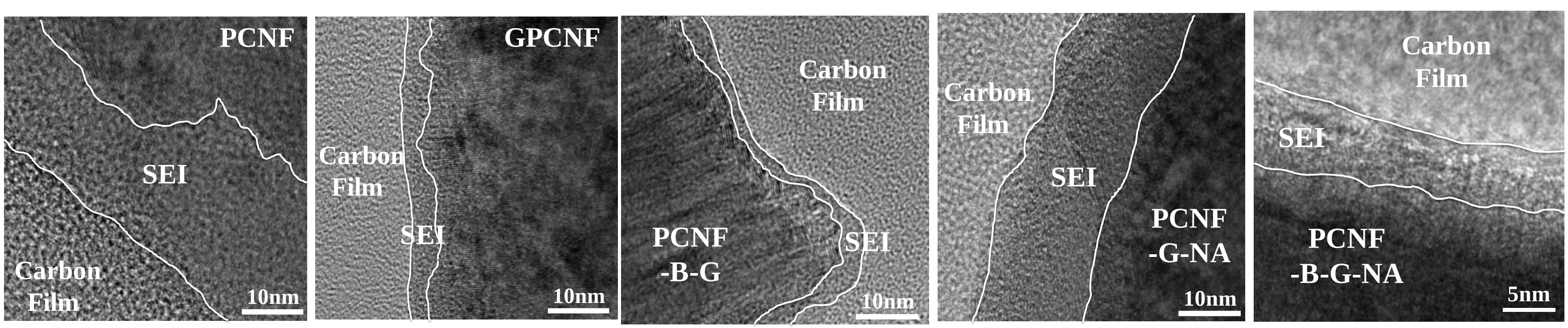


Microscopic observation of PCNFs

PCNF | PCNF-G | PCNF-G-NA | PCNF-B-G | PCNF-B-G-NA



PCNF | PCNF-G | PCNF-B-G | PCNF-G-NA | PCNF-B-G-NA

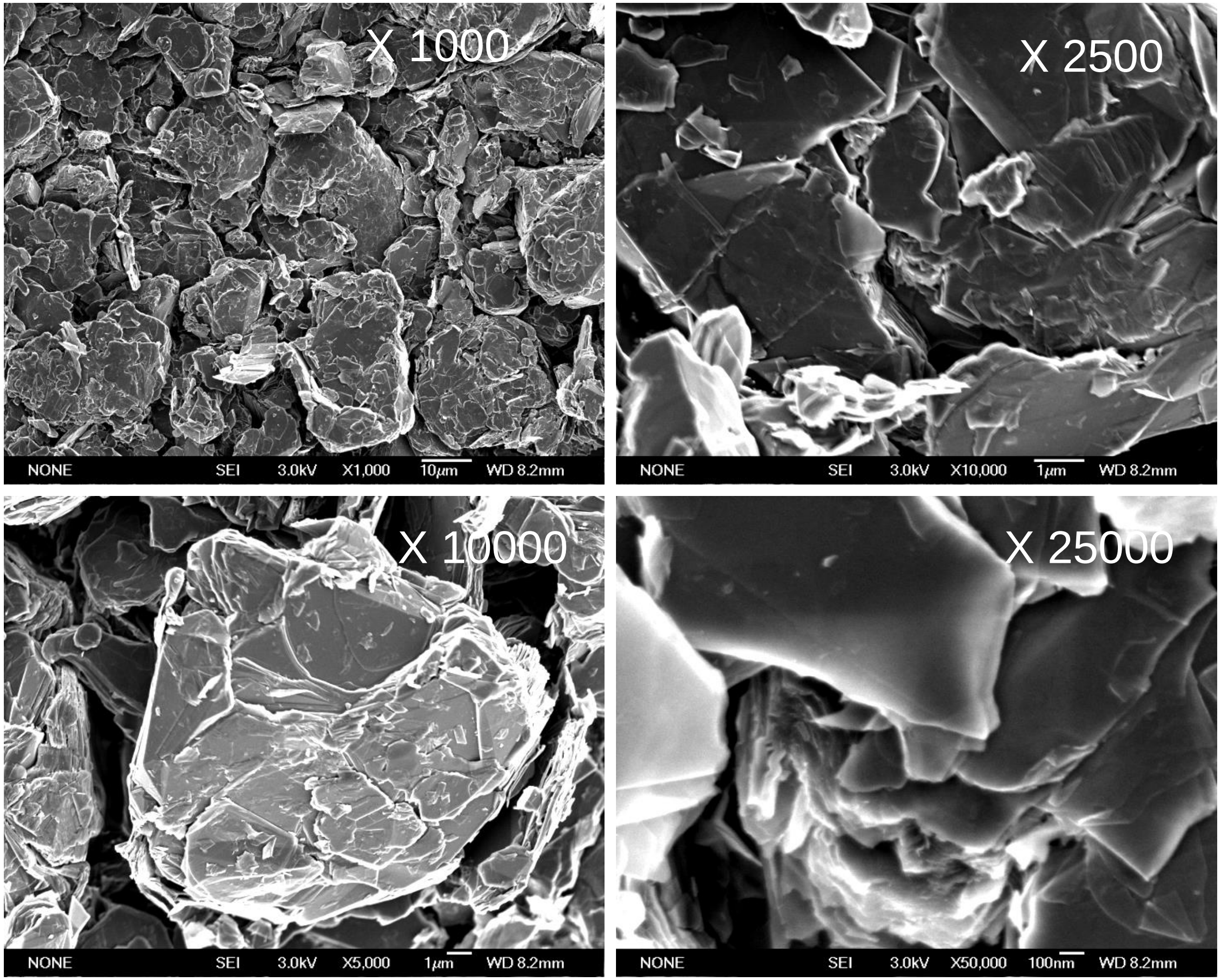


SEI thickness : 15 ~ 25 nm | SEI thickness : 3 ~ 5 nm | SEI thickness : 2 ~ 5 nm | SEI thickness : 14 ~ 16 nm | SEI thickness : 5 ~ 7 nm

J PHYS CHEM B 108 (5): 1533-1536 FEB 5 2004

Typical Synthetic Graphite

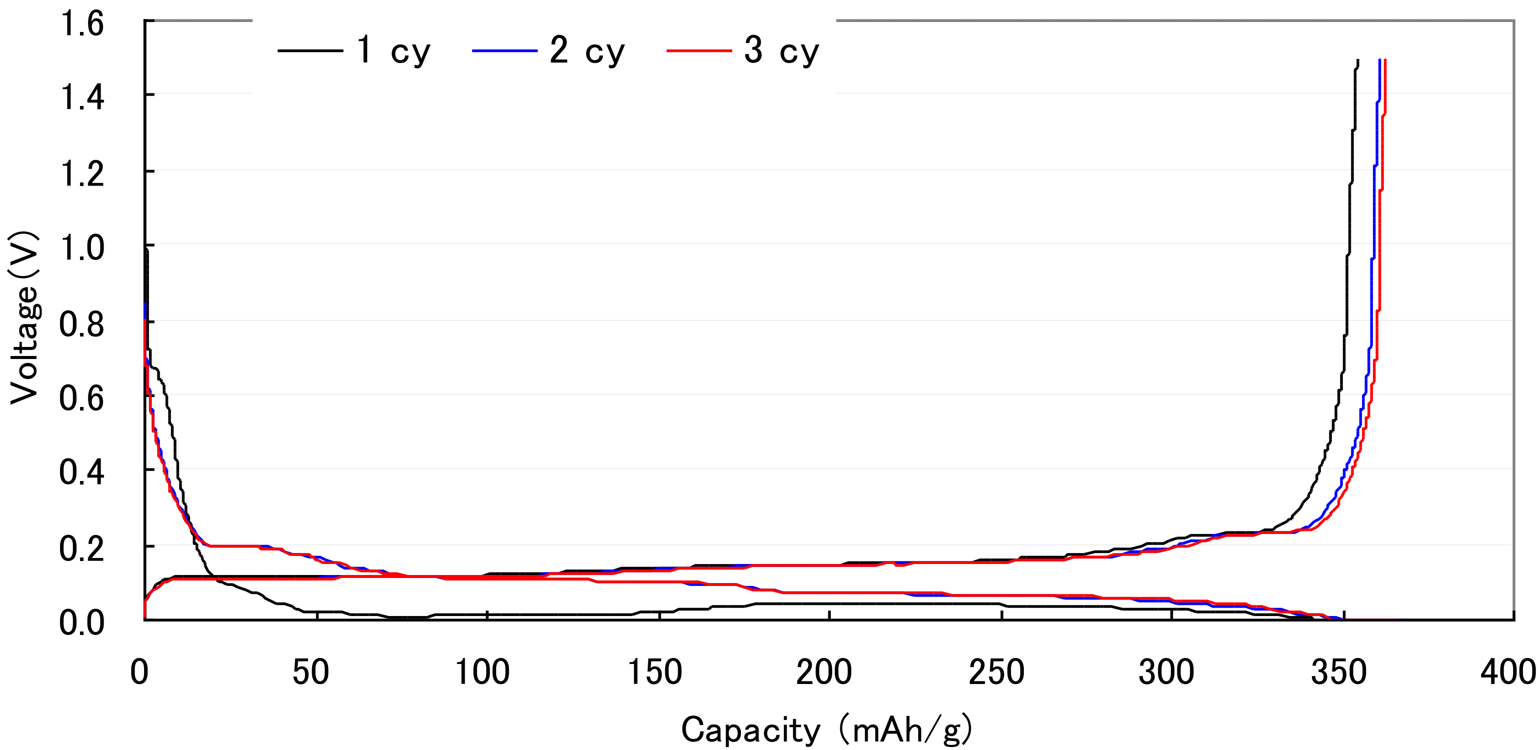
(MAG; Hitachi Chemical Co.)



Typical Synthetic Graphite

(MAG; Hitachi Chemical Co.)

0.1C, Half Cell Test, LiPF6 1M, EC+DEC



Unique application to CNF structure

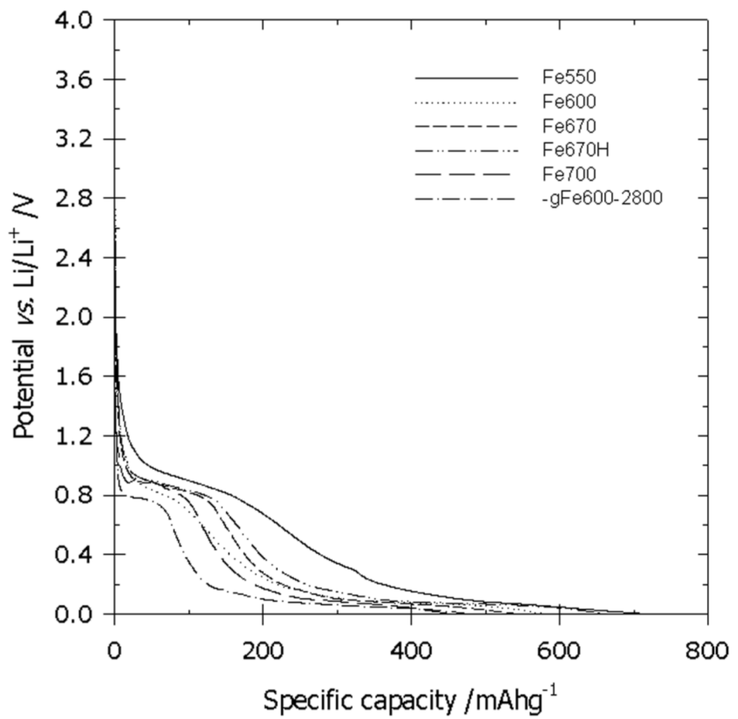
Electrode Materials for Li-ion Batteries

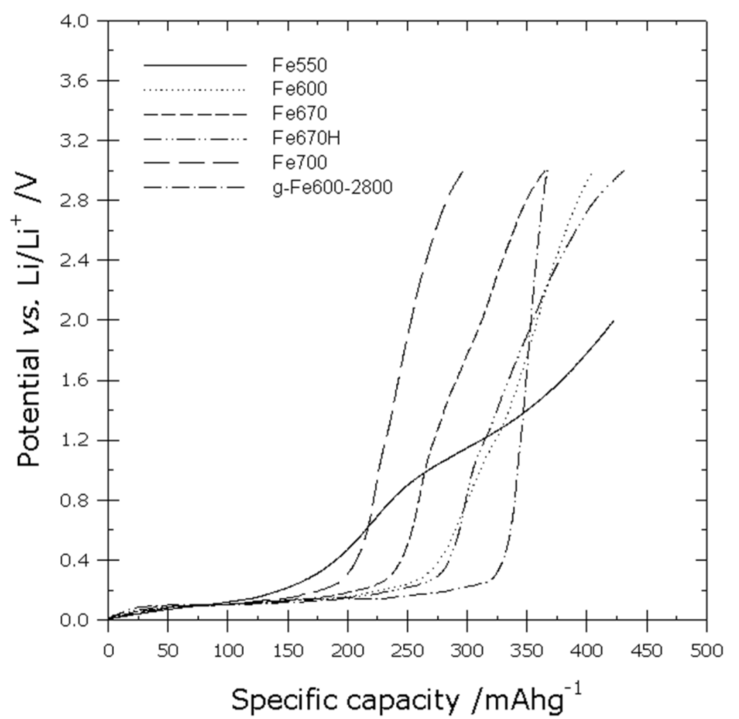
Application sections	Energy sources for the next generation mobile machines：PC, Small TV, PDA, EV, CC
High Capacity	2900mAh/18650 type → 3600mAh/18650 type Over 2 times capacity should be improved in anode materials
High Power	CNF + Graphite + ? : for high power Demands for high speed charge and discharge：Hybrid Vehicle, UPS, PC

Applying CNF Composites for Problems Solving

Unique application to CNF structure

Electrode Materials for Li-ion Batteries (Basic Property)



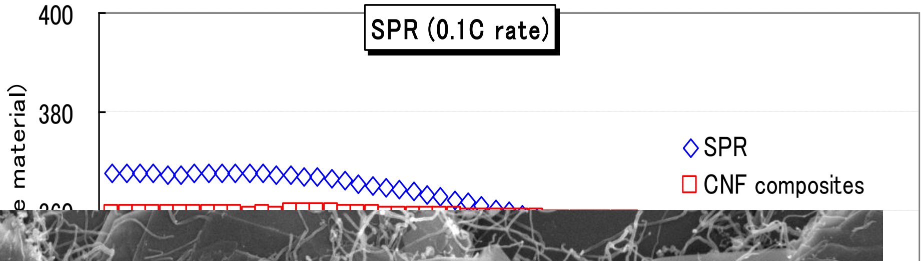


100% of PC Solvent for Electrolyte can be used to P-CNF anodic carbon

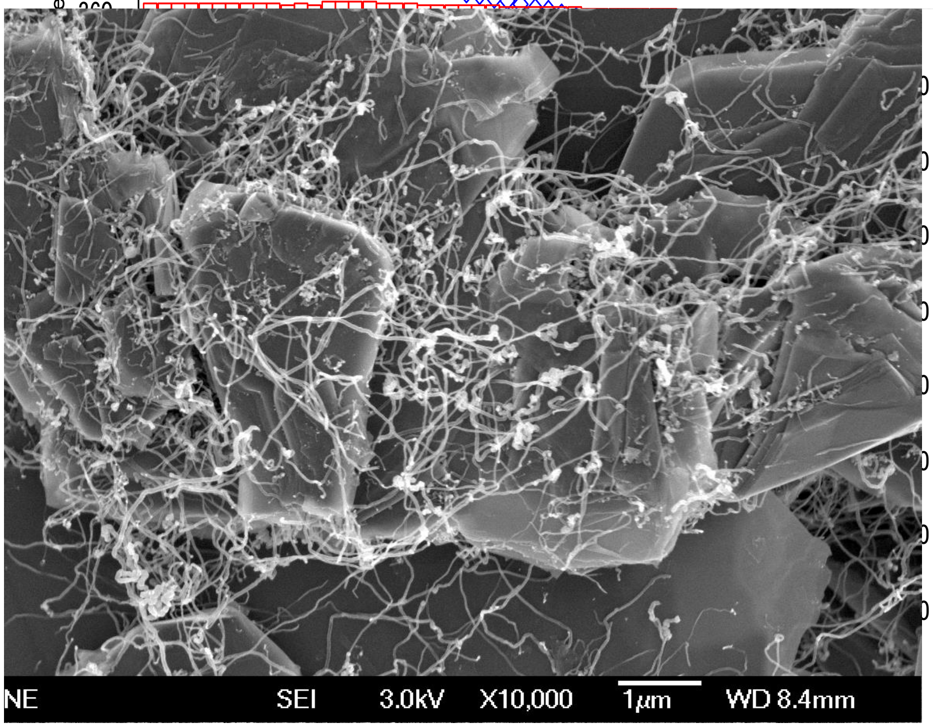
- Development of anodic composite materials for high power using very small crystallinity (Containing the modification of natural graphite)
- Development of anodic composite materials for ultra high capacity using CNF composition (Now on the field testing)

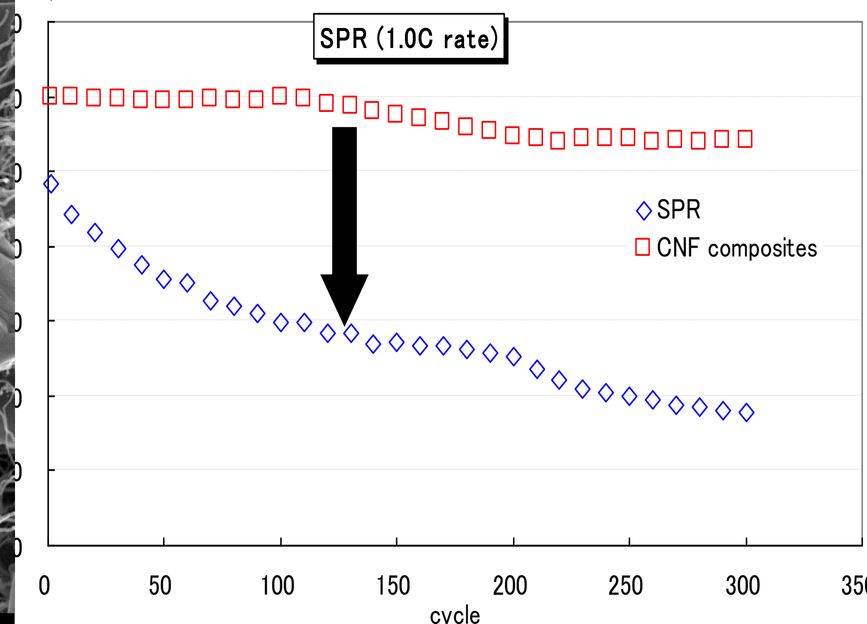
Rate Characteristics of SPR & SPR-CNF Composites

Half cell test: SPR(Natural graphite: Li metal; Coin Cell, LiPF6 (EC+DEC)



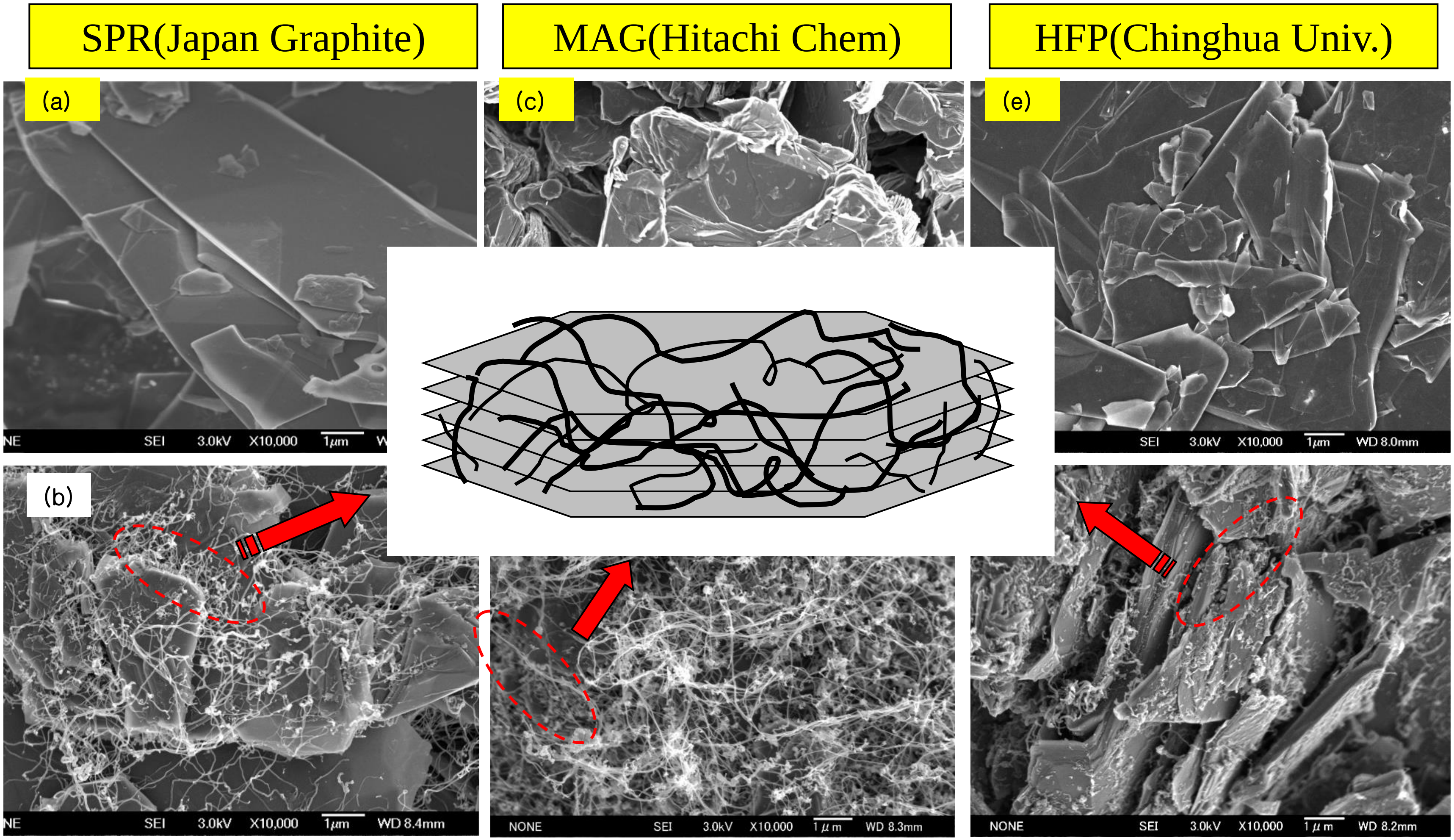
CNF composites are more stable both 0.1C and 1.0C rate





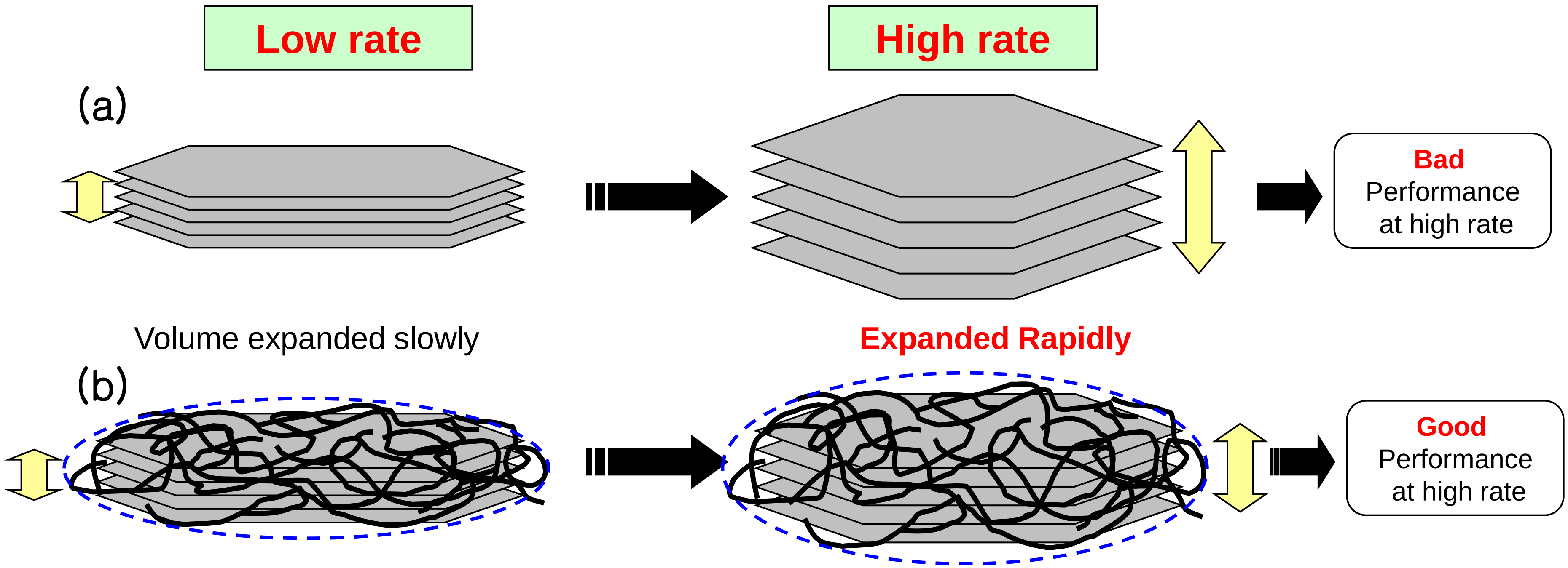
Cycle of discharge capacity at different rate(0.1C, 1.0C rate) of SPR and SPR-CNF composites

SEM photographs of graphites and CNF-graphite composites



SEM images of SPR(a), MAG(c), HFP(e), and their CNF composites(b, d, f)

Schematic models of charge states



CNF relaxes the electrode breaking down which is induced by graphite expansion → **CNF makes effective steric effect for protecting electrode**

(a) Graphite **(b) Graphite - CNF composite**

Anode for Next Generation

- **Glassy Carbon**;

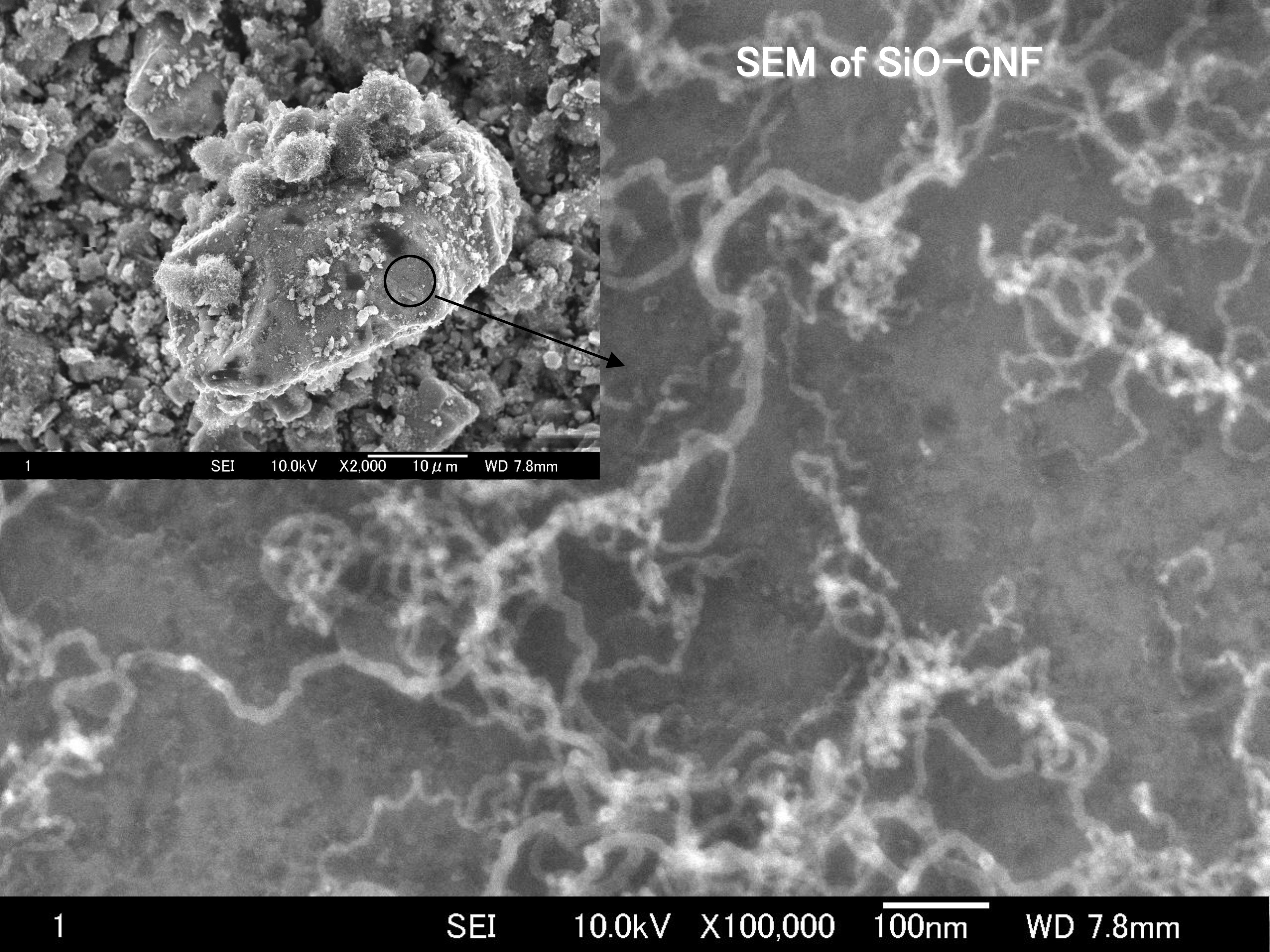
  Larger Capacity per Weight

  → Larger Capacity per Volume

- **Non-carbon Materials**;

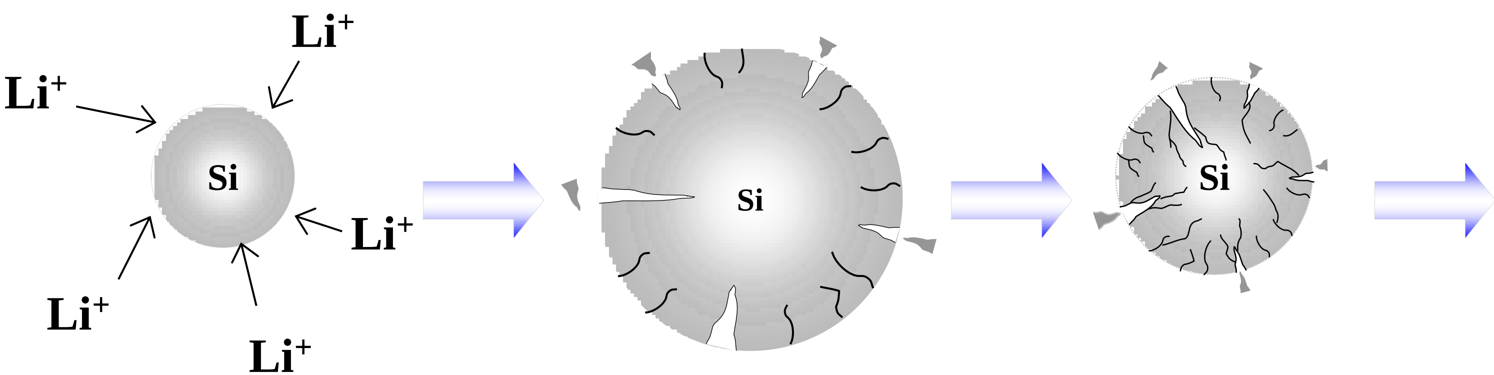
  Si Materials
  Sn Materials } Large Expansion

  → Poor Cycle Stability


SEM of SiO-CNF
1 SEI 10.0kV X2,000 10 μm WD 7.8mm
1 SEI 10.0kV X100,000 100nm WD 7.8mm

Structural Problem in CH-DCH processes

Li^+ insertion → **Cracking** → **Small Particle**



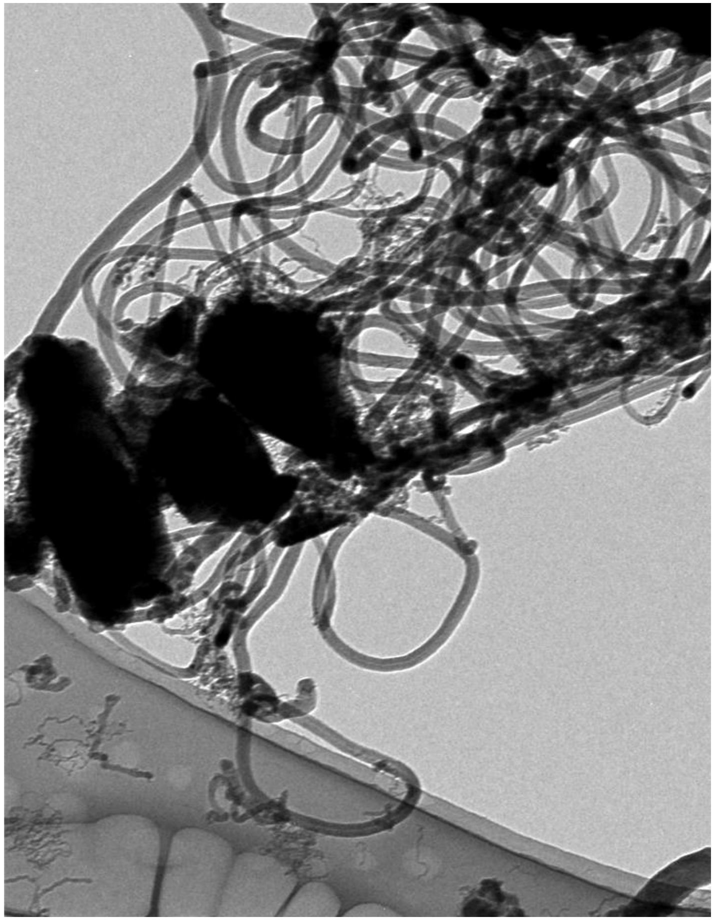
Poor Cycle Life

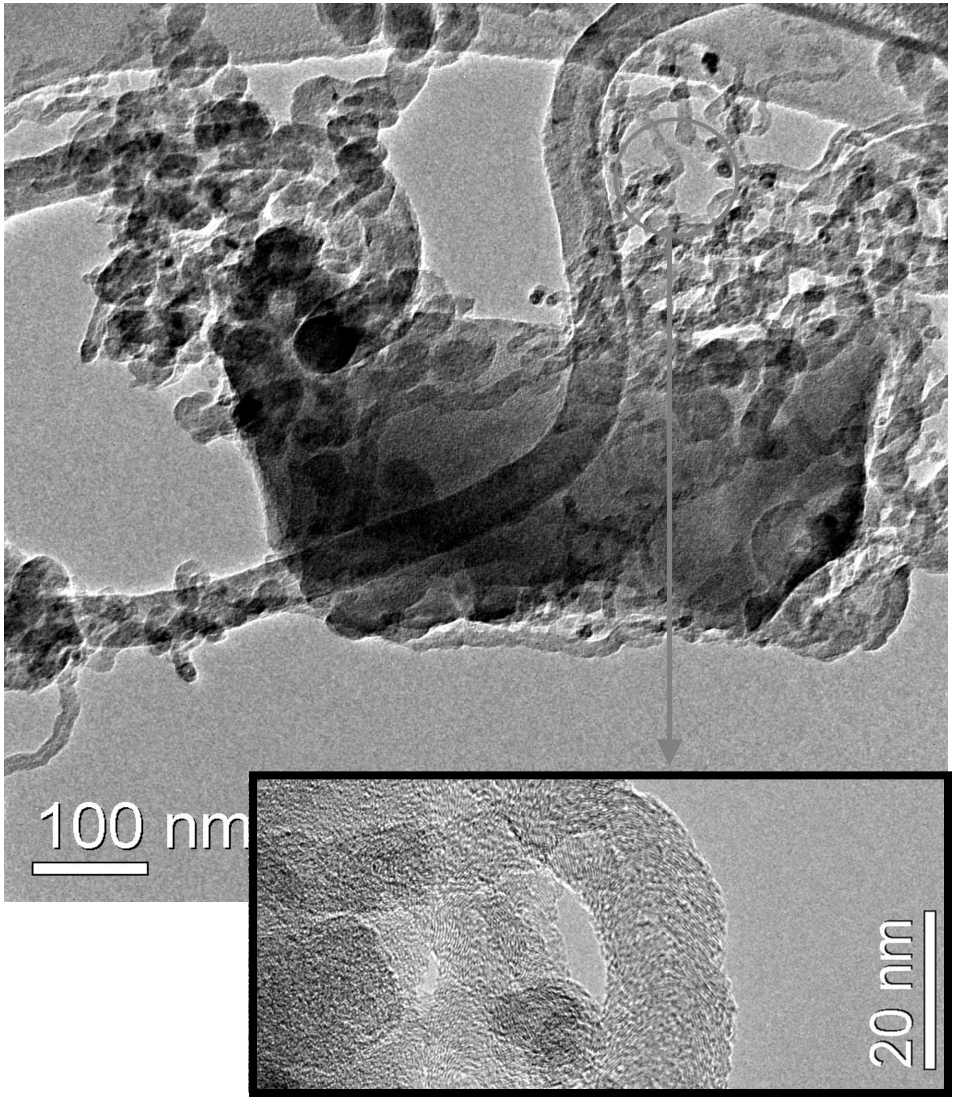
Volume expansion

Si particles became smaller and smaller by cycling

Increasing resistance bet. Si and current collector
Capacity was decreased

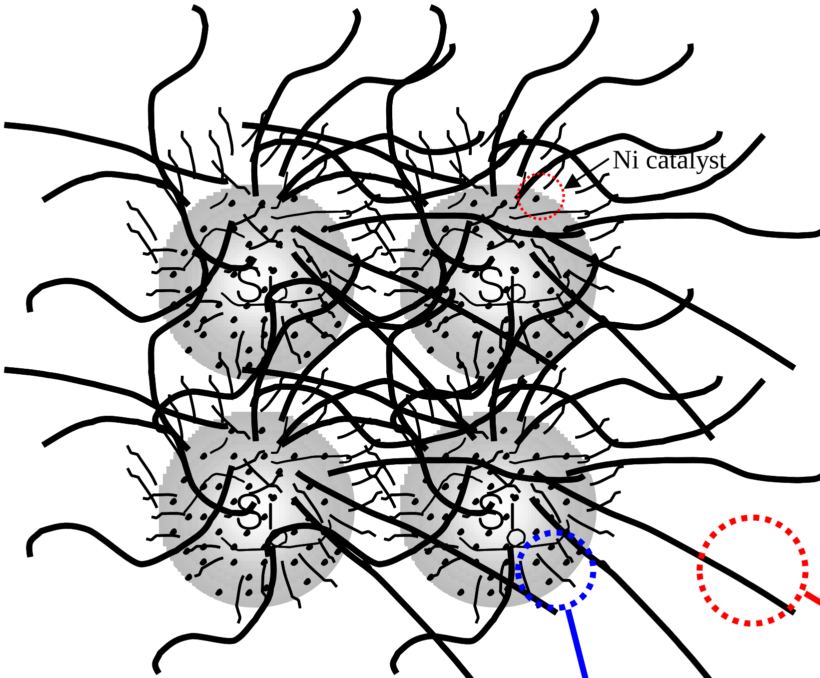
TEM images of Si-CNF composites

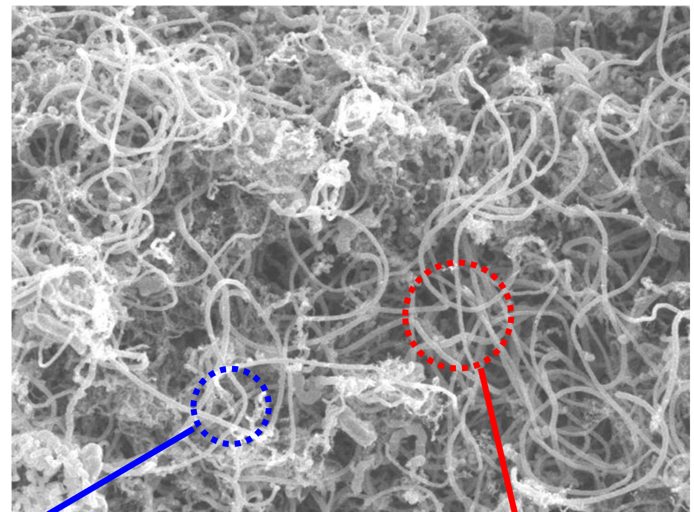




Schematic Model of CNF synthesized Si

Conjectured mechanism of composed CNF to improve electrochemical properties





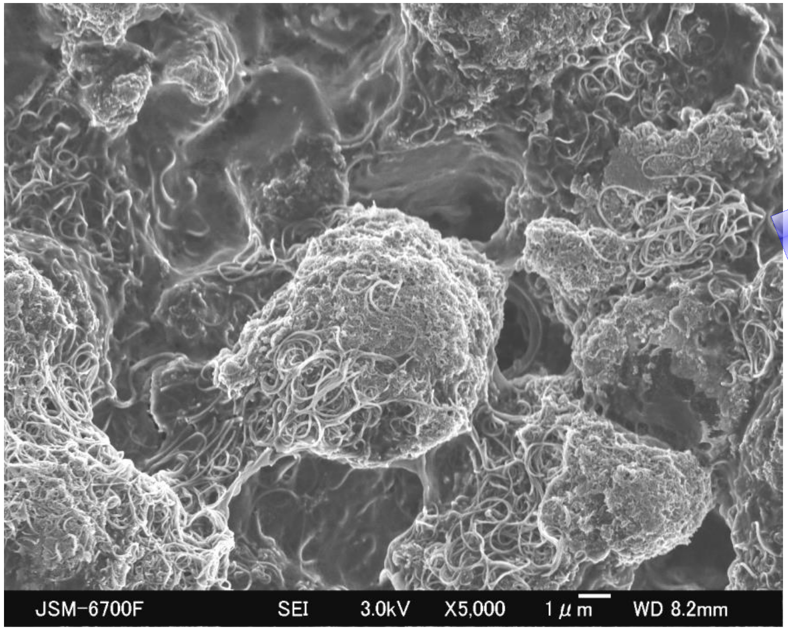
1. Thin CNFs

Thickness : 10~50㎚
Seems Like Ivy
Afford the **electric conductive path** of Si powder.

2. Thick CNFs

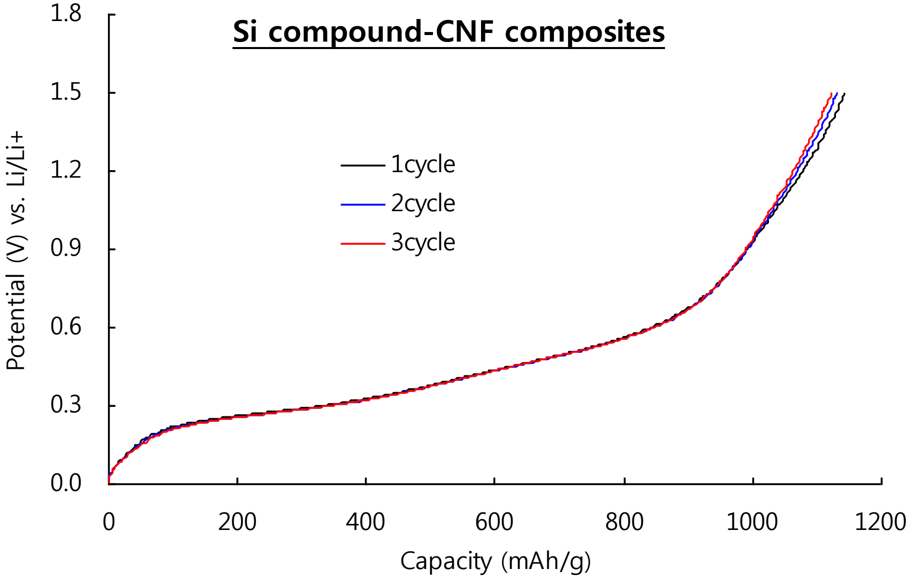
Thickness : 100~300㎚
Channeling effect between the particles
⇒ Compose conductive network

Schematic Model of CNF synthesized Si



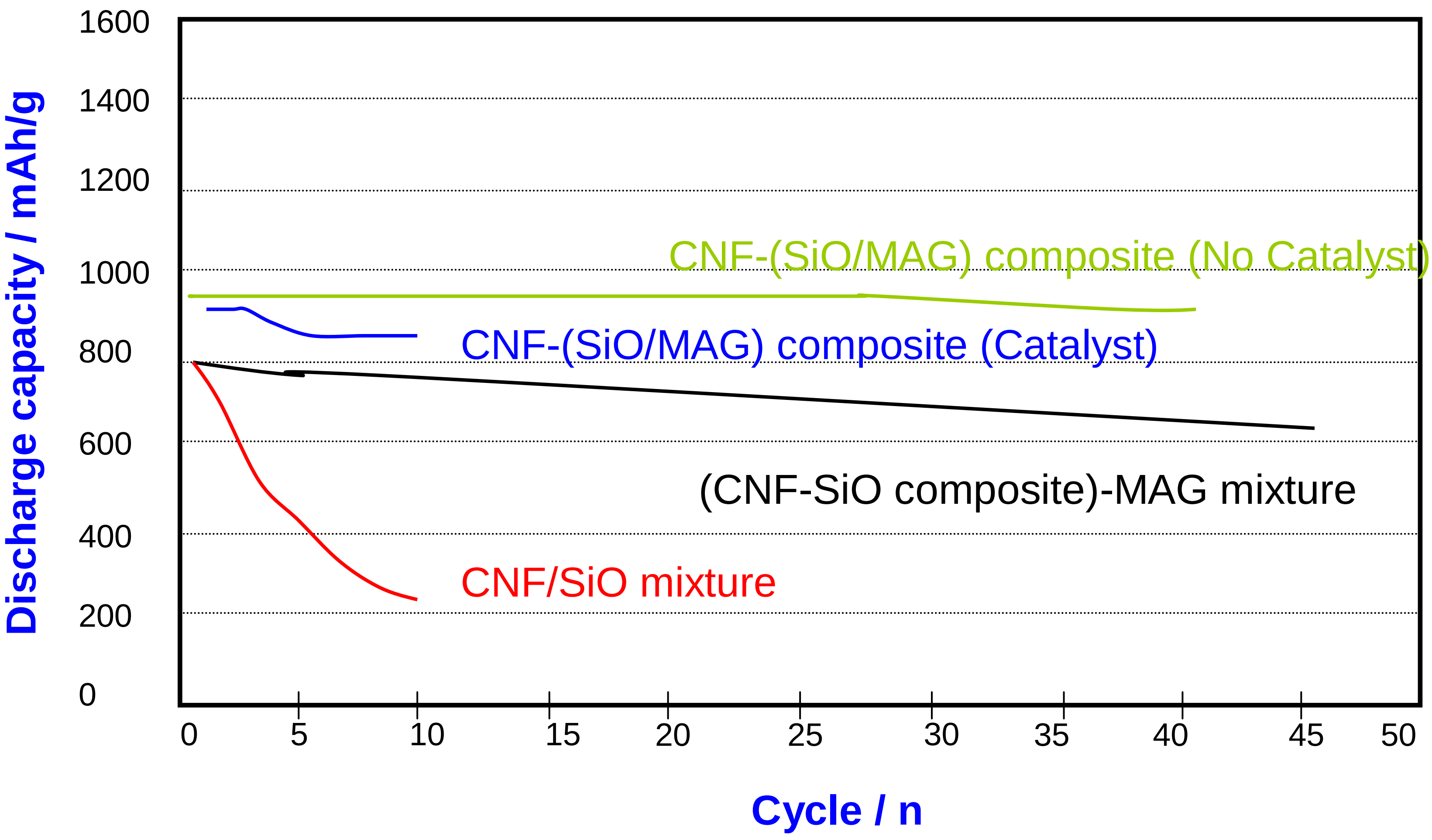
3. Steric effect

Can establish the relaxation spaces for relieving volume expansion in charge process

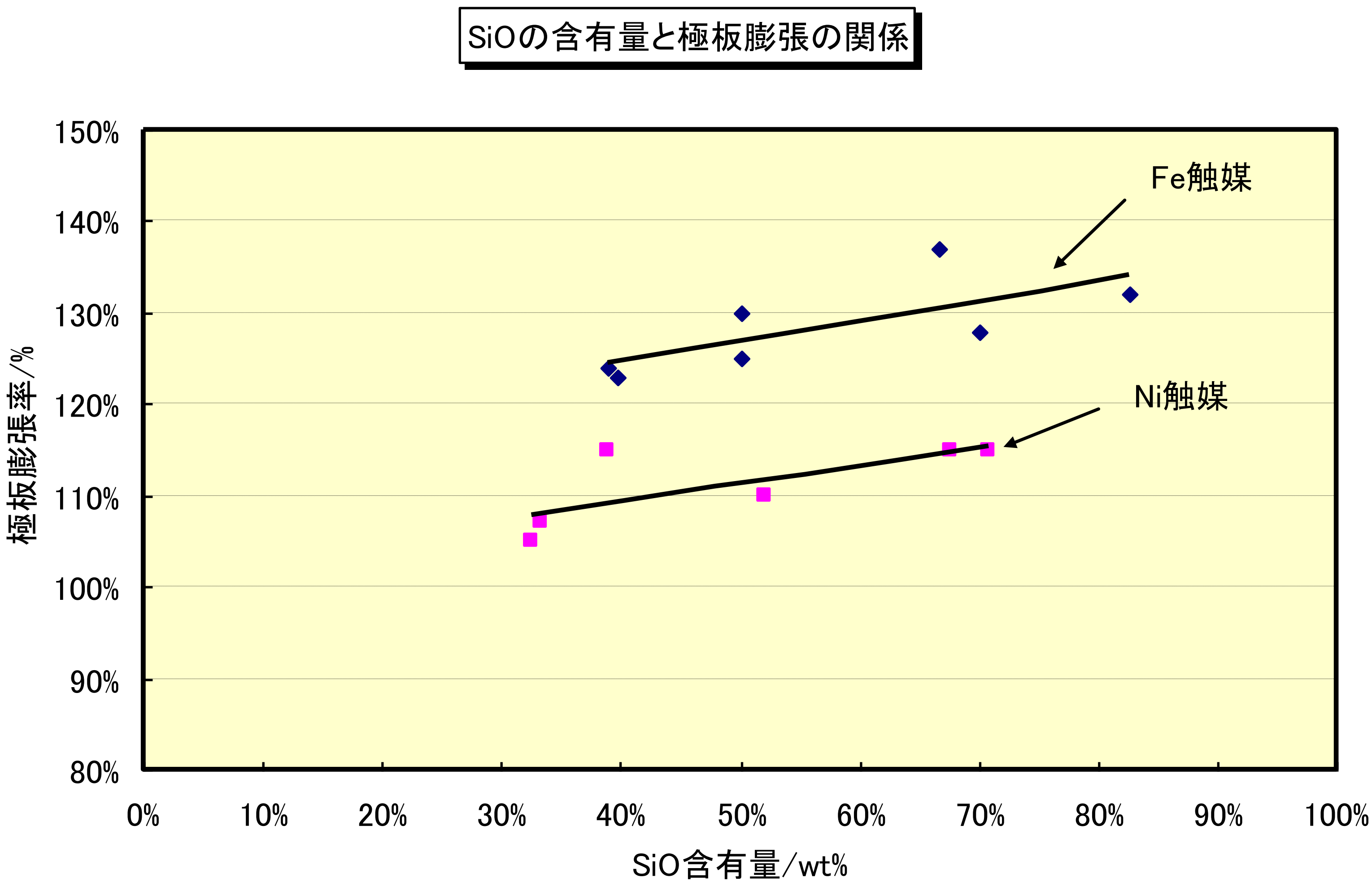


Optimization of Si -CNF composition Shows almost perfect cycle life.

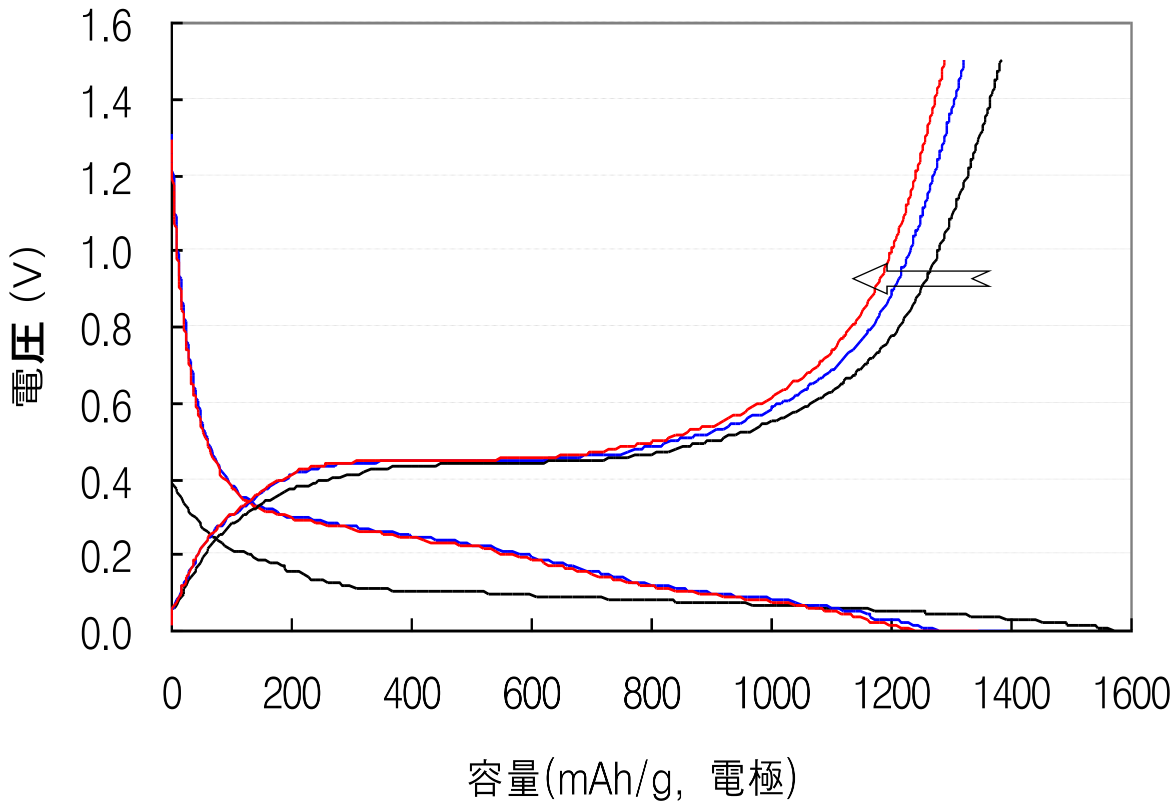
Cycle ability

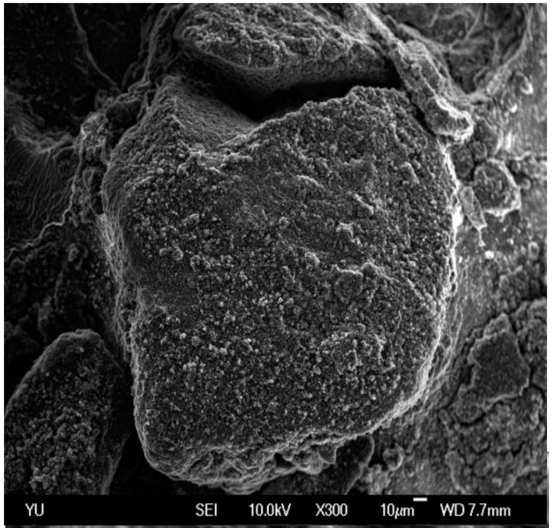


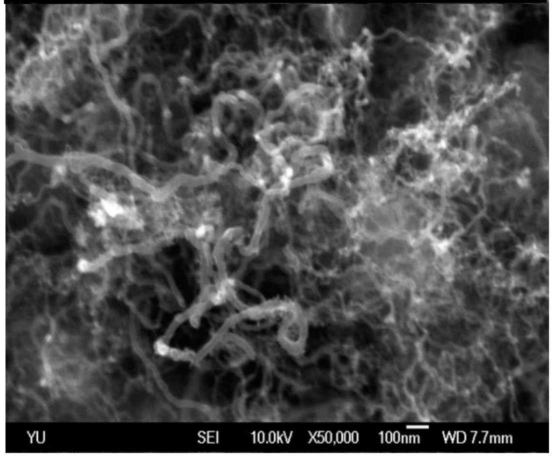
Expansion Ratios



Si-CNF





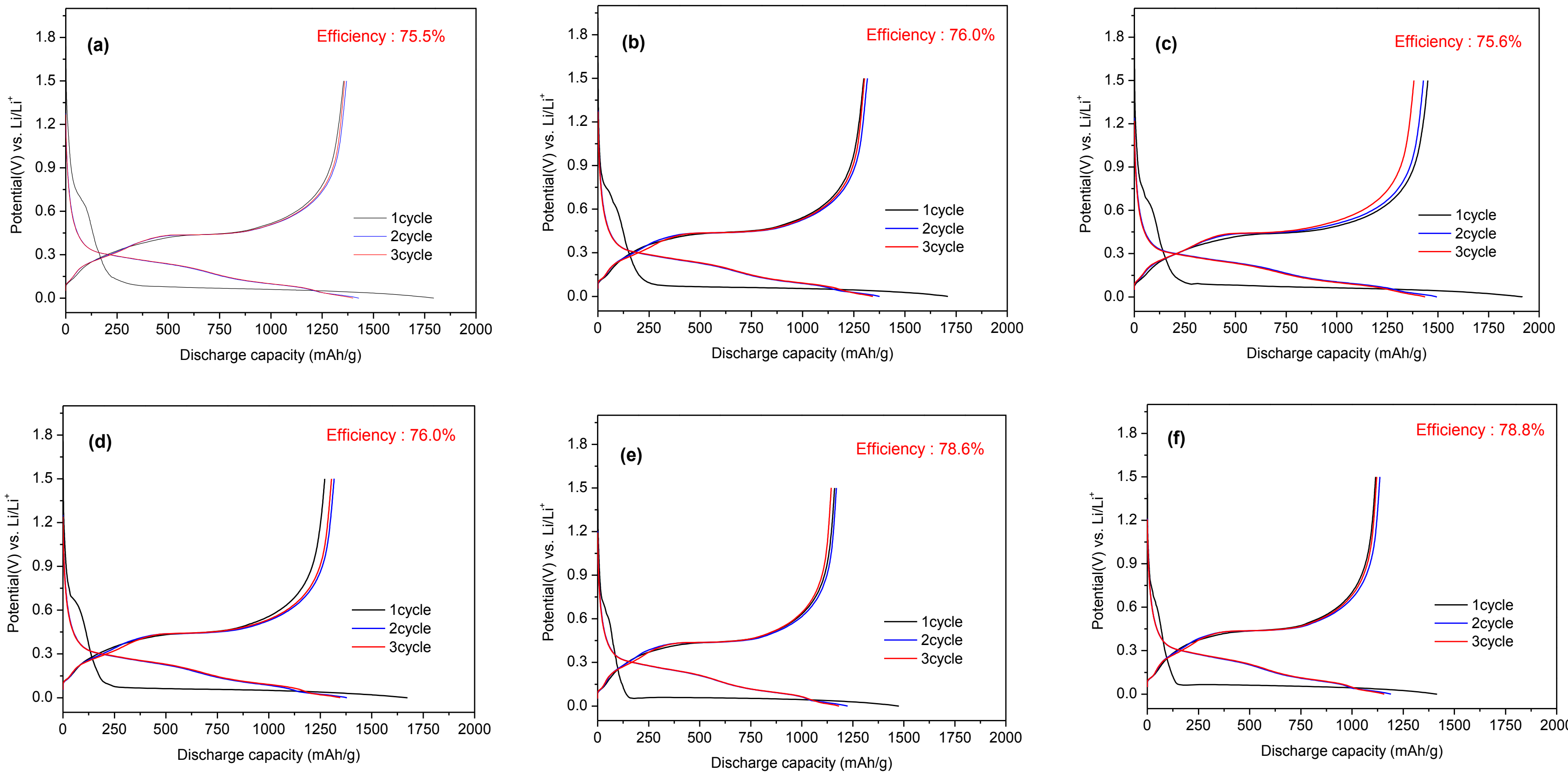


サイクル特性はまだ完全ではない。

改善

Siの適切なAmorphous化が必須
表面密着性の改善が必要

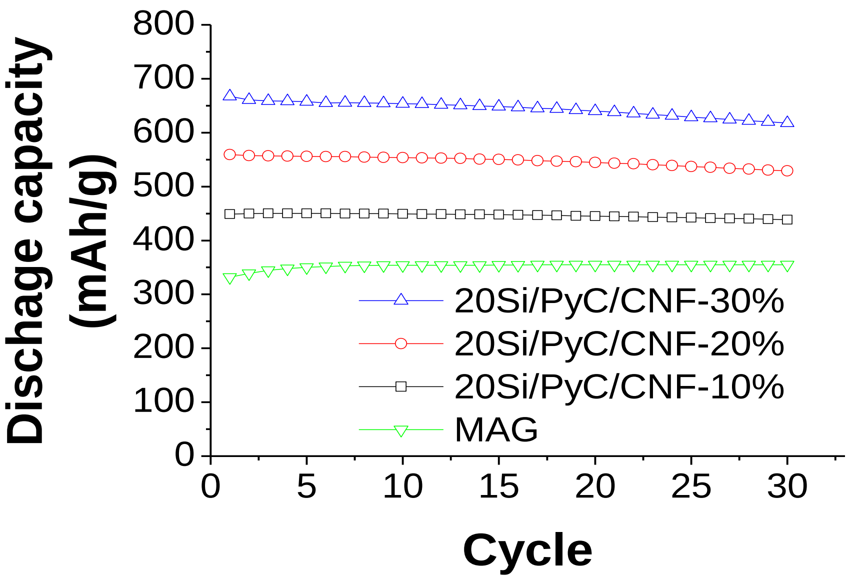
0.4μm Siの P/C形成 段階別 3cycleまでの特性評価

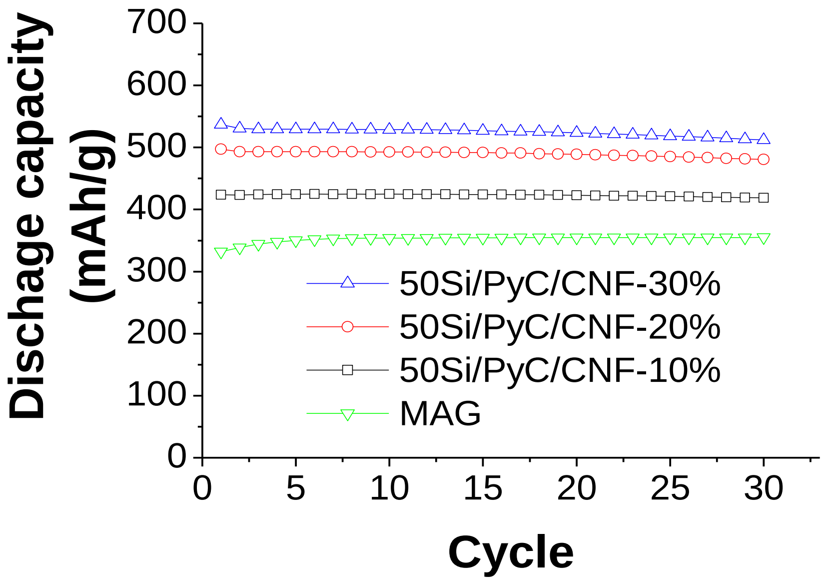


(a, c, e) : 0.4μm Si(As received), (b, d, f) : P/C形成された 0.4μm Si

a, b : Si-CNF 複合体, c, d : 触媒除去, e, f : P/C 再形成

Si-CNF composite / Graphite Hybridization





CNF for Capacitor

Edge effect

Polarization

Pseudo Capacitance

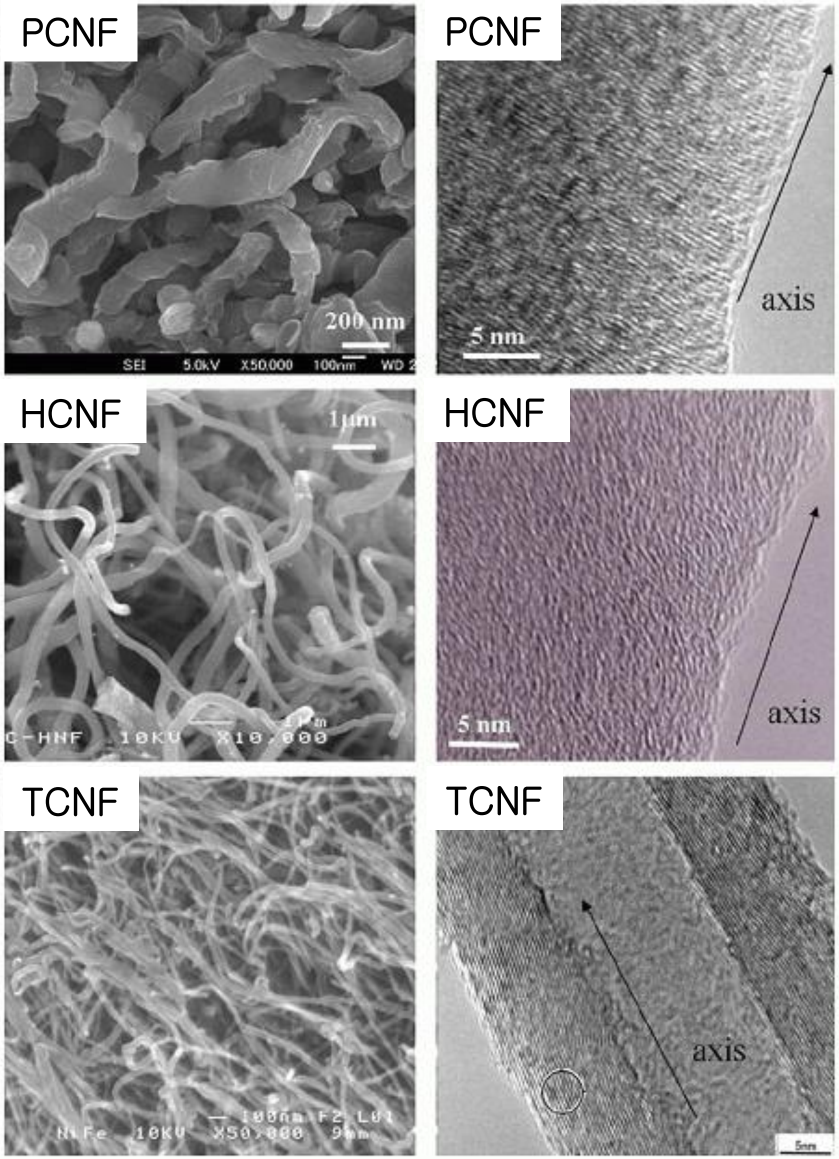
Capacitance over Graphitic Surface

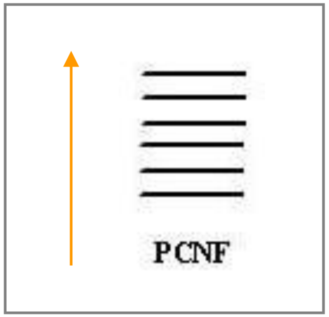
Basal } of Hexagonal Planes
Edge }

Typical Surface of Carbon Nano Fibers

Strong Dependence of Capacitance over Graphite Surface Structure

Various CNFs



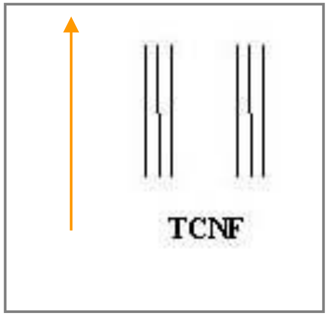


Surface edges

Perpendicularity to the fiber axis

Surface edges

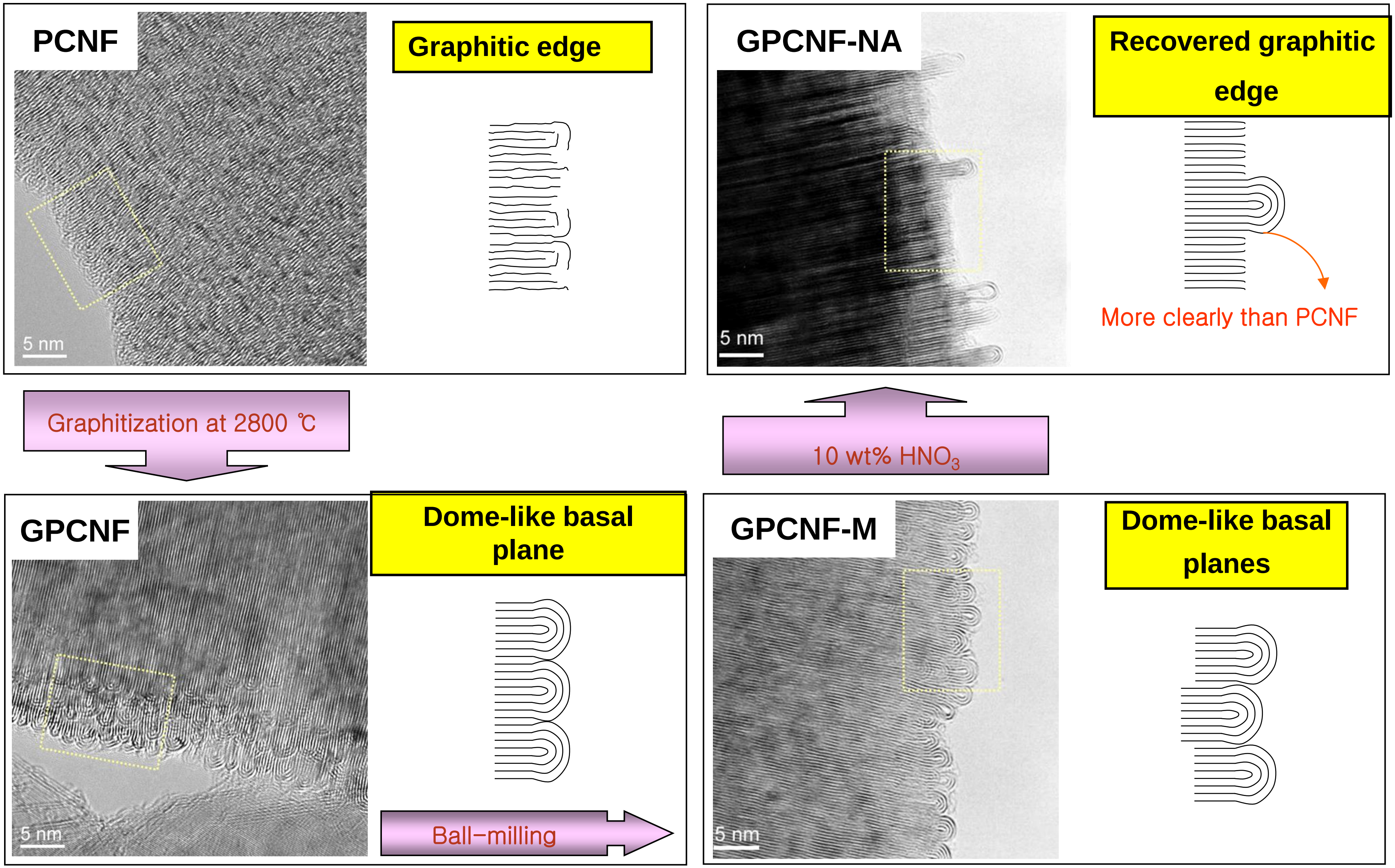
Decline to the fiber axis



Surface basal planes

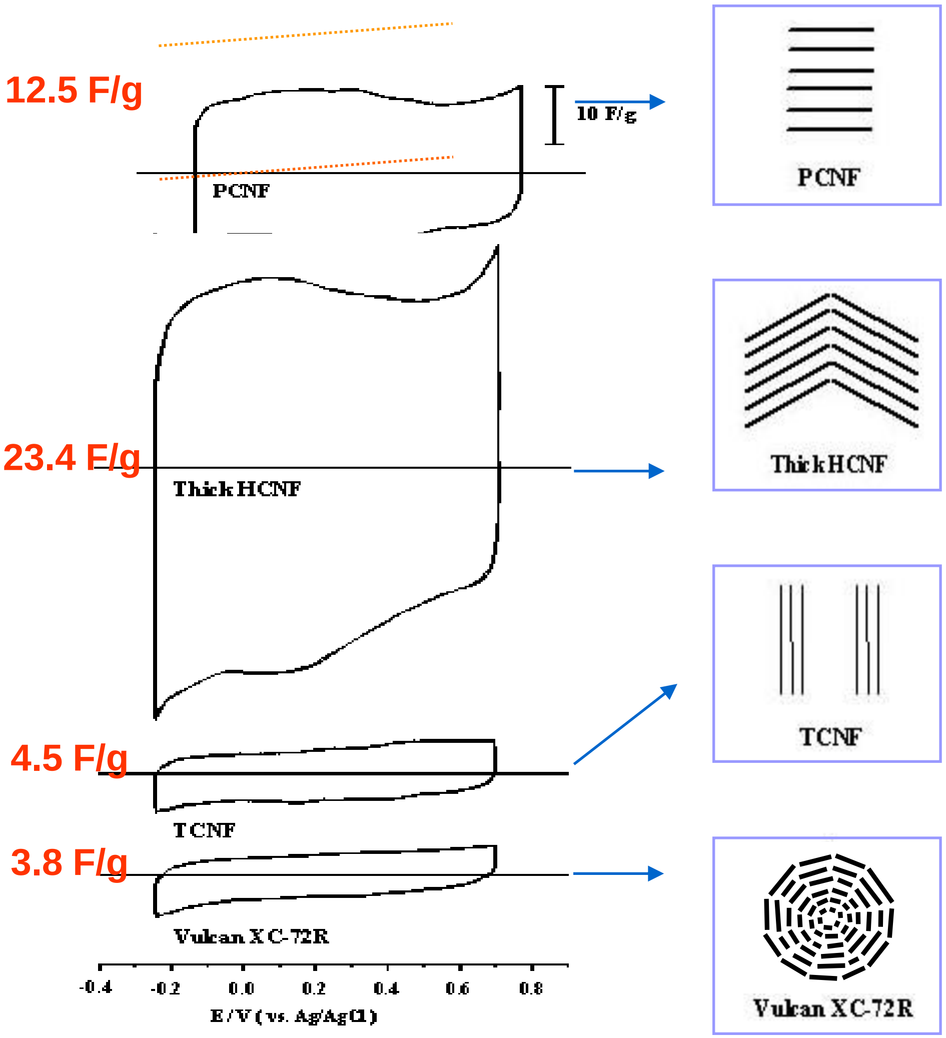
Parallel to the fiber axis

Surface-modified PCNFs



Capacitances of various CNFs

Cyclic voltammograms of various carbon nanofibers in 0.5 M H_2SO_4 solution, scan rate : 10 mV/sec.



※ Capacitance values :

Thick HCNF > PCNF > TCNF > XC-72R

Graphitic edges > Basal planes

※ Capacitive behaviors

Basal plane surface → Capacitive charging current

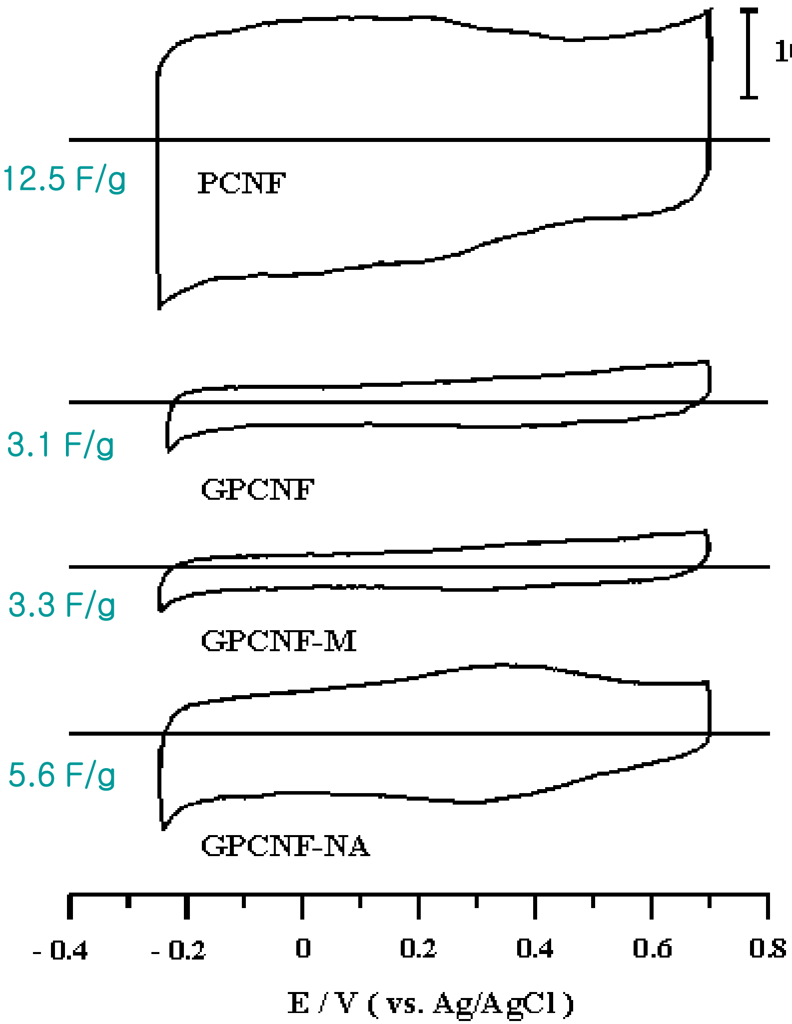
Graphitic edge surface

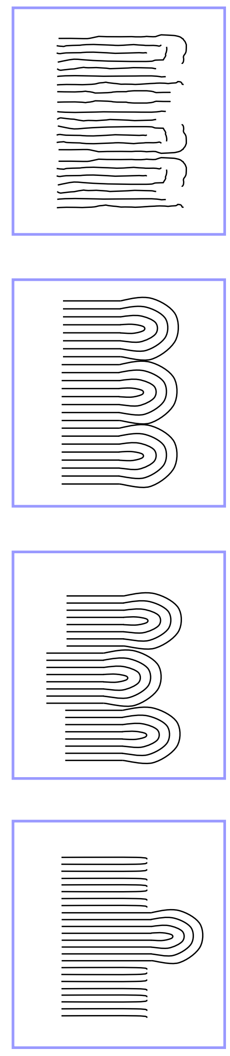
- **Reversible redox peak at about 0.1 V**
- **Pesudocapacitance by effect of edge surface**

• Capacitances were calculated with current values from cyclic voltammetry at 0.45 V

Capacitances of modified PCNFs

Cyclic voltammograms of surface modified carbon nanofibers in 0.5 M H2SO4 solution, scan rate : 10 mV/sec.





Reconfirmation dependence of the capacitance on the surface structure

※ Capacitance values :

PCNF > GPCNF-NA > GPCNF-M > GPCNF

Graphitic edges > Basal planes

※ Capacitive behaviors

Dome-like basal planee (GPCNF, GPCNF-M)

→ Capacitive charging current

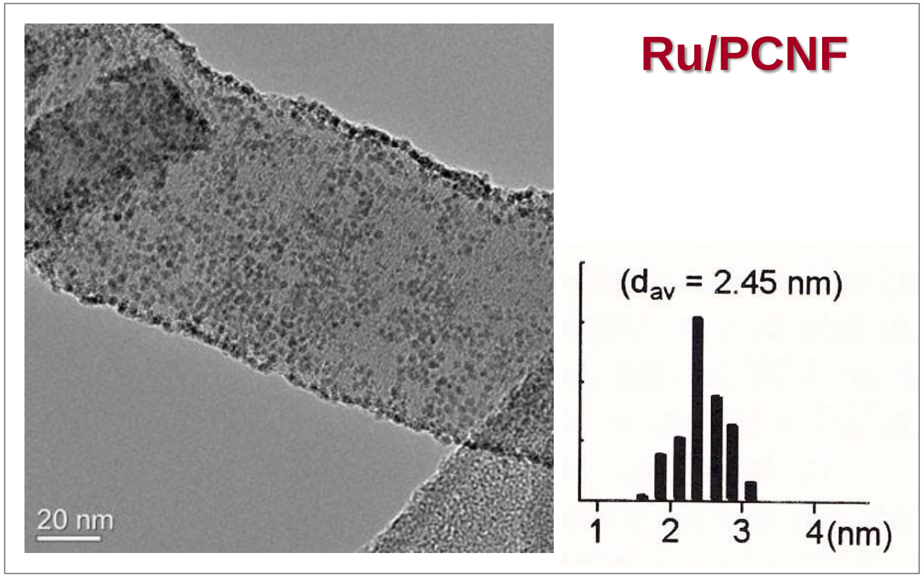
Graphitic edge surface (GPCNF-NA)

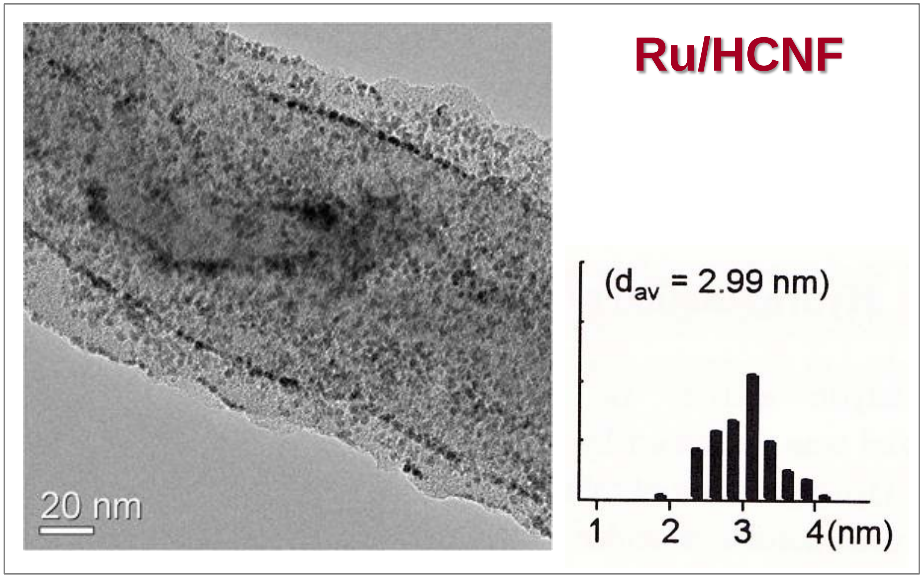
→ **Reversible redox peak at about 0.3 V**

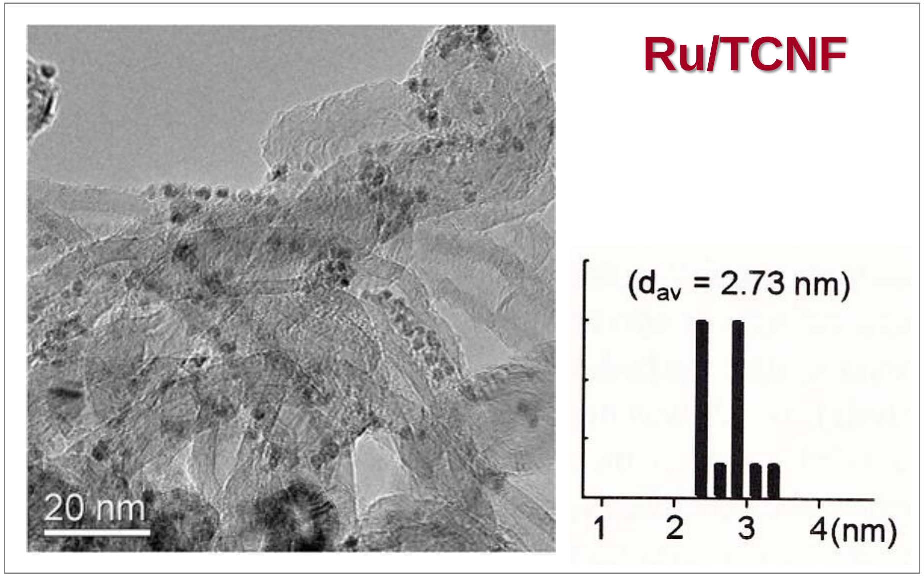
→ **Pesudocapacitance by effect of oxygenated surface species**

- Capacitances were calculated with current values at 0.45 V, except for GPCNF-NA (at 0.58 V)

TEM and ICP-MS results of Ru/CNFs







ICP-MS analysis of Ru/CNFs

Catalyst	Ru amounts (wt%)
Ru/PCNF	1.7 (± 0.1)
Ru/HCNF	1.4 (± 0.4)
Ru/TCNF	2.5 (± 1.9)

Cyclic voltammograms of Ru/CNFs

Electrochemical capacitance of Ru/CNFs (F/g)							
	Pristine CNFs	Non-polarized Ru/CNFs	Increase ratio by Ru effect (calculated from CNF (times))	Polarized Ru/CNFs	Increase ratio by polarization (calculated from Ru/CNF (times))	After Ru stripping	Decrease ratio by Ru stripping (calculated from polarized Ru/CNF (times))
Ru/PCNF	12.5	62.6	**5.0**	75.7	**1.2**	19.5	**1 / 3.9**
Ru/HCNF	23.4	54.7	**2.3**	67.4	**1.2**	44.0	**1 / 1.5**
Ru/TCNF	4.5	38.4	**8.5**	47.1	**1.2**	28.6	**1 / 1.6**

CNF Supports in DMFC

Fuel Cell

- **Roles of Carbon**

  Activation of Noble Metal

  High Dispersion, Chemical Activation, Edge of Carbon Plane!

  Support/Metal Interaction

- **Transferring Proton of Noble Metal to Membrane**

  Proton Conductor

  Good Bridging with Proton Conduction Binder

- **Electron Conductivity**
- **Chemical Stability**
- **Surface and Pore of Carbon**

  Finer Carbons to Satisfy Both Requirements

  Dispersion of Noble Metal on Carbon with Smaller Size

  → Carbon Nanofibers

Objective and Approach

Objective

Development of highly active catalyst for DMFC anode using carbon nanofiber (CNF)

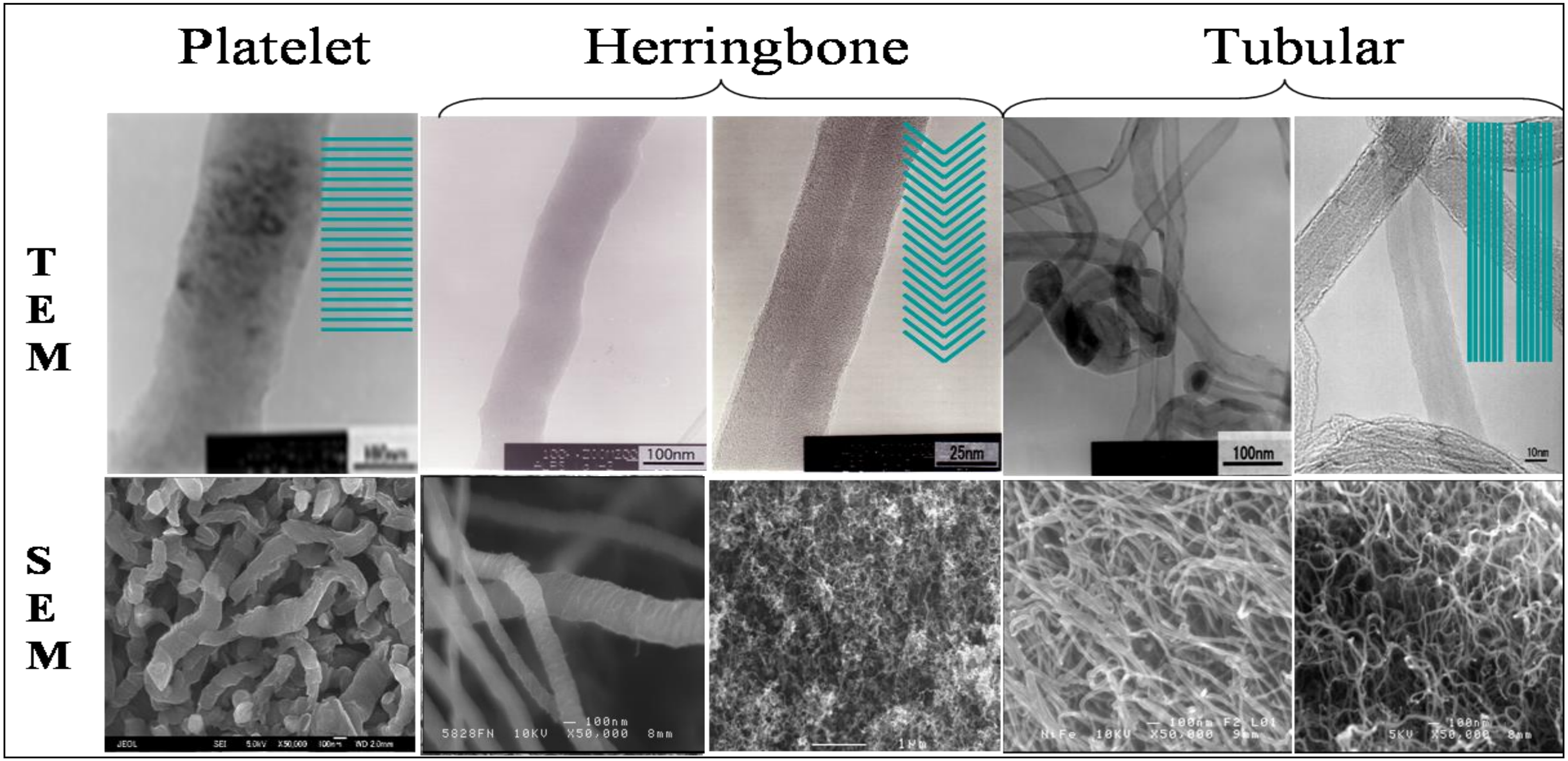
Approach

Synthesis:	Selective Syntheses, Various Structure, Diameter of CNFs…
Selection:	Best structure, Diameter, Surface, Surface area, functional group…
Modification:	**Introduction of Mesoporosity onto CNF to increase the Effective surface Area**
Analysis:	Half & Full cell tests, SEM, TEM, …
Further study:	Searching further increasing methods for catalytic activity

Carbon nanofiber vs. Carbon black

Advantage	Disadvantage
Active Hexagonal Edges Relatively high graphitizability Relatively high electric conductivity	Low Effective Surface Area Nanofibrous Entanglement (Difficulty of dispersion) Low contents of secondary structure and functional groups

Selective Synthesis of Carbon Nanofibers



Dia. (nm)	150	150~200	10~70	20~40
Code	P-CNF	Thick H-CNF	Thin H-CNF	T-CNF

CNF	**Diversity of structure, diameter, and surface**	Merit	**High methanol oxidation activity, Graphitizability, conductivity**	Demerit	**Agglomerated structure: low effective surface area Low surface energy**

Experiments

Preparation of Catalysts

Carbon nanofibers + H_2O

↓ ← $RuCl_3$-xH_2O + H_2O

↓ ← H_2PtCl_6-6H_2O + H_2O

0.1~0.5M $NaBH_4$

↓

Filtering

↓ ← Washing

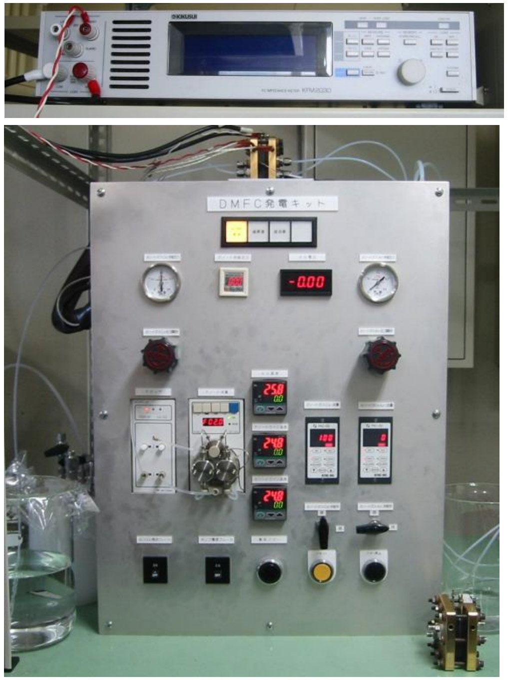
↓ ← Nafion Ionomer

Brushing on Carbon Paper

↓ ← Drying at 80℃

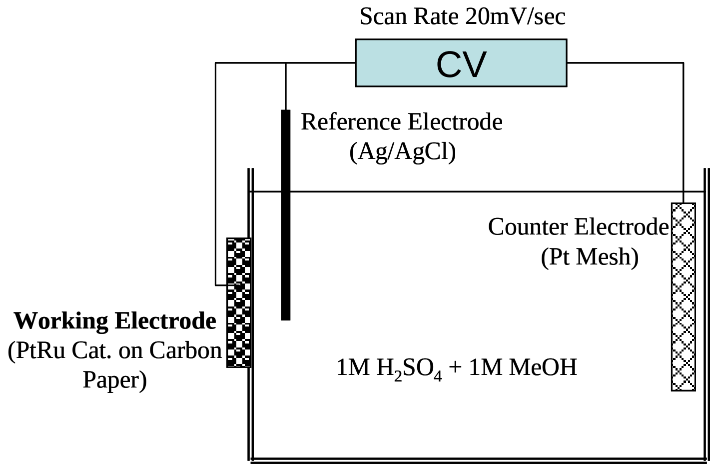
Cyclic Voltammetry

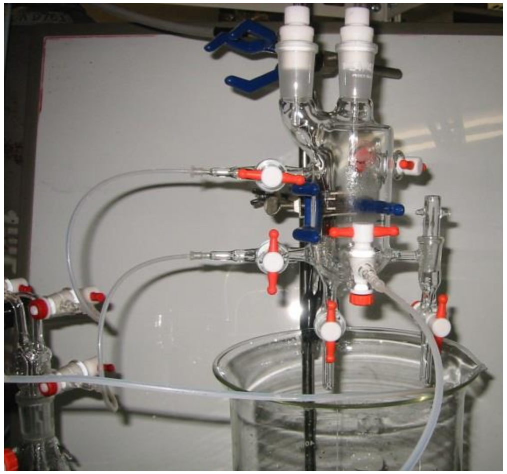
Equipments



Single Cell Test Kit

Half Cell Test

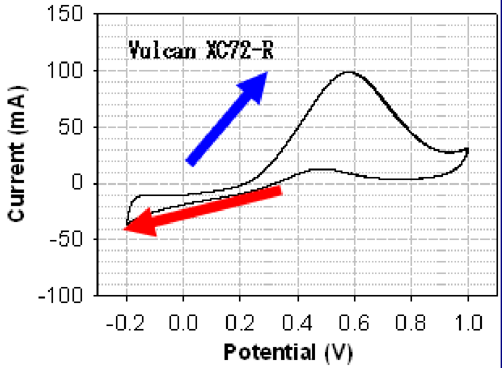


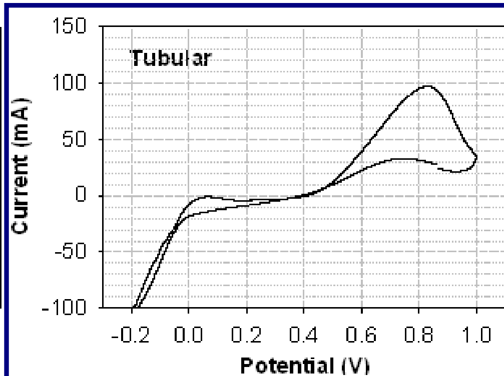


Electrode	Carbon Paper (ϕ1cm)				Gold (ϕ1cm)			
Catalyst Amount (mg)	PtRu 60wt% 5mg Slurry	Pt	Ru	C	PtRu 40wt% 0.3mg Slurry	Pt	Ru	C
		2	1	2		0.08	0.04	0.18

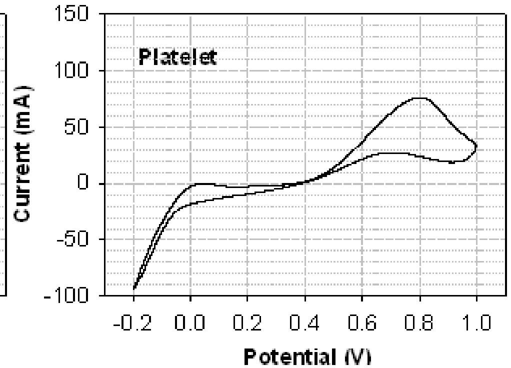
Methanol Oxidation Property

Evaluation by Half Cell Test : 1mol MeOH + 1mol H_2SO_4, 25℃

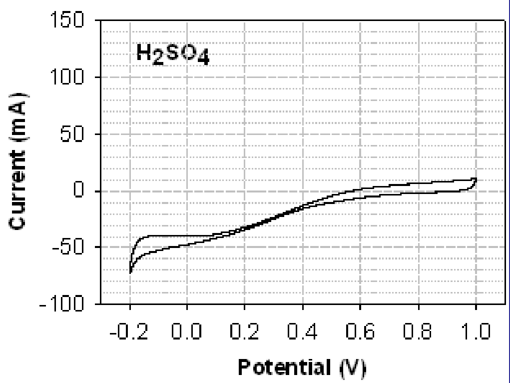


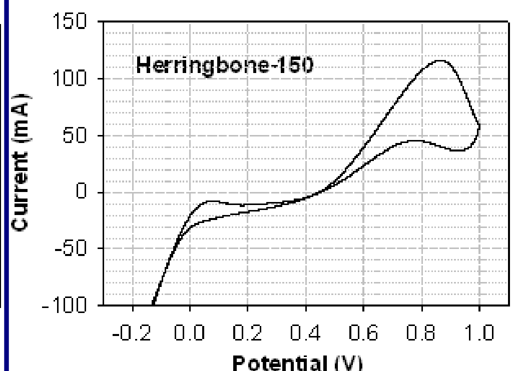


Tubular, 30nm dia.

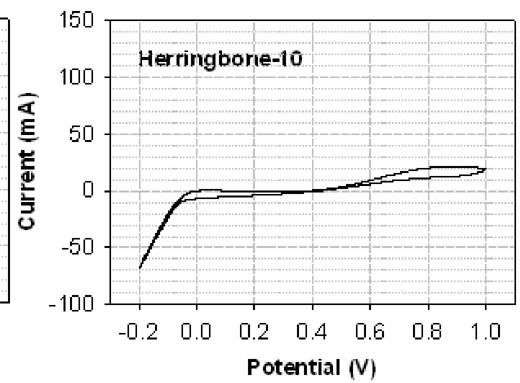


Platelet, 200nm dia.





Thick-Herringbone, 250nm dia.



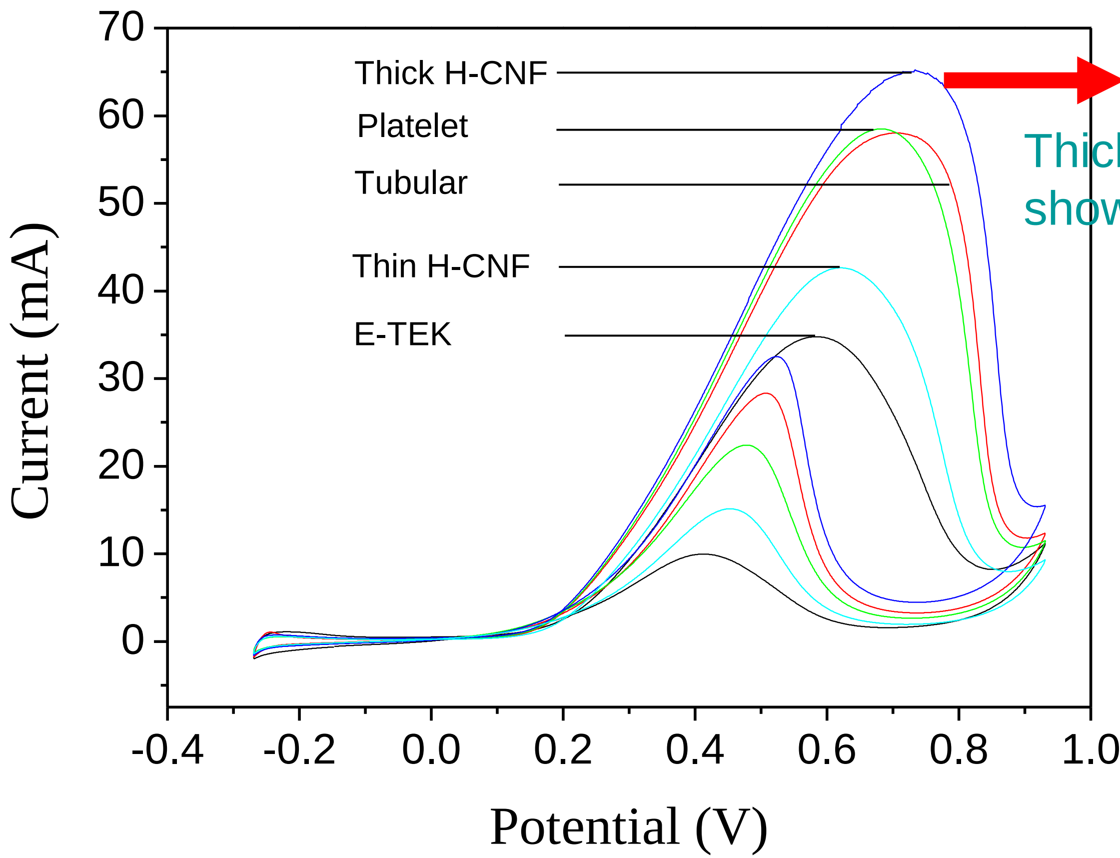
Thin-Herringbone, 10nm dia.

Thick Herringbone CNF showed relatively high activity

Noble Metal Content	Slurry Amount (mg/cm^2)	Pt	Ru	C
		(mg/cm^2)		
PtRu 60wt%	5	2	1	2

Methanol Oxidation Property

Evaluation by Half Cell Test : 1mol MeOH + 1mol H_2SO_4, 25℃

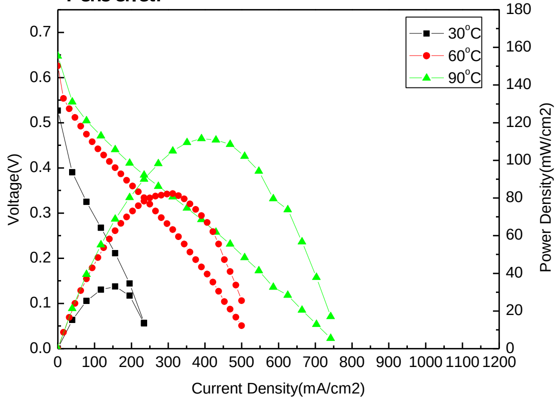


Thick Herringbone CNF showed relatively higher activity

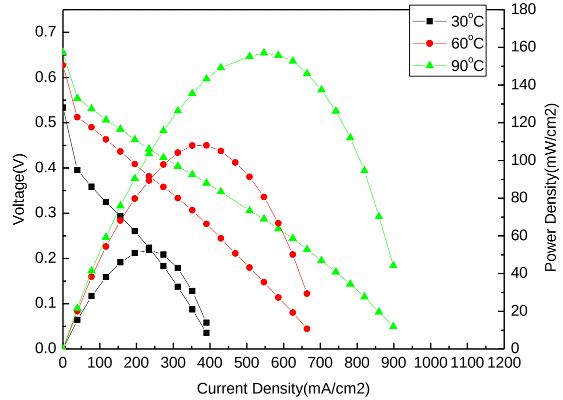
Noble Metal Content	Slurry Amount (mg/cm²)	Pt	Ru	C
		(mg/cm²)		
PtRu 40wt%	0.3	0.08	0.04	0.18

Single Cell Test of Various CNFs

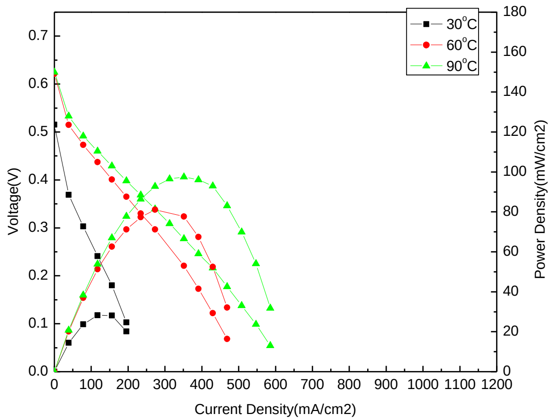
Tubular



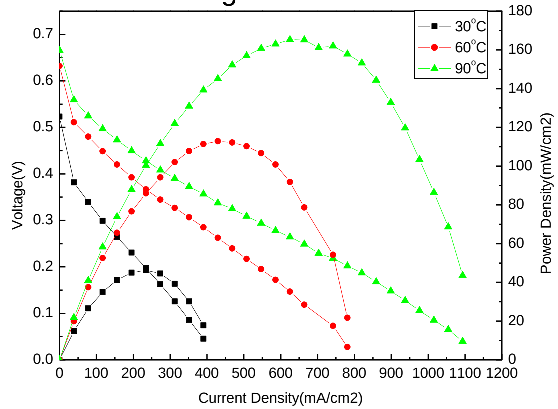
Platelet



Thin Herringbone



Thick Herringbone



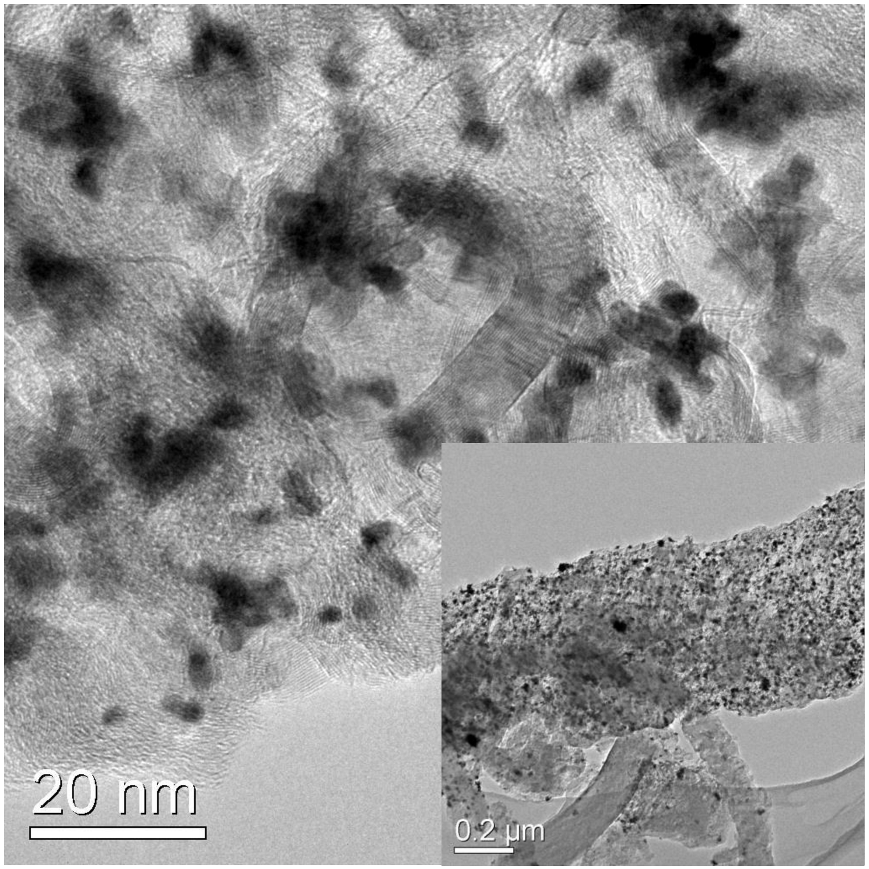
Noble Metal Content	Slurry Amount (mg/cm^2)	Pt	Ru	C
		(mg/cm^2)		
PtRu 40wt%	7.5	2	1	4.5

Code	Maximum Power Density (mw/cm^2)		
	30°C	60°C	90°C
Tubular	33	82	112
Platelet	52	108	157
Thin Herringbone	28	81	97
Thick Herringbone	46	113	165

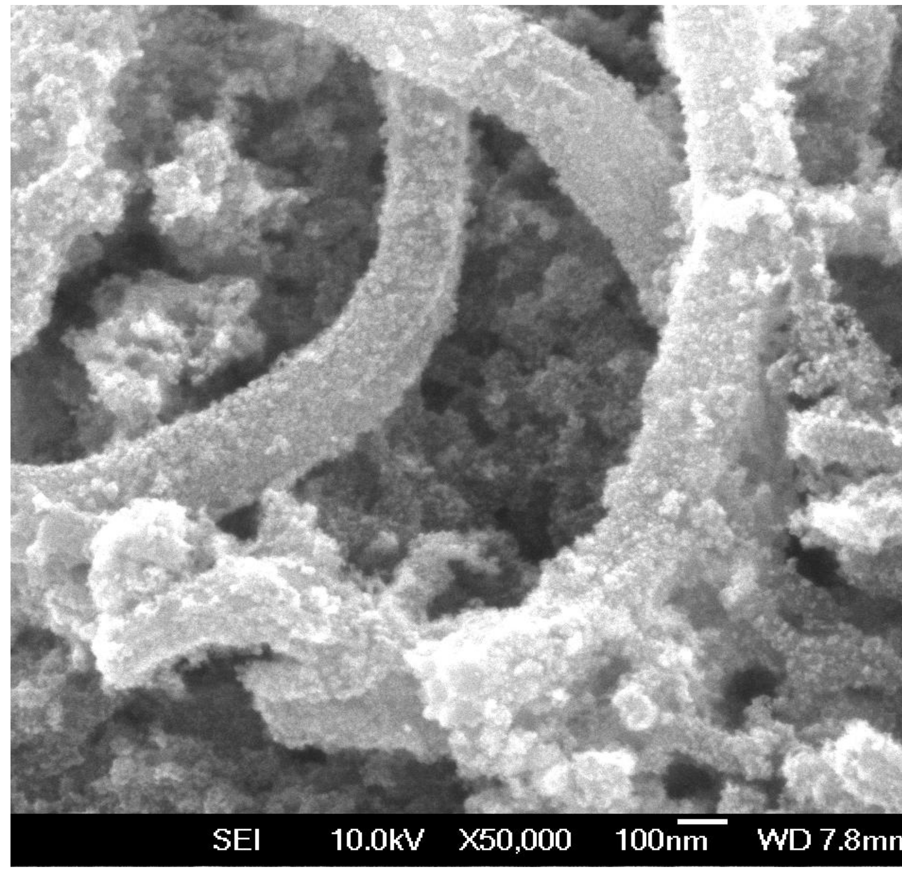
PtRu Catalyst on Mesoporous CNF

貴金属含有量	Slurry量 (mg/cm^2)	Pt	Ru	C
		(mg/cm^2)		
PtRu 40wt%	5	1.33	0.67	3

TEM

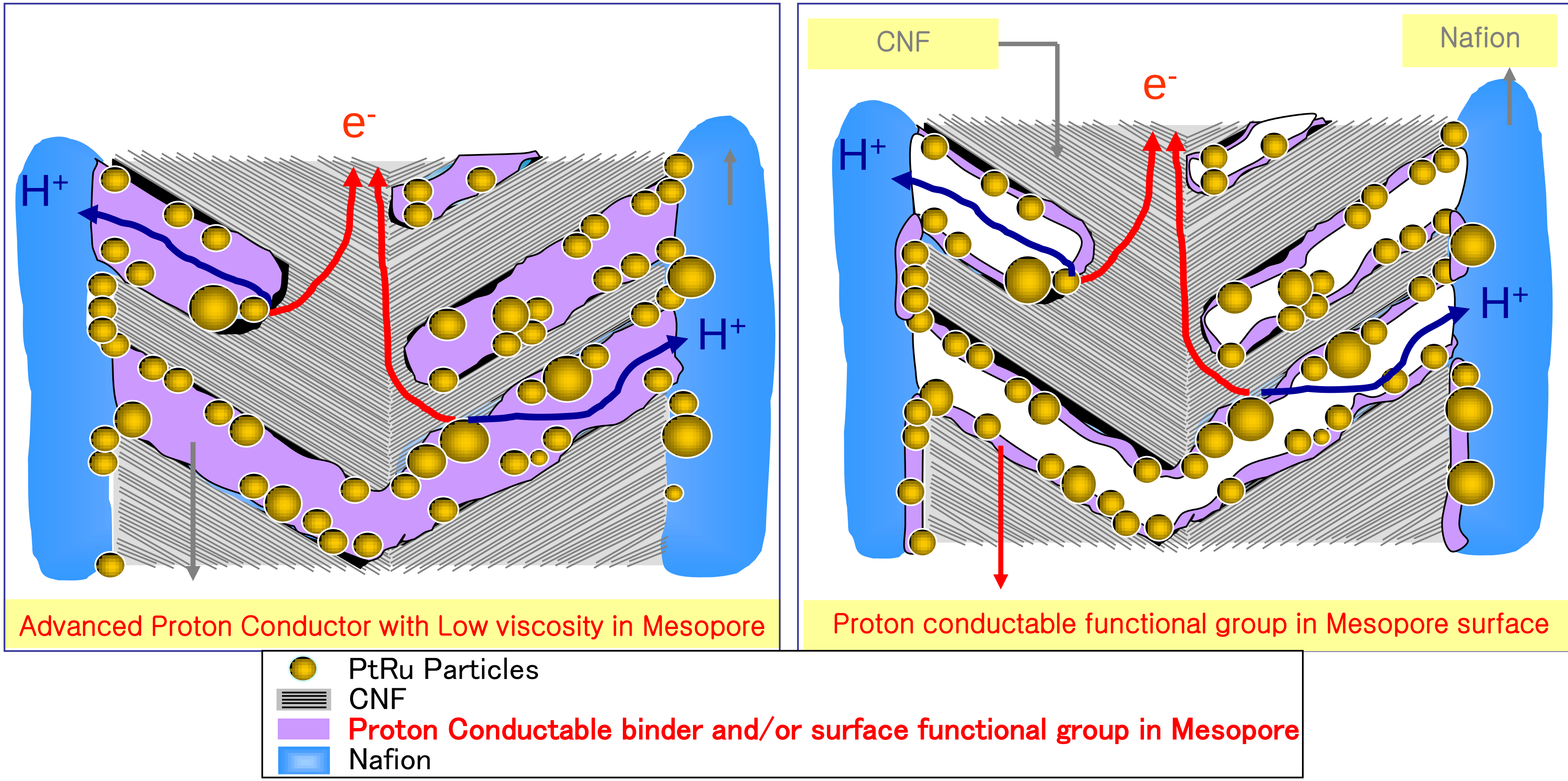


SEM



Well dispersed PtRu catalyst was observed in the TEM photographs. The average size of catalyst particles was about 3nm. Catalysts should be existed in the mesopores as well as on the exterior surface.

Model for Meso-porous H-CNF with Proton Conduction in Mesopore



Discrepancy of Single cell and half cell

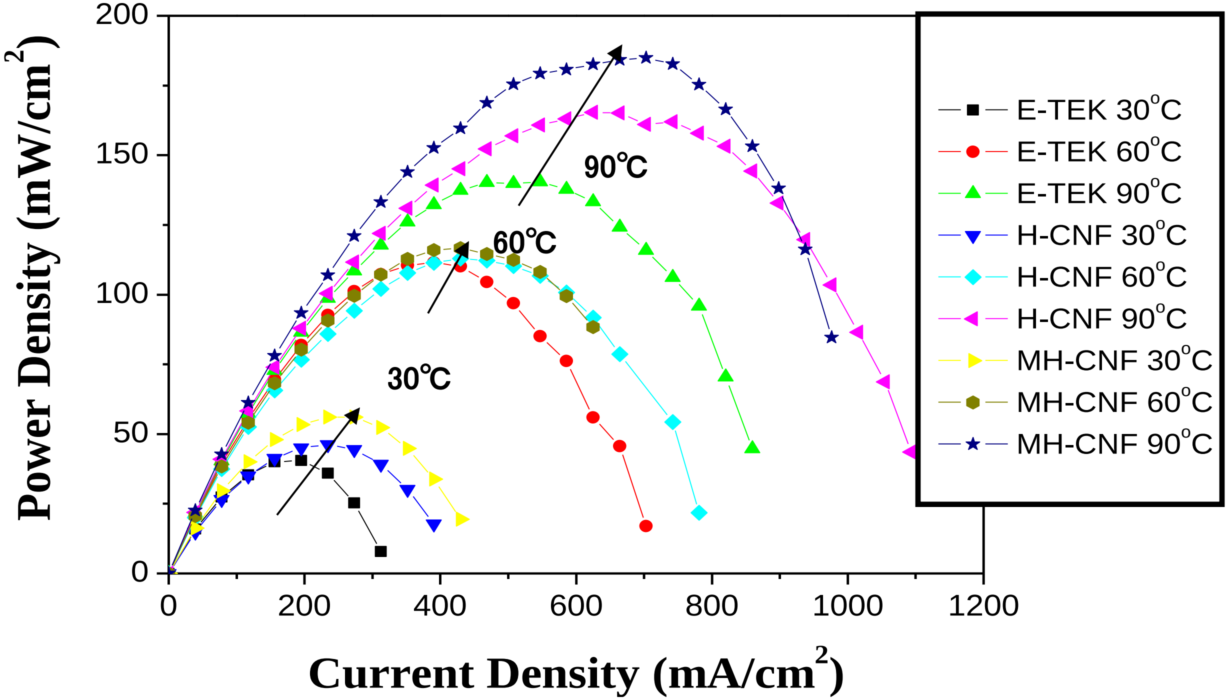
3 times increase of methanol oxidation in half cell

30% increase of single cell performance

→ Studying about new proton conduction system in Mesopore

Single Cell Performance

60wt% Pt-Ru/C E-TEK
40wt% Pt-Ru/C Herringbone-CNF
40wt% Pt-Ru/C Mesoporous H-CNF



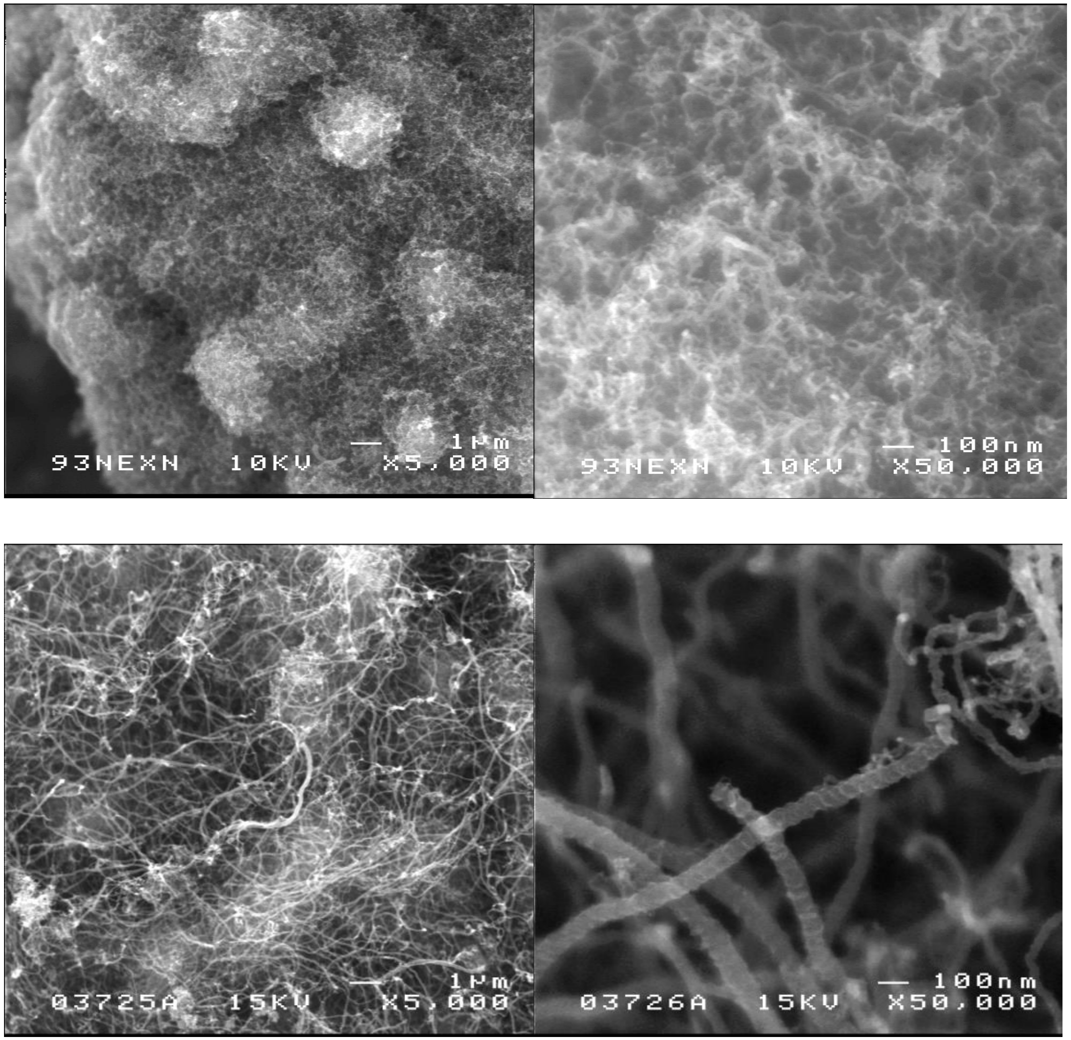
Catalyst	Noble Metal Content (wt%)	Maximum Power Density (mW/cm²)		
		30℃	60℃	90℃
E-TEK	60	41	102	140
H-CNF	40	46	113	165
Mesoporous H-CNF	40	56	117	185

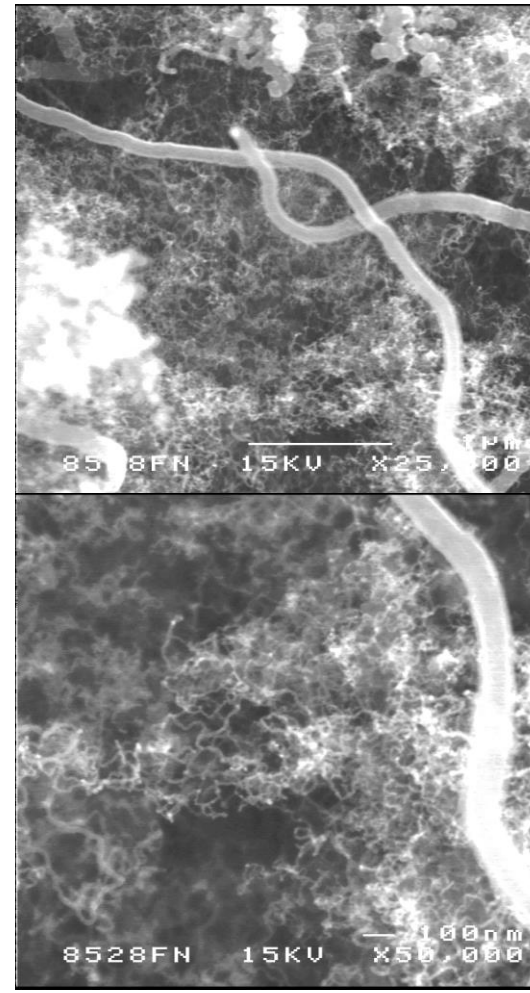
Discrepancy of half cell and full cell performances

Preparation of Thin H-CNF

Under 30 nm Diameter of H−CNF、Difficulty of Dispersion

FeNi Catalyst, Thin H-CNF

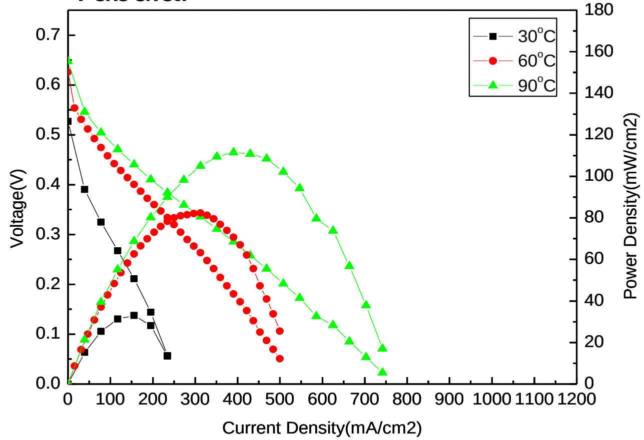




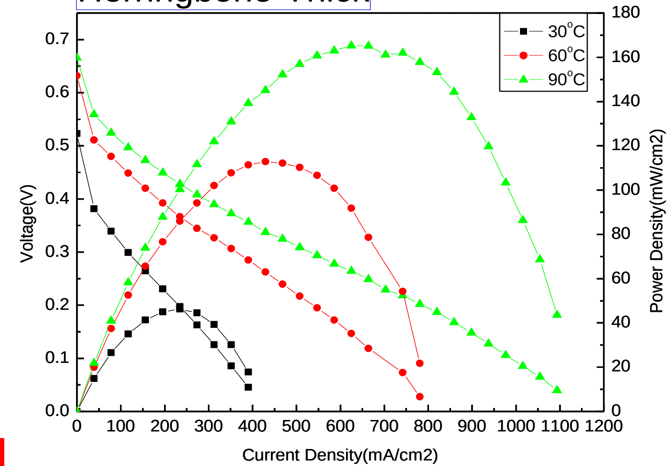
Thin H-CNF as Support Material

Various Structures of CNFs, Single Cell Performances

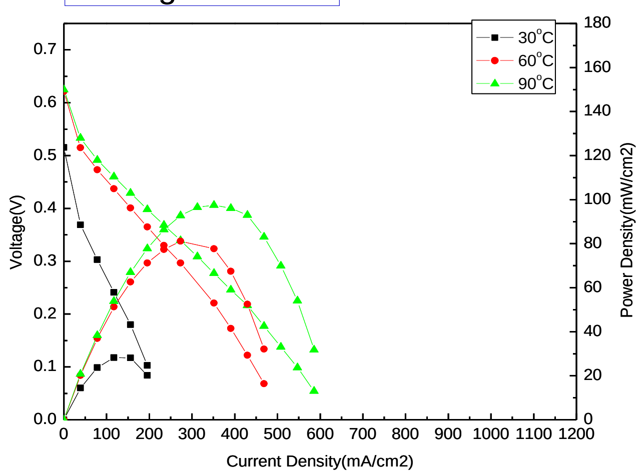
Tubular



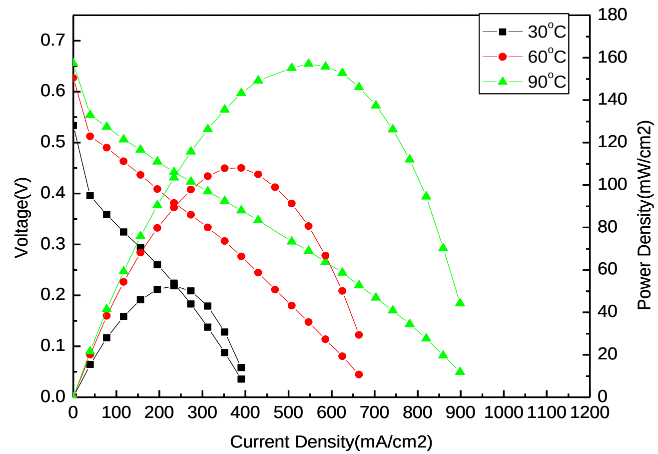
Herringbone-Thick



Herringbone-Thin



Platelet



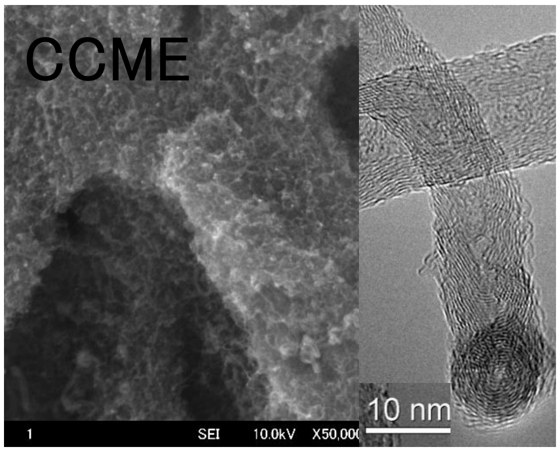
The Lowest Performance of Thin H-CNF may be attributed to the Difficulty of Dispersion

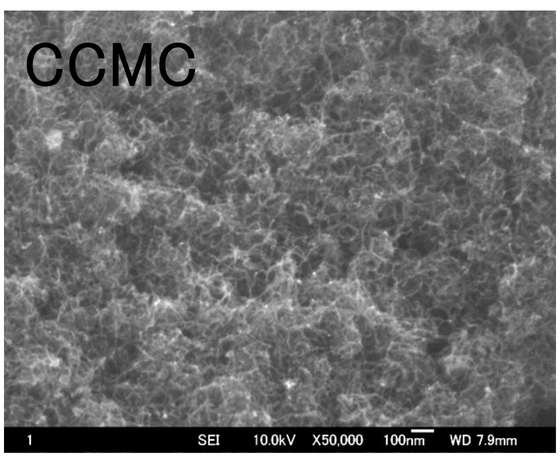
Catalyst	Noble Metal Content	Slurry Amount (mg/cm^2)	Pt	Ru	C
			(mg/cm^2)		
CNF	PtRu 40wt%	5.0	2	1	4.5

Preparation of Various Diameters of H-CNF

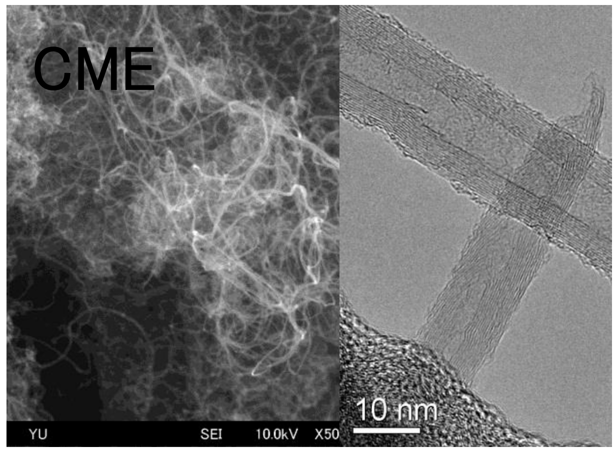
Difficulty of Dispersion in Thin H−CNF、Good Dispersion of Medium and Thick H−CNF
Optimization of Catalyst Preparation

(Thin H−CNF、φ 5~30nm)

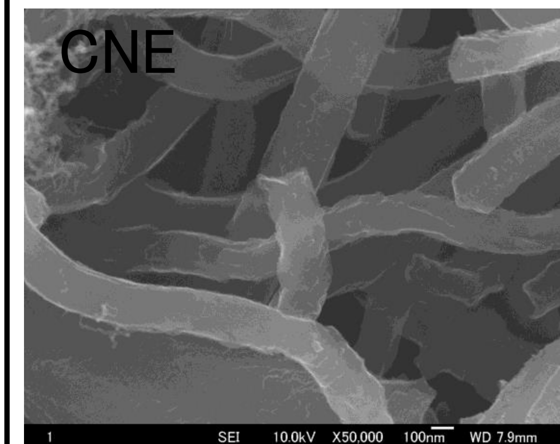


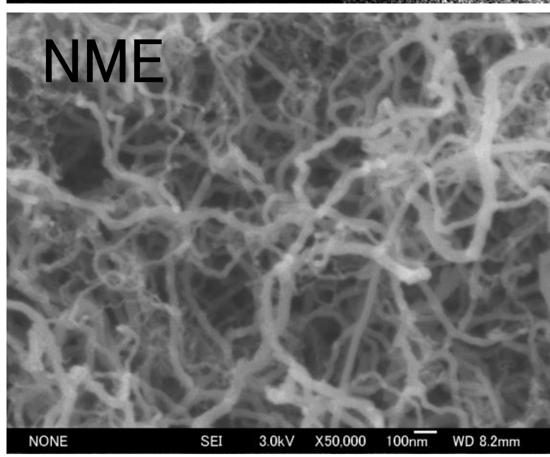


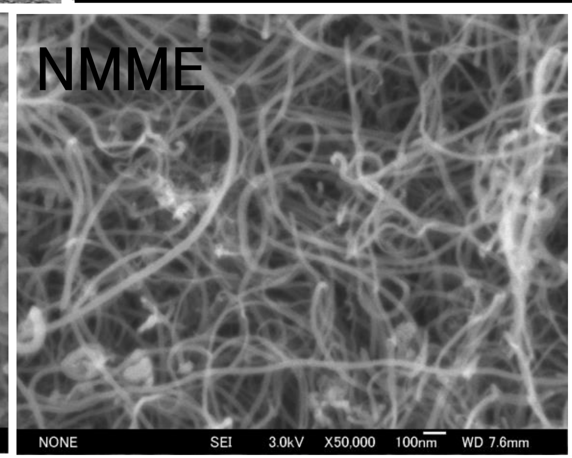
(Medium H−CNF、φ 30~70nm)



(Thick H−CNF、φ 70~300nm)







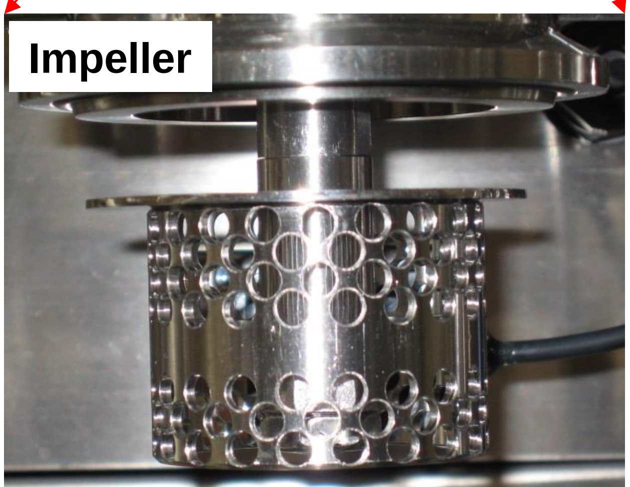
Difficult Dispersion

Good Dispersion

Catalytic Activity of Highly dispersed Thin H-CNF

Nano−dispersed Equipment、16500rpm、1min、30 times

ⓐ NM55(Ni:MgO = 5:5) ⓑ NMM415(Ni:Mo:MgO = 4:1:5) ⓒ FMM415(Fe:Mo:MgO = 4:1:5)
ⓓ NFM415(Ni:Fe:MgO = 4:1:5) ⓔ CM55(Co:MgO = 5:5)、40%Pt-Ru/C, pH3-pH4, 60℃ Preparation

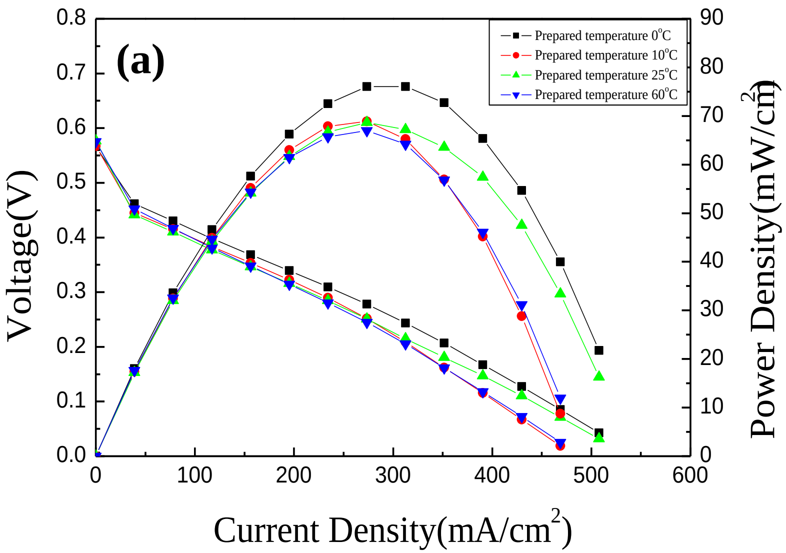


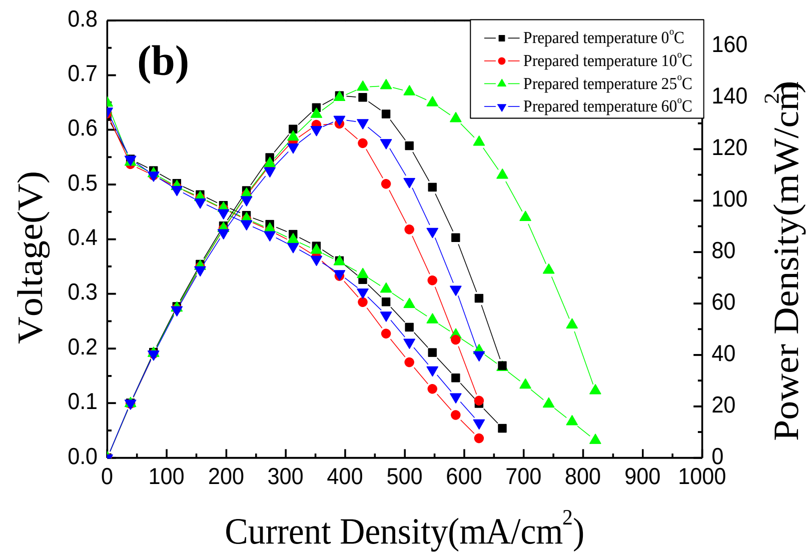
	Single Cell Max. Power density (mW/cm^2)		
	30℃	60 ℃	90 ℃
Not treated	28	81	97
NM55	52	108	182
NMM415	34	95	168
FMM415	40	92	158
NFM415	56	118	184
CM55	49	108	176
Johnson M. 60wt%, Pt $2 mg/cm^2$	55	121	162

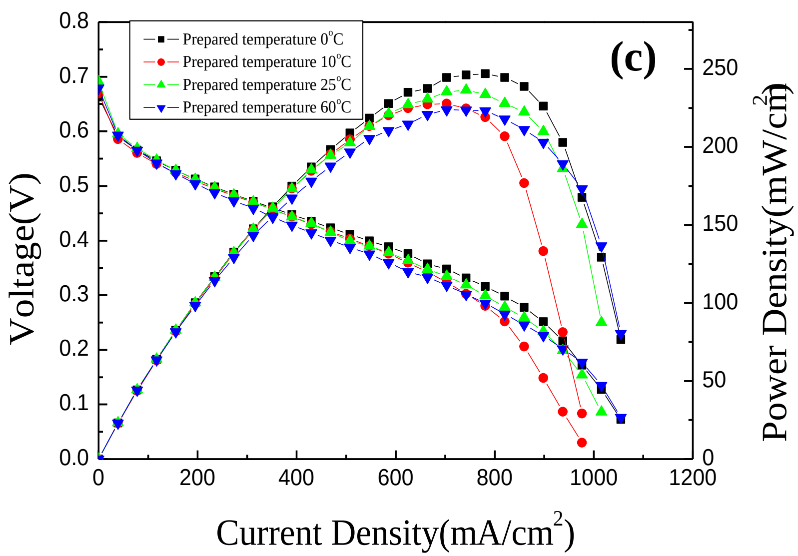
貴金属含有量	Slurry量 (mg/cm^2)	Pt	Ru	C
		(mg/cm^2)		
PtRu 40wt%	5	1.33	0.67	3

Single cell performance of NFM- catalyst

based on the unit electrode area



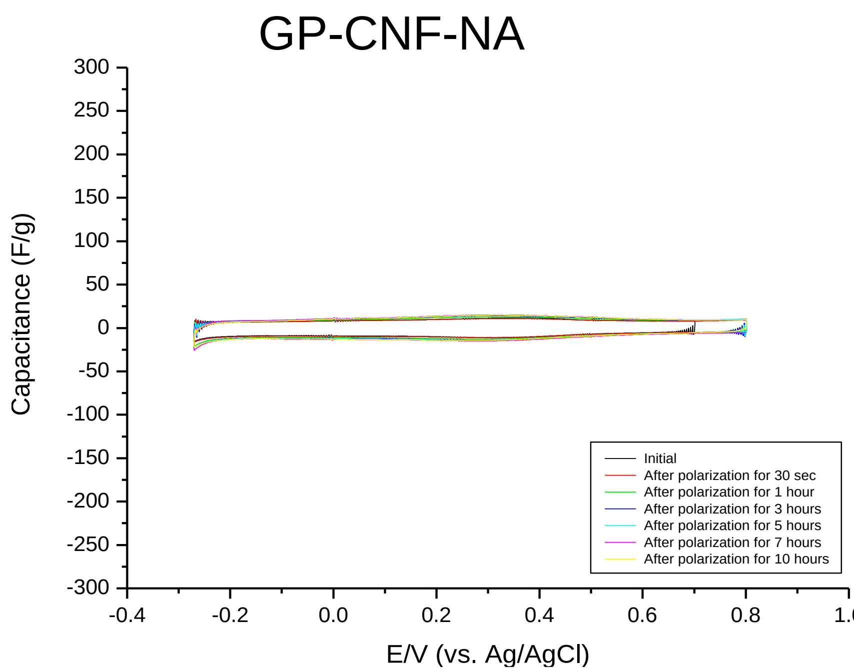


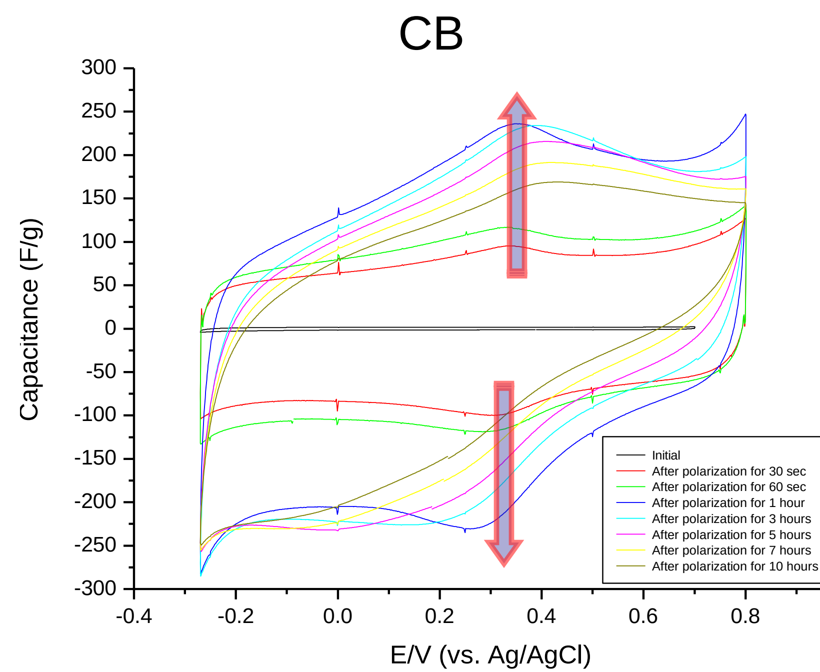


Single cell performance of catalyst supported on NFM examined at (a)30°C, (b) 60°C, and (c) 90°C.

	Single cell Power density. Max(mW/cm2)		
	30°C	60°C	90°C
Not dispersion prepared temperature 25oC	56	118	184
Prepared temperature 0oC	76	140	246
Prepared temperature 10oC	68	129	227
Prepared temperature 25oC	68	144	236
Prepared temperature 60oC	66	131	223
60%Pt-Ru/C (Johnson matthey)	55	121	162

Oxidation Stability of CNF



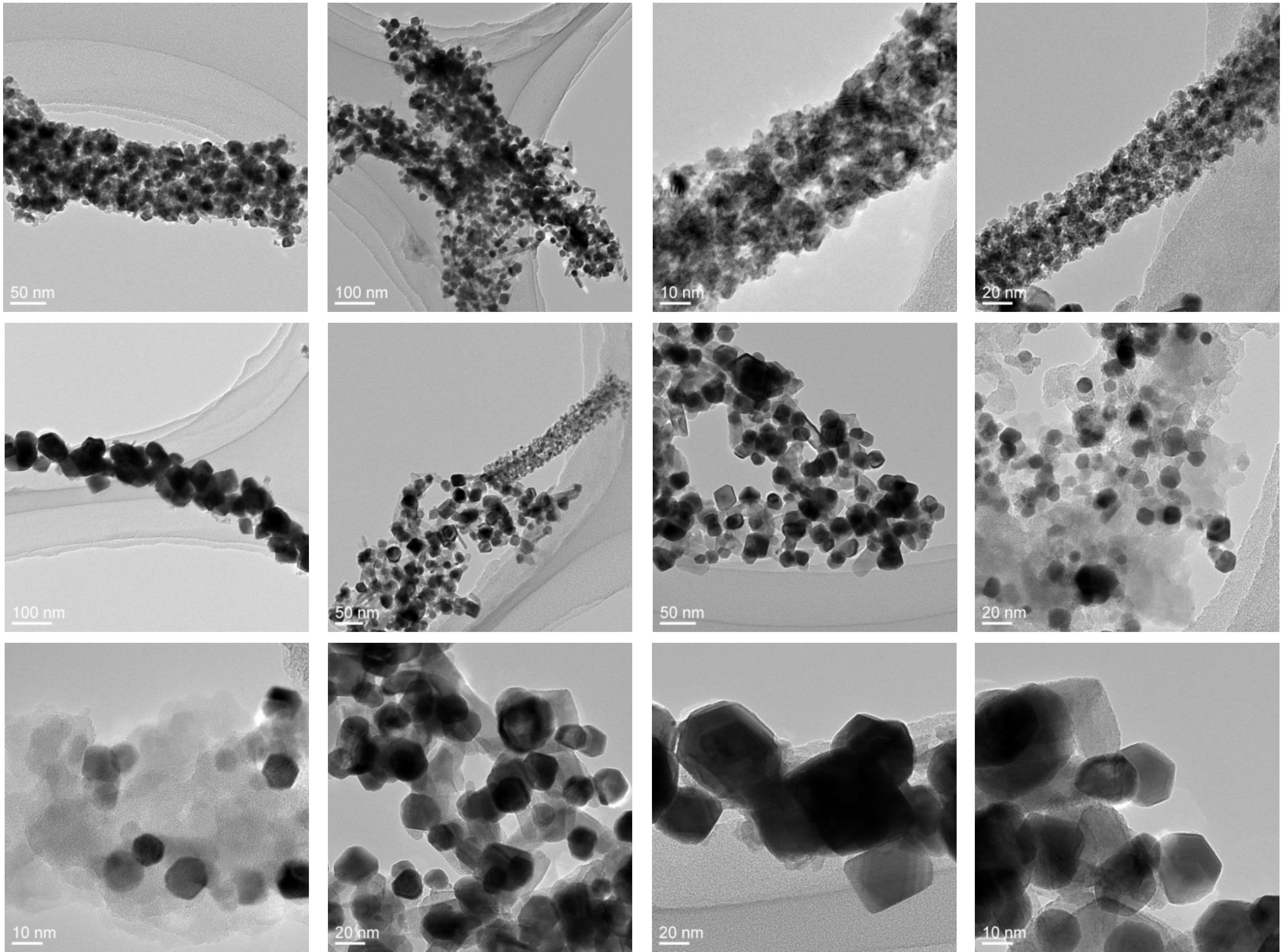


◆ カーボンブラックは電気化学的な酸化還元反応が起こり、キャパシタンスが増加する。

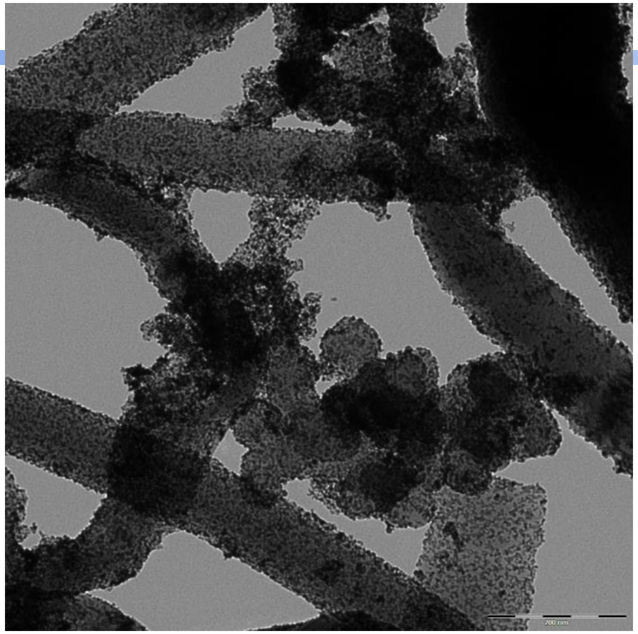
◆ GP−CNF−NAは電気化学的な酸化還元反応が起こらないためプロファイルがほとんど変わらない。

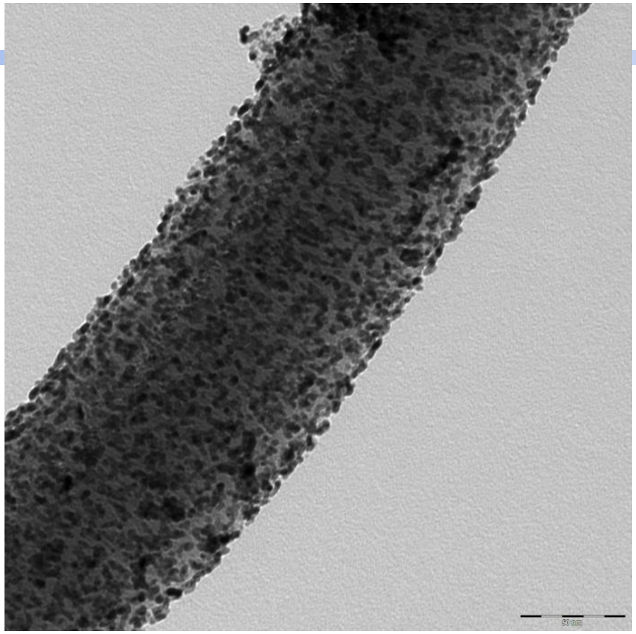
PtRu Nano-chains

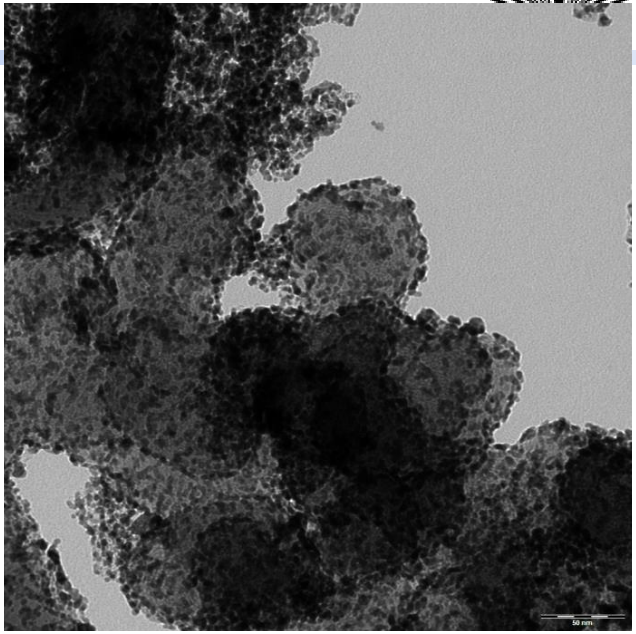
10 wt% PtRu nanochain

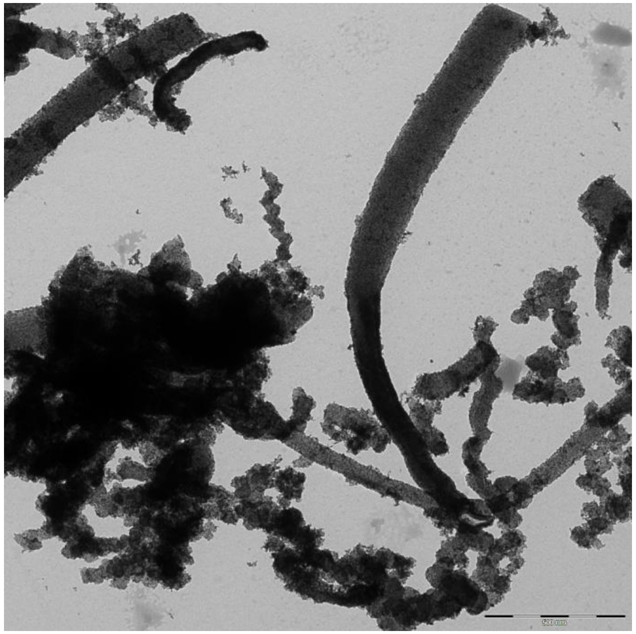


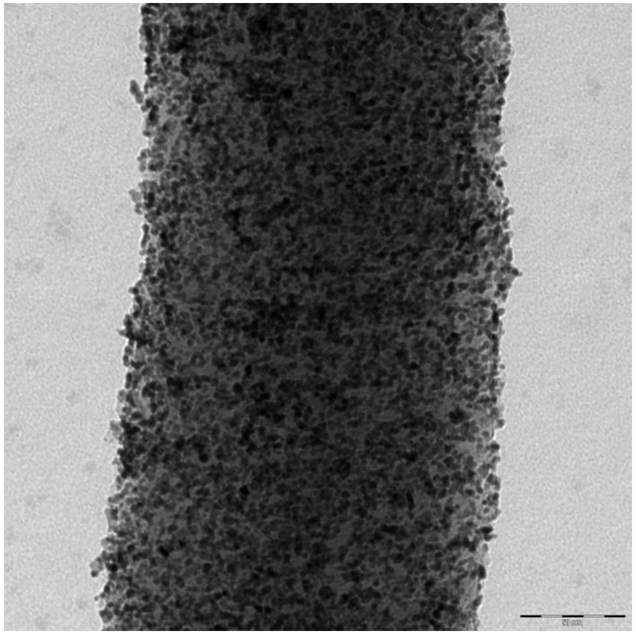
TEM images of 40%Pt/PCNF+CB

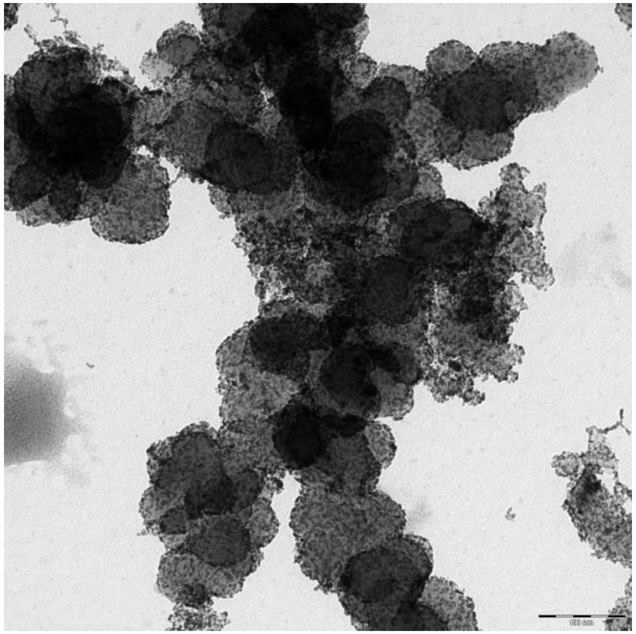




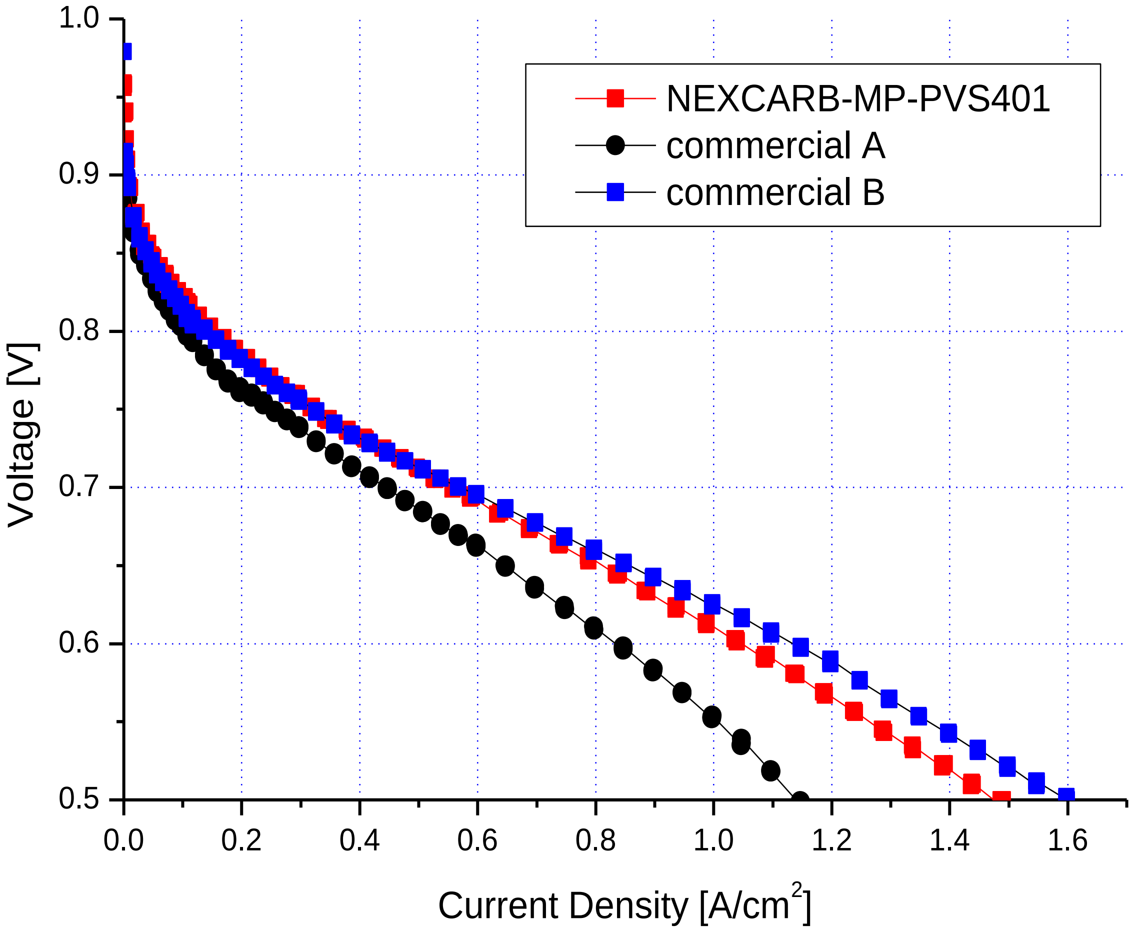








Evaluation of 40%Pt/PCNF+CB



Operating Condition

1) Cell Temp' : 70℃
2) Humidifier Temp'
   Anode / Cathode = 70 ℃ / 60 ℃
3) Flow H2/Air = ×1.4/×2.5
4) Ambient pressure
5) Electrode Size : 25㎠
6) Min flow : 400㎃/㎠

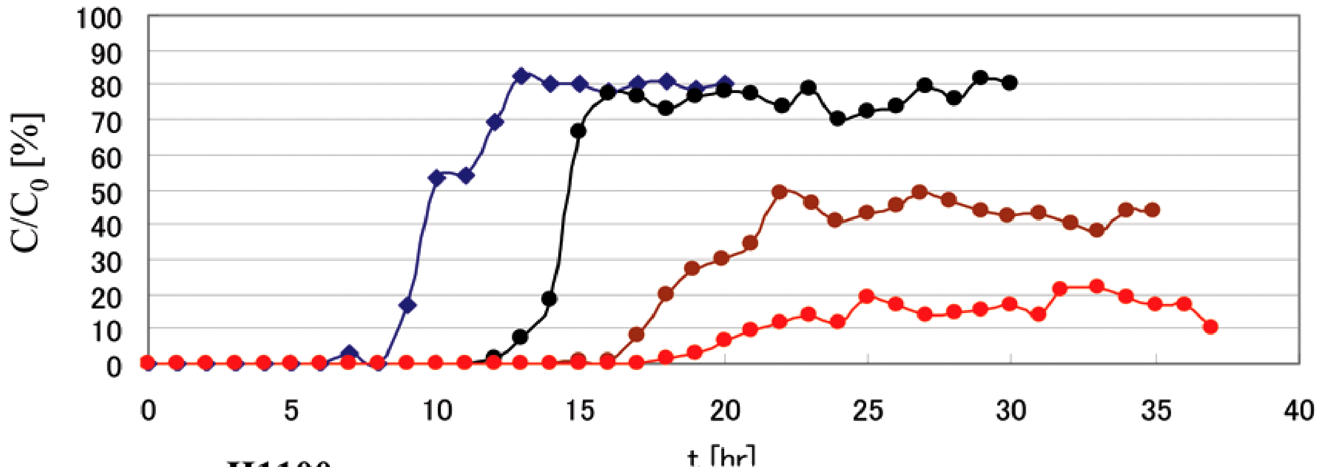
Very similar performance with Gore Japan MEA

Data from Suntel Co. Ltd.

CNF for Air Purification

ACF–CNF

メタロセン担持量変化による脱硫結果の比較
(析出温度600℃、実験温度70℃)



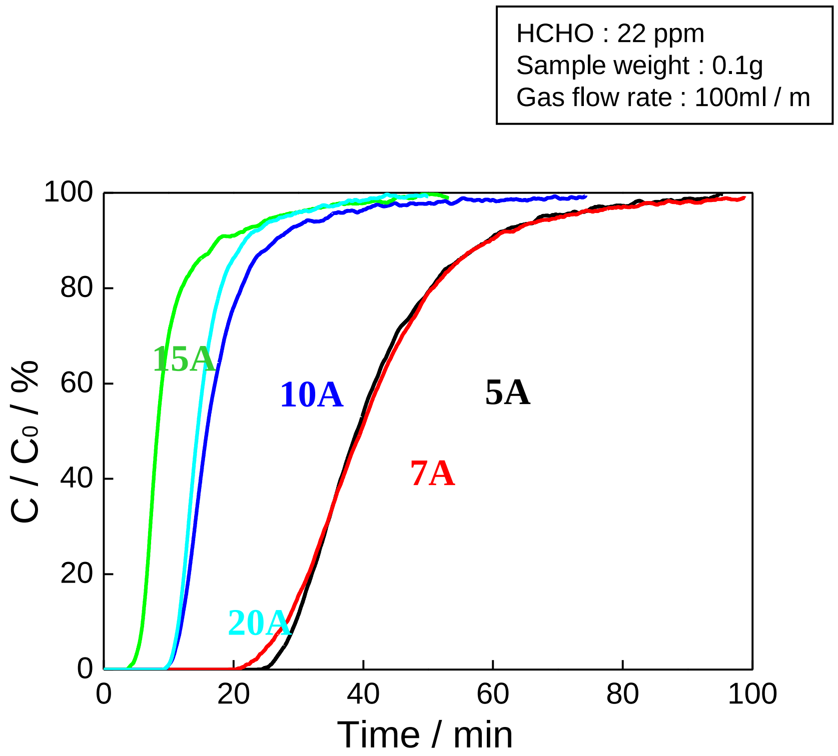
	Breakthroght time[hr]	Steady state activity [%]	Surface Area [m^2/g]
H1100(ACF)	6	80	1500
0.5%Metallocene (5min)	12	75	1130
1%Metallocene (5min)	16	45	1120
5%Metallocene(5min)	17	20	1116

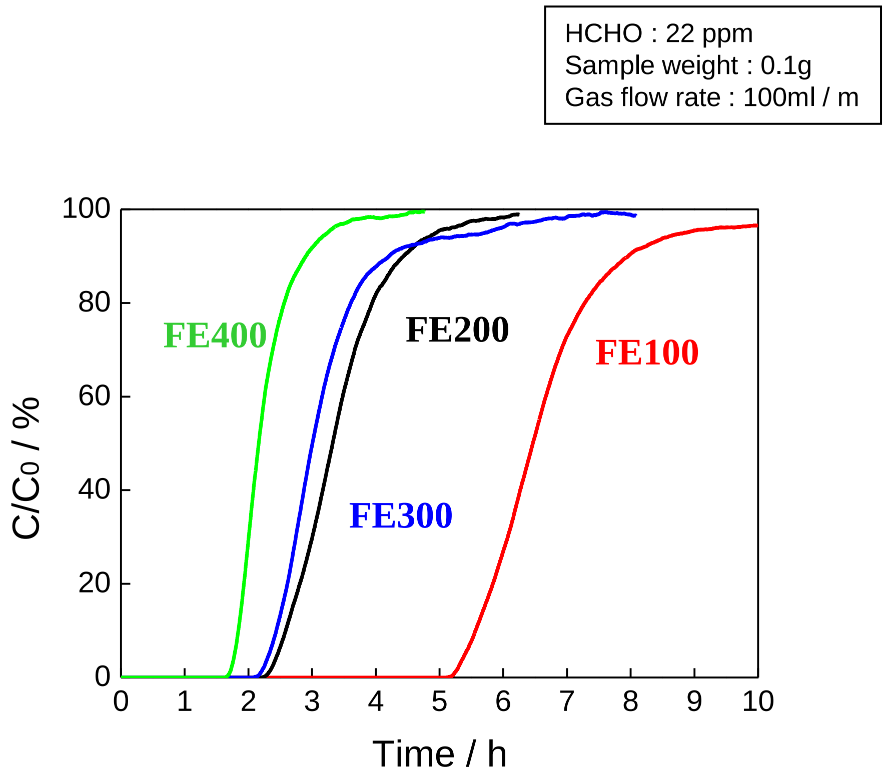
Some Properties of ACFs

Pitch based ACF	BET (m^2 / g)	Elemental analysis (wt %)				N / C
		C	H	N	O	
OG5A	563	92.4	0.6	0.7	6.0	0.007
OG7A	901	93.0	0.6	0.8	5.4	0.007
OG10A	1085	95.3	0.6	0.5	3.4	0.004
OG15A	1606	95.2	0.6	0.3	3.4	0.003
OG20A	1924	94.1	0.6	0.4	4.8	0.003

PAN based ACF	BET (m^2 / g)	Elemental analysis (wt %)				N / C
		C	H	N	O	
FE100	450	70.9	2.0	8.4	17.3	0.102
FE200	650	72.5	1.8	4.8	17.9	0.057
FE300	880	74.3	1.6	3.3	17.2	0.038
FE400	1020	76.8	1.6	2.3	19.4	0.026

HCHO adsorption characteristics of ACFs





Break through time

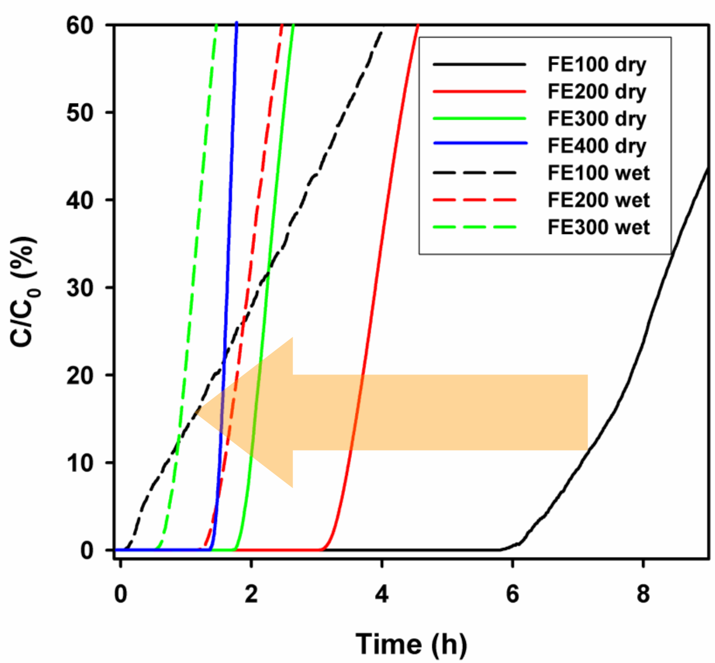
♦Pitch-based ACF : 15A < 20A < 10A < 7A < 5A

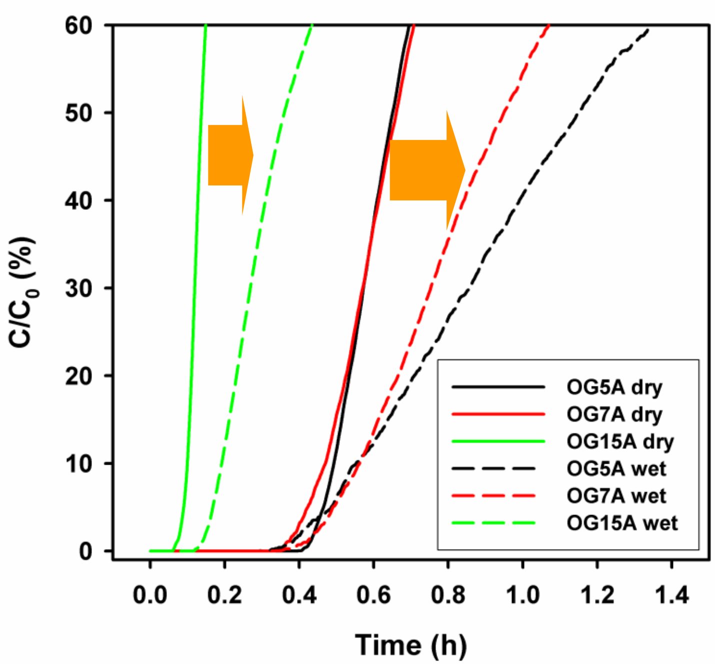
♦PAN-base ACF : FE400 < FE300 < FE200 < FE100

Breakthrough curves of formaldehyde adsorption

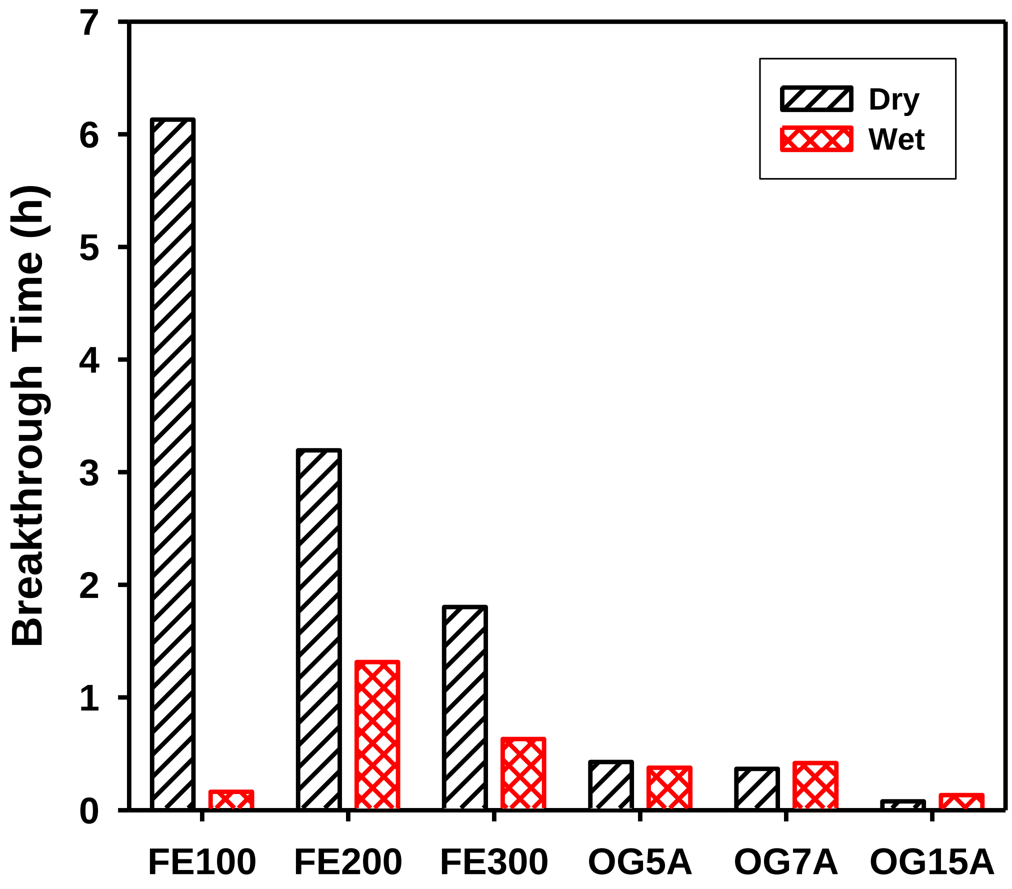
WATER Competitive adsorption decreases the adsorption amount of HCHO

Dry condition (solid line) and wet condition (dashed line) for the different kinds of a) FE series and b) OG series



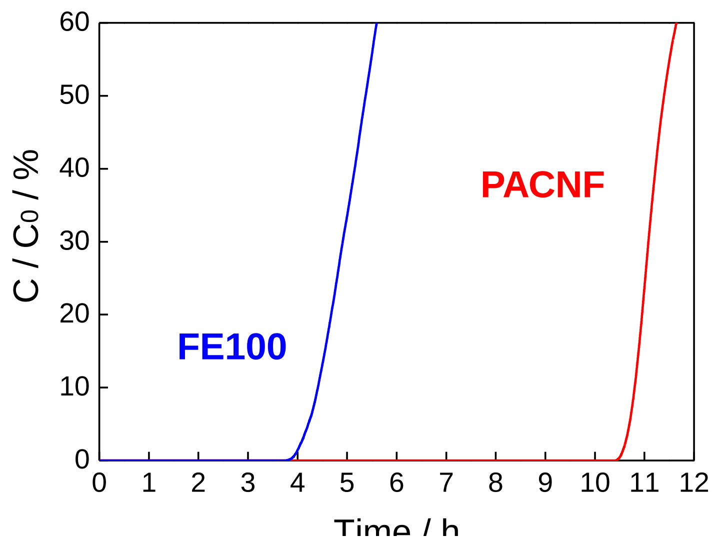


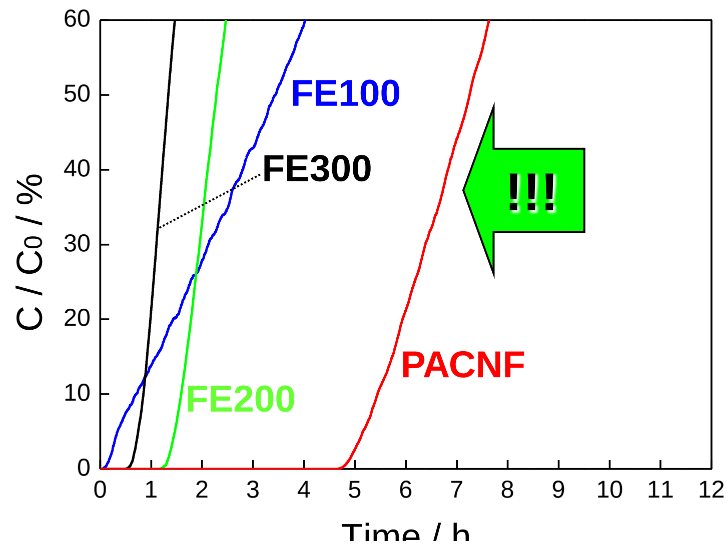
Comparison of formaldehyde adsorption in different ACFs between dry and wet condition



HCHO adsorption characteristics of PACNF in humidified atmosphere

RH	BET	Elemental analysis (wt%)						Microporous
	(m2 / g)	C	H	***N***	***Odiff***	ash	N / O	ratio (%)
90%	375	68.06	1.19	***18.02***	***11.41***	1.32	1.80	94.7%





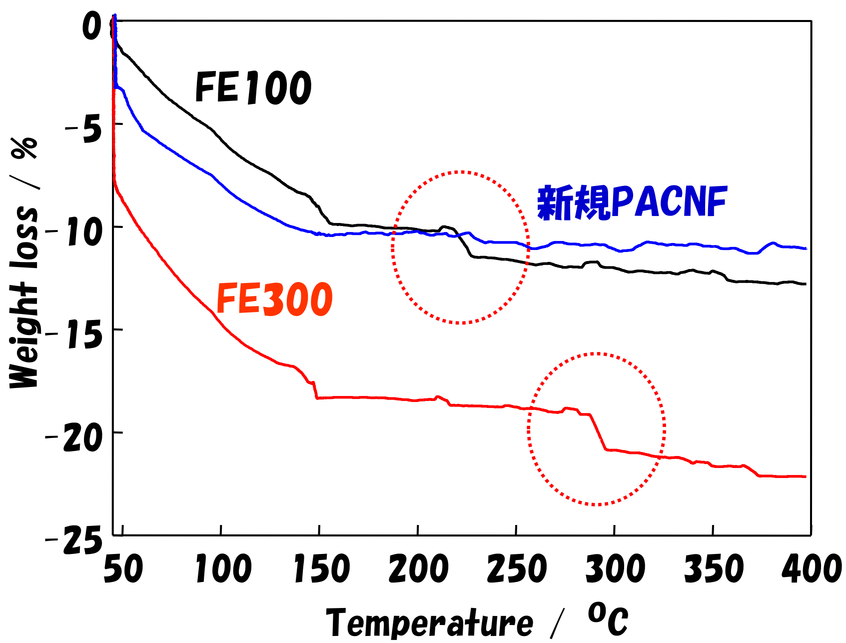
Experimental
HCHO : 11 ppm
Sample weight : 0.05g
Gas flow rate : 100ml / ml
Humidity of condition : 0%

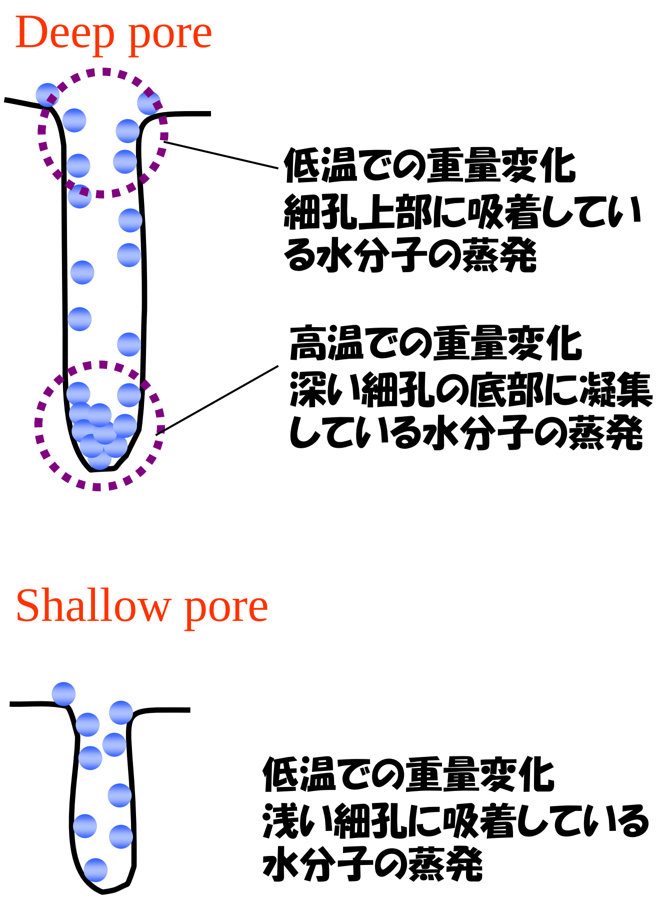
Experimental
HCHO : 11 ppm
Sample weight : 0.05g
Gas flow rate : 100ml / ml
Humidity of condition : 50%

Under the circumstances of humidity (RH=50%),
PACNF shows specific prominent adsorption characteristics for formaldehyde.

Water adsorption property

水分を飽和吸着させたサンプルを
アルゴン中で400℃まで昇温させ、
重量変化を観察





CNF Support for Heterogeneous Catalysts

Oxidation and/or Reduction

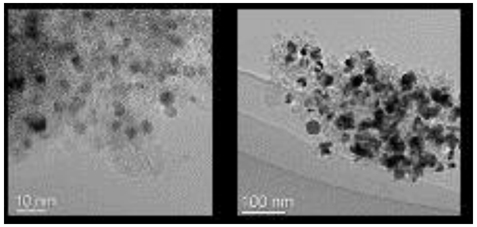
Desulfurization/Denitrogenation

Demetallization

Reduction Catalyst

高分散かつサイズ制御された金属ナノ粒子の創製と触媒作用

市販の活性炭担持触媒



不均質な炭素表面

不均質な担持

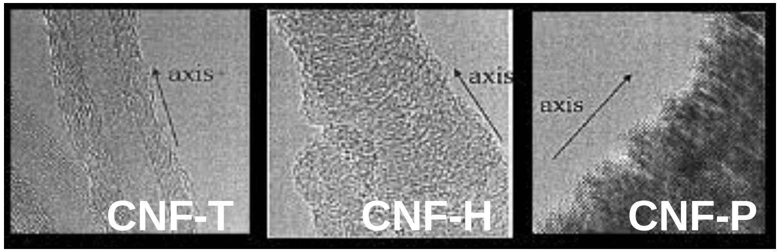
活性・効率・再現性に問題

高分散
サイズ制御

⟹

“ナノ on ナノ”
アプローチ

炭素ナノ繊維（CNF）：表面構造制御

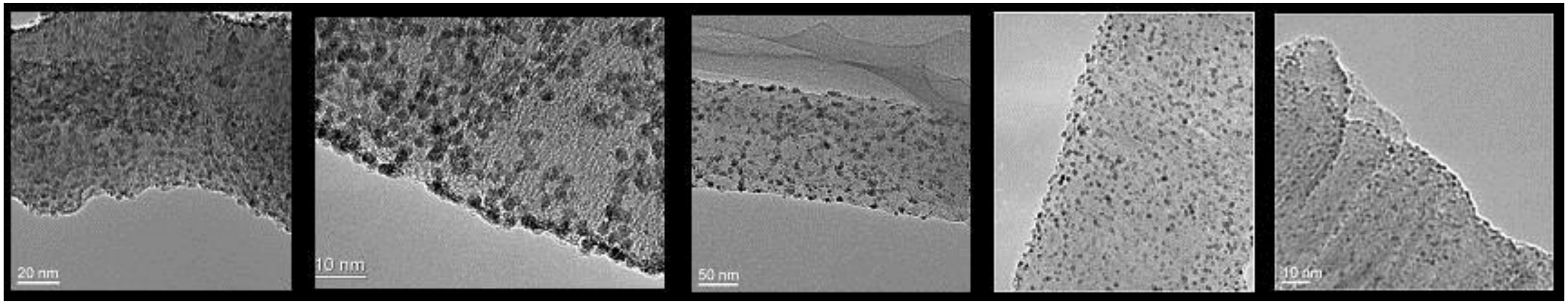


＋

L_nM- -CO （カルボニル錯体）

L_nM- - -|| （オレフィン錯体）

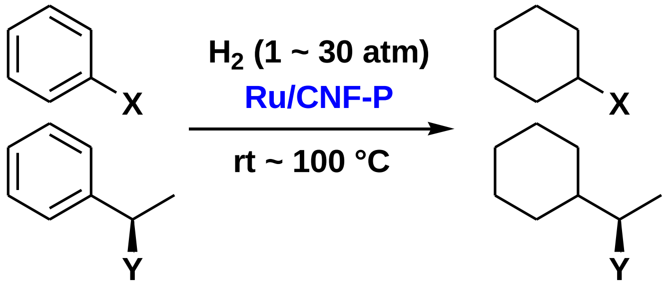
0価有機金属錯体：熱・水素化分解



Fe/CNF-P	Ru/CNF-P	Rh/CNF-P	Pd/CNF-P	Pt/CNF-P
d_{av} = 5.0 nm	d_{av} = 2.5 nm	d_{av} = 7.6 nm	d_{av} = 4.2 nm	d_{av} = 1.4 nm

金属ナノ粒子担持炭素ナノ繊維の応用例

高活性芳香環水素化触媒
高耐久性・高選択性

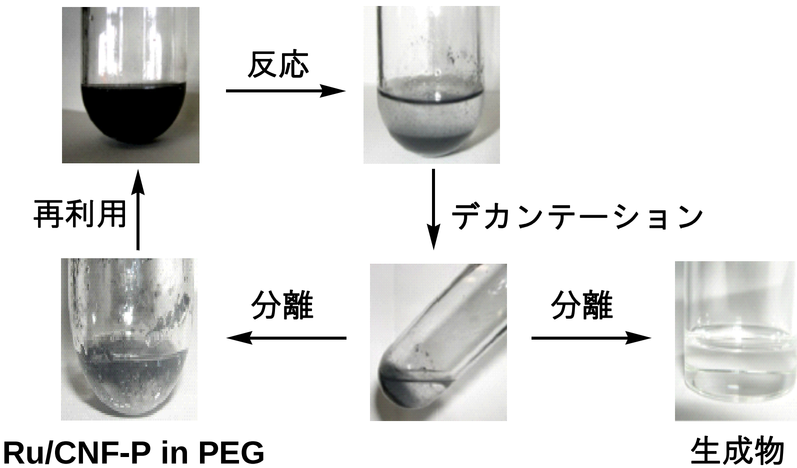


>99.9% ee, *R* 　　 >99.9% ee, *R*

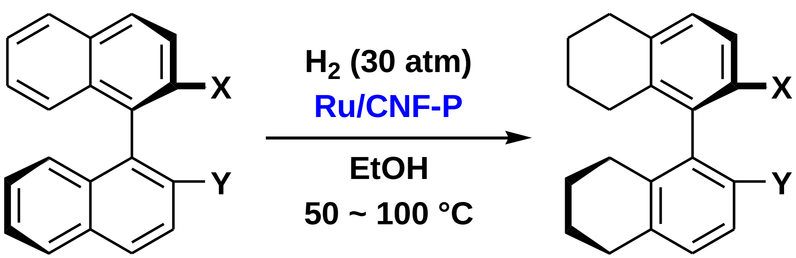
X = OR, CO_2R, NR_2;　Y = OH, NH_2

S/C = 5,300 ~ 36,000 [mol (substrate)/mol (Ru)]

PEGを用いた容易な触媒再利用システム



ビナフチル化合物の部分水素化による
光学活性H_8-ビナフチル誘導体の効率合成

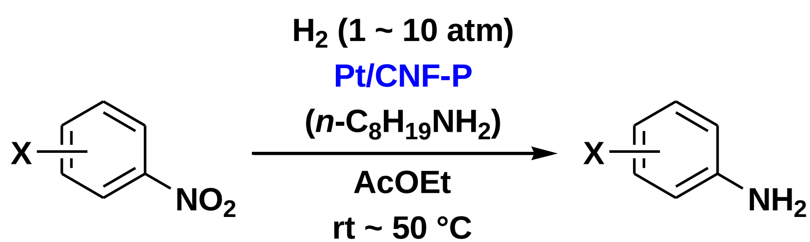


>99.9% ee, *R* 　　 >99.9% ee, *R*

X, Y = OH, OMe, OPiv, OMOM, NH_2

S/C = 150 ~ 1,400 [mol (substrate)/mol (Ru)]

官能基化された芳香族ニトロ化合物の
還元による置換アニリンの高選択的合成



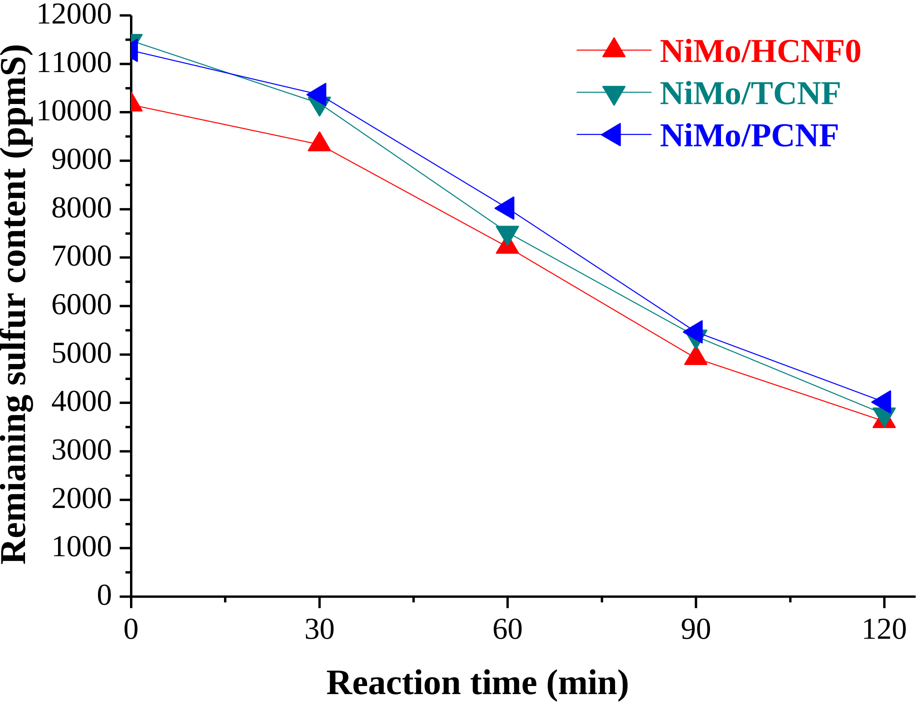
X = Cl, Br, I
$CONH_2$, CO_2R, COR

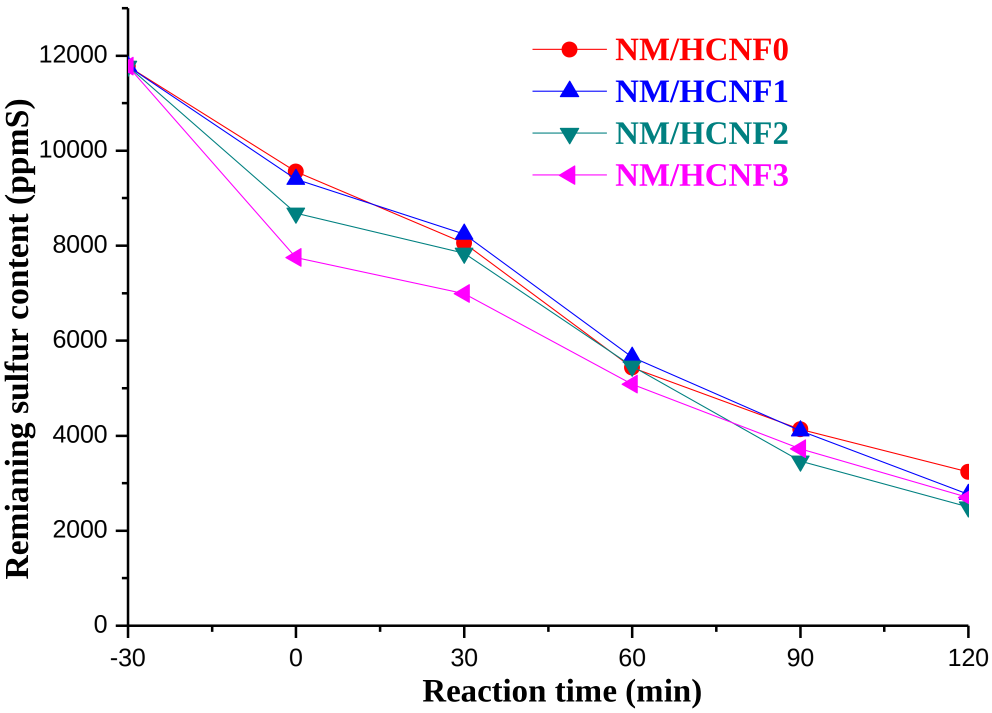
96 ~ 100% selectivity

CNF as supports for NiMo catalysts

- The potential of several kinds of carbon Nanofiber as supports for NiMo catalysts in hydrodesulfurization of SRGO (Straight Run Gas Oil) and HSRGO (Hydrotreated Straight Run Gas Oil)
- The performance were compared with NiMo/Al_2O_3 commercial catalyst to get the relationship between the some supports materials physical -chemical character, active metal dispersion and HDS activity of catalysts

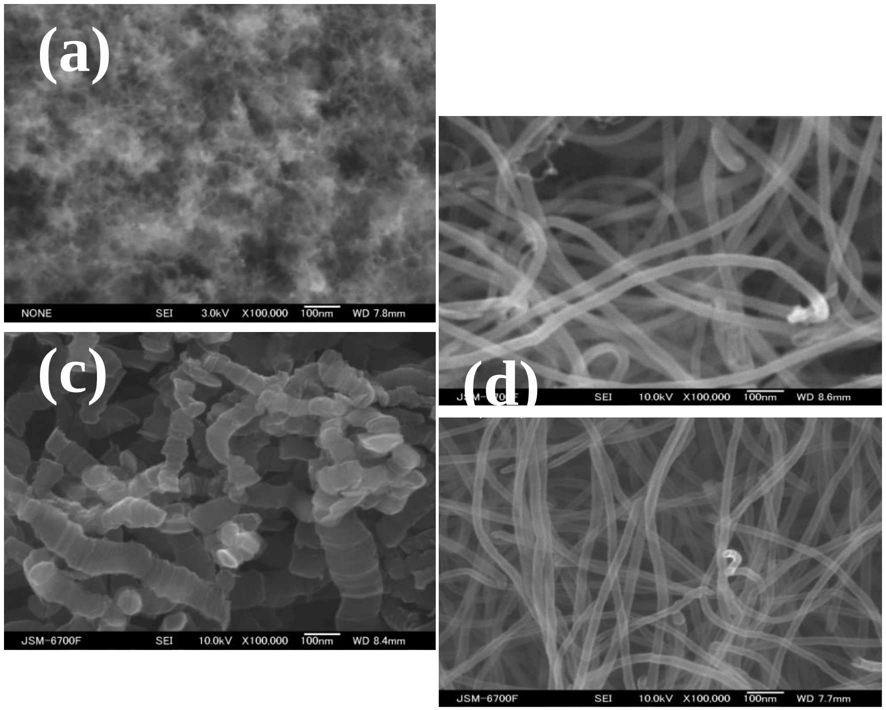
Catalytic activity of NiMoS catalyst on HDS of SRGO





- **NiMo/HCNF, showed higher activity for HDS of SRGO than NiMo/TCNF, NiMo/PCNF**
- **NiMo/HCNF2 and NiMo/HCNF3 with higher surface area showed higher activity than NiMo/HCNF1**

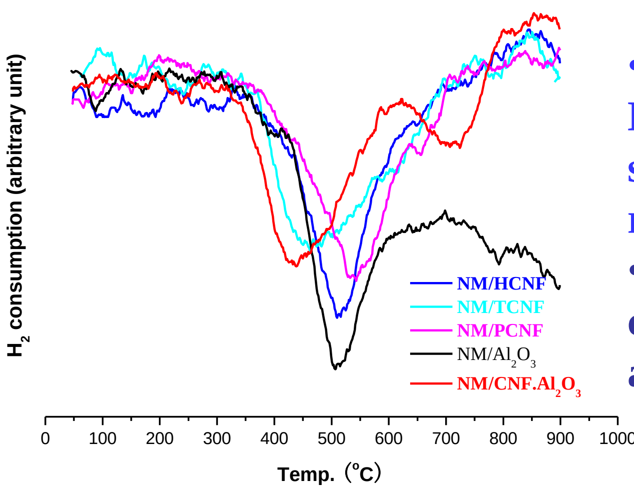
Physical and chemical characteristics of supports and catalyst



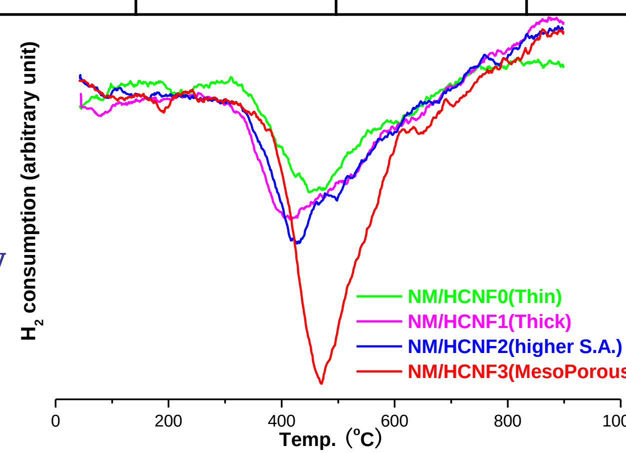
(a)$HCNF/Al_2O_3$(b)HCNF
(c)TCNF (d)PCNF

LN_2 adsorption-desorption test result of support materials calculated by BJH desorption method

Sample	R_p (nm)	S(m^2/g)	V_p(cc/g)
Al_2O_3	8.0	231	0.914
HCNF0	9.2	105	0.593
TCNF	2.1	59	0.568
PCNF	2.4	59	0.534
HCNF1	1.7	271	0.270
HCNF2	1.7	303	0.301
HCNF3	1.9	312	0.343



- HCNF3 supported NiMo catalysts showed higher reducibility
- H_2-TPR results show consistencywith HDS acivity



CNF for Luminescence

FEBL

Objective

- Development of FEBL using CNF instead of CNT

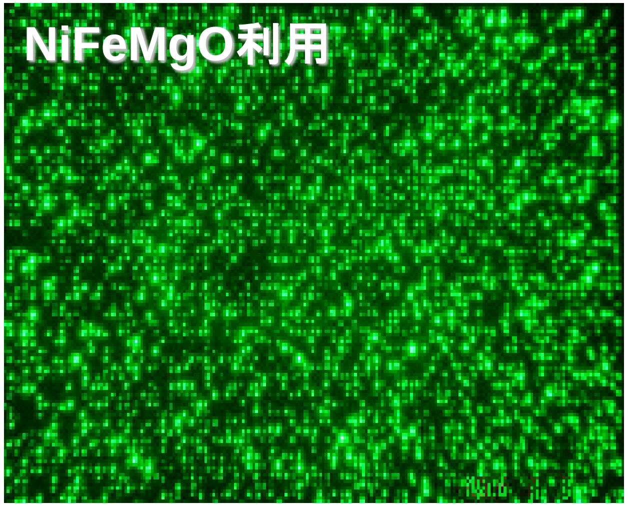
Expectation

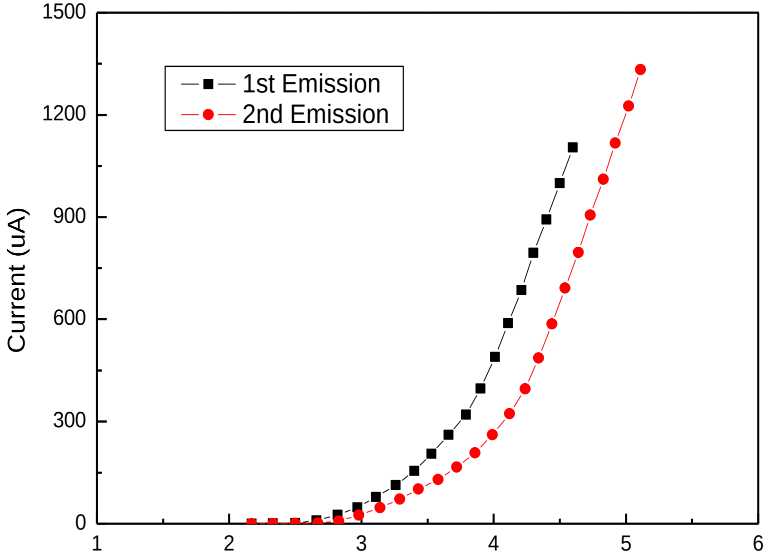
- Patent
- Activation of nano-materials

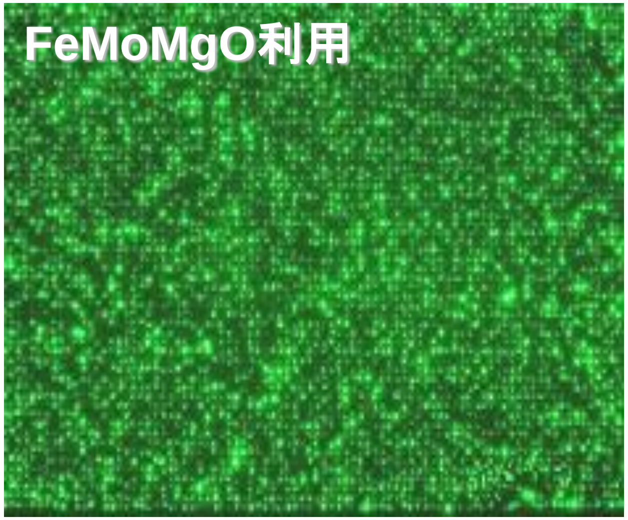
Final Target

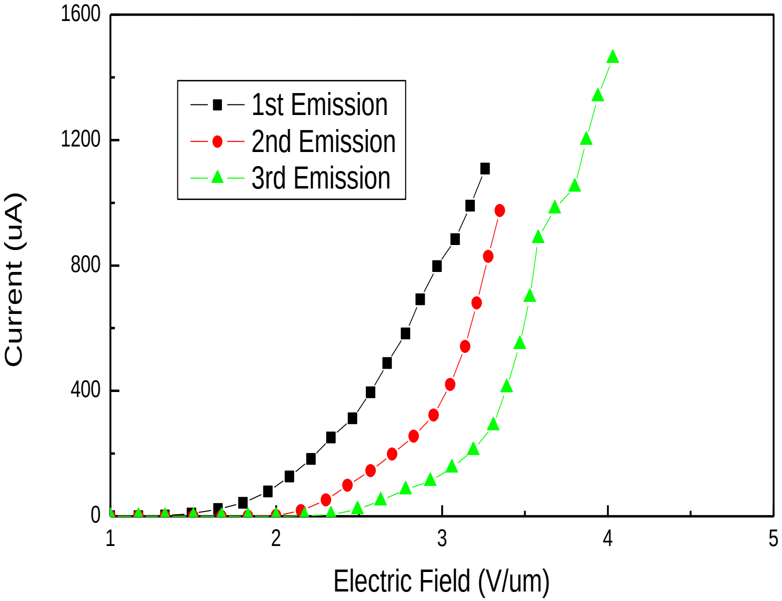
- CNF Paste
- 10 - 50nm(Aspect ratio over 150)
- 7 inch panel using CNF
- Fill factor: over 80%
- Homogeneity: over 90%
- Brightness: over 6000cd/m^2 (12000 V)

CNF Development



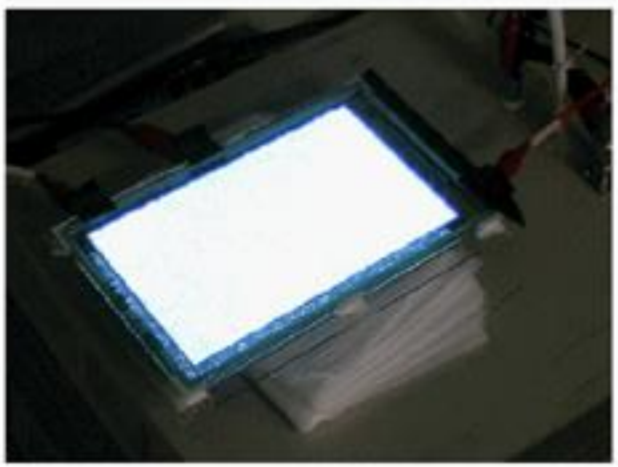






3 E system 7 inch Panel

Cathode 電位、Anode 電位、電流



Diffuser使用

CNF for Composites

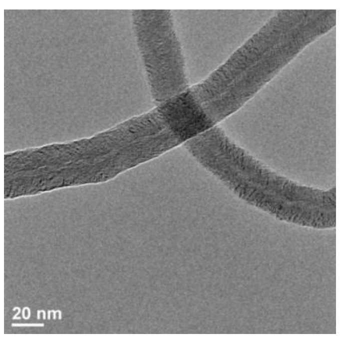
Electric conductivity

Thermal Conductivity

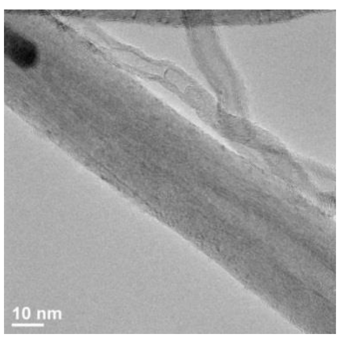
Tensile Strength and Modulus

Electric Conductivity for Polymer Composites

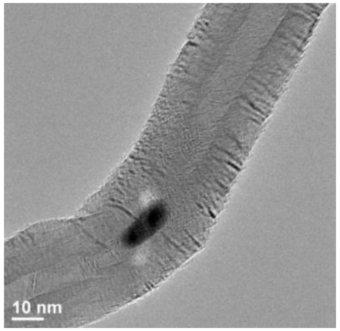
触媒	合成条件	平均収率	繊径	CNF 構造	電気伝導度
Co:Fe:Cr:Mg=4:2:2:2 (重量比) [触媒前処理: Air, 600℃, 4h]	**460℃**, 60min, **C_2H_4**:H_2=160:40	23.1倍	40nm	**Herring-bone**	**Out of range**
	600℃, 60min, **C_2H_4**:H_2=160:40	26.5倍	40nm	**Tubular**	**4.1**
	600℃, 60min, **C_3H_8**:H_2=160:40	25.1倍	40nm	**Tubular**	**5.1/5.6**
	700℃, 60min, **C_3H_8**:H_2=160:40	21.5倍	70nm	**Tubular**	**4**



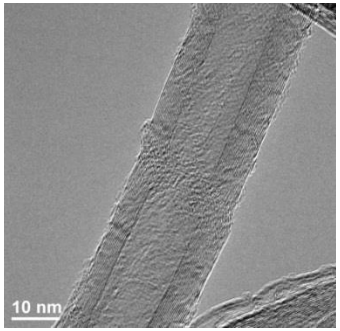
460℃ C_2H_4



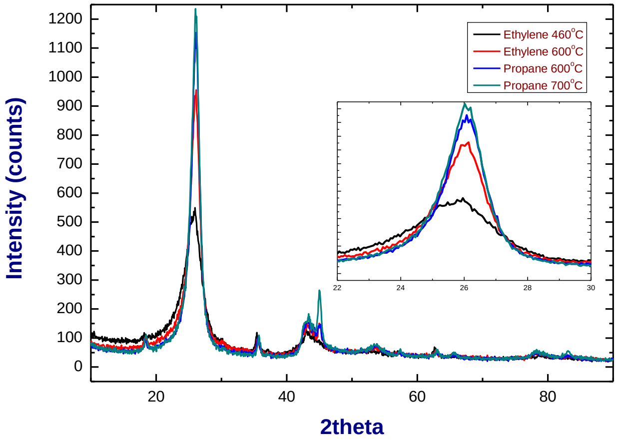
600℃ C_2H_4



600℃ C_3H_8



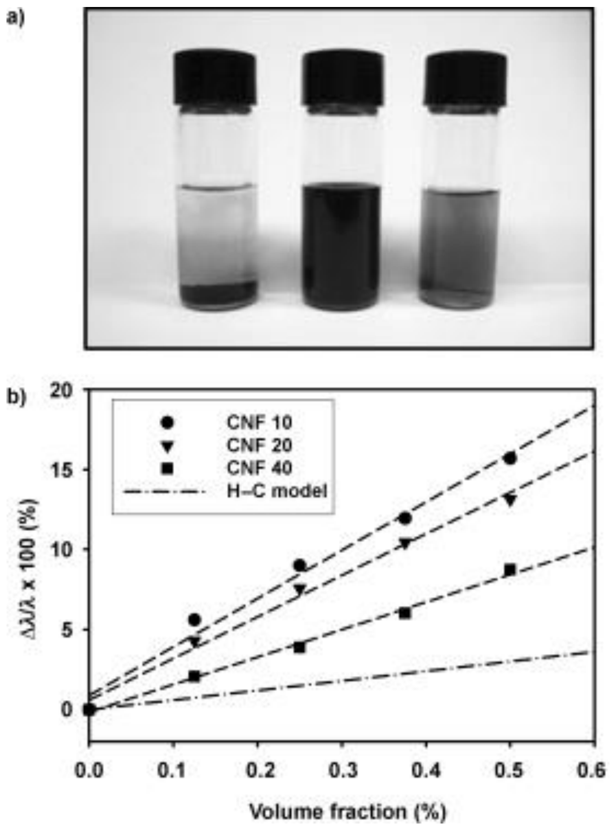
700℃ C_3H_8



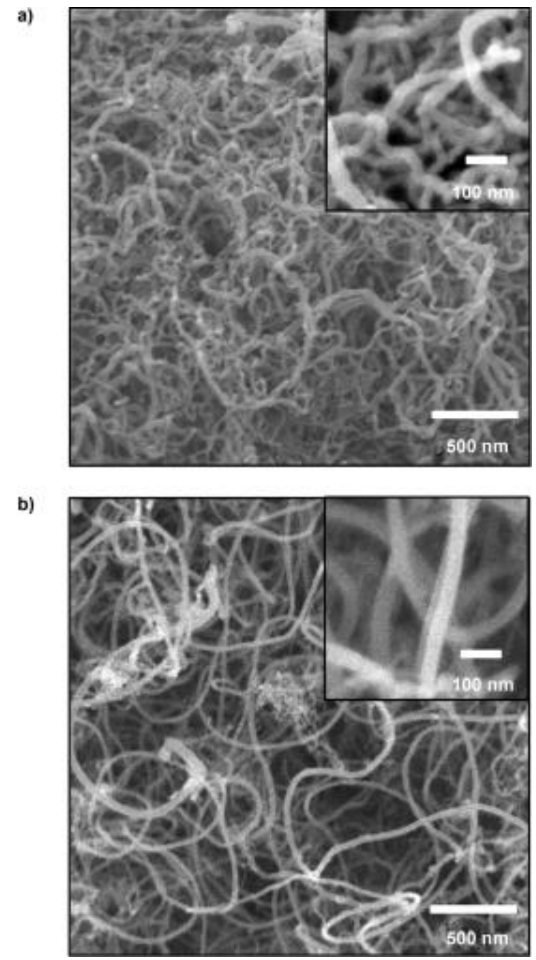
Nano fluid

A Novel Nanofiller for Nanofluid Applications

Small, Volume 3, Issue 7, Date: July 2, 2007, Pages: 1209-1213



a) Photograph of CNF-10-water suspensions. Left: pristine CNFs (0.5 vol %); middle: TCNFs from plasma oxidation for 30 min (0.5 vol %); right: TCNF-water suspension diluted 20 times. b) TC enhancement of nanofluid containing various contents of CNFs. The dot-dashed line indicates the theoretical prediction for TC enhancement based on the Hamilton-Crosser (H-C) equation



SEM images of a) pristine CNFs and b) TCNFs (CNF-10).
Insets: higher-magnification SEM images

Thermal Conductivity for Rubber Composites

CNF 適用配合

		1	2	3	4	5
MB	Butyl rubber	100	100	100	100	100
	Filler	60	60	60	60	60
	MB 薬品	13	13	13	13	13
	CNT	0	10	10	10	10
		現用	JEIO	KKPC-1	KKPC-2	KKPC-3 *
FM	FM	12	12	12	12	12

Heat conductivity	TMCD	0.296	0.378	0.331	0.342	0.334
	%	100	128	112	116	109

1番　　: control

2番　　: control + JEIO 10 phr

3番 ~ 4番 : control + KKPC sample 10 phr

1. KKPC-1: 120nm 繊径(AS-prepared) – **Fe:Ni:Co:Mg=7:0.5:0.5:2** 触媒を用いて C_2H_4 ガスで合成した太いTubular

2. KKPC-2: KKPC-1を2800℃熱処理

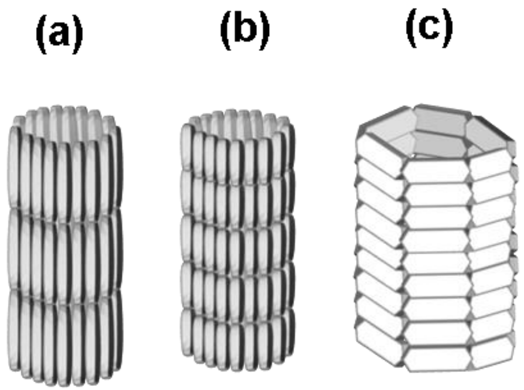
3. KKPC-3: KKPC-1の触媒を除去したもの

Experimental

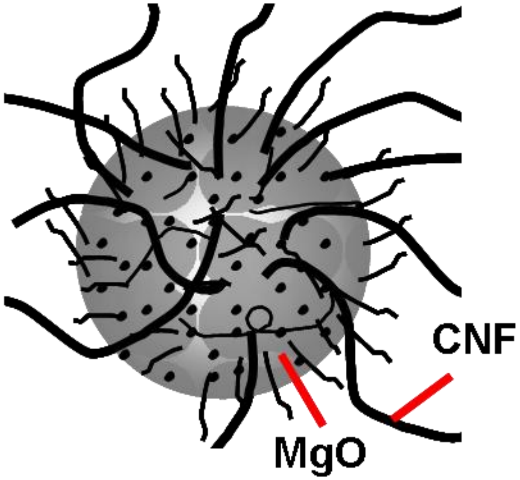
Preparation of CNF-MgO composites

Catalysts

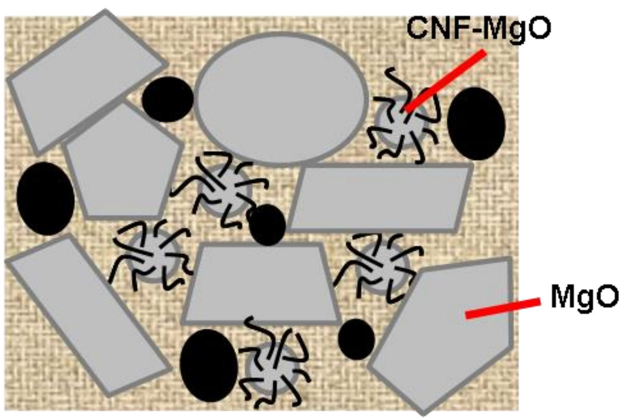
- KNF003(Fe/Mo/MgO) (a)
- CoCrMgO (6/2/2) (b)
- FNMgO(Fe/Ni/MgO) (c)



Schematic pictures of CNF structures
(a) CNF composed of long nano-rod
(b) CNF composed of short nano-rod
(c) CNF composed of nano-plate



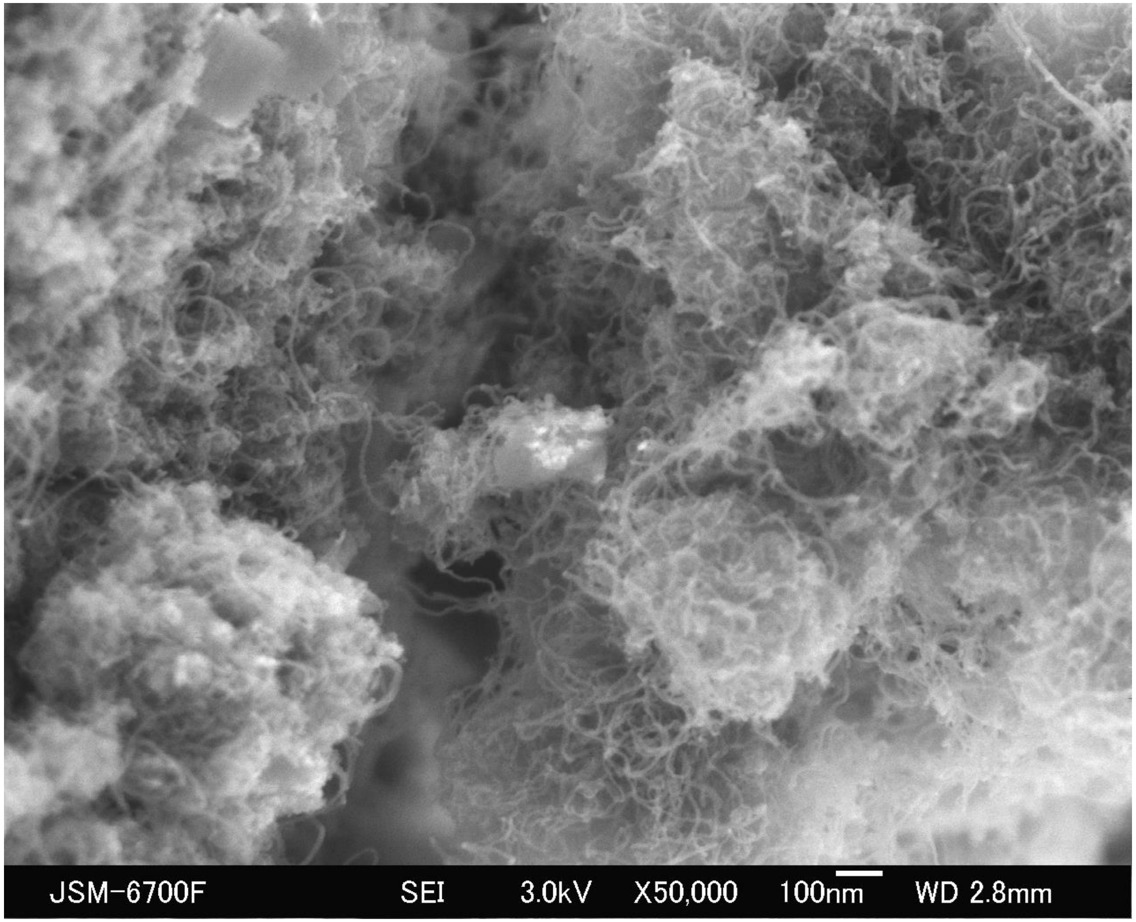
MgO-CNF

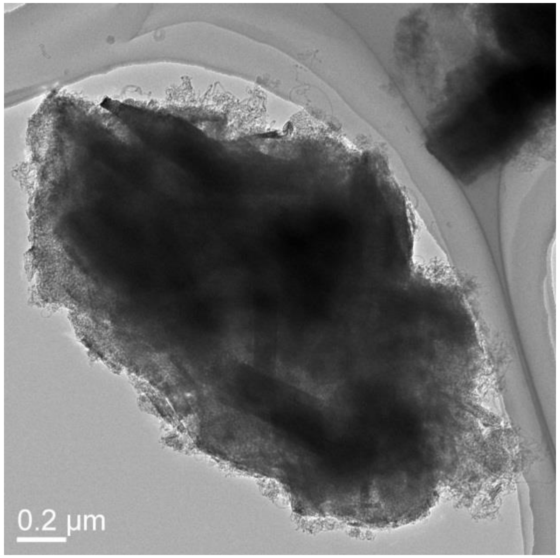


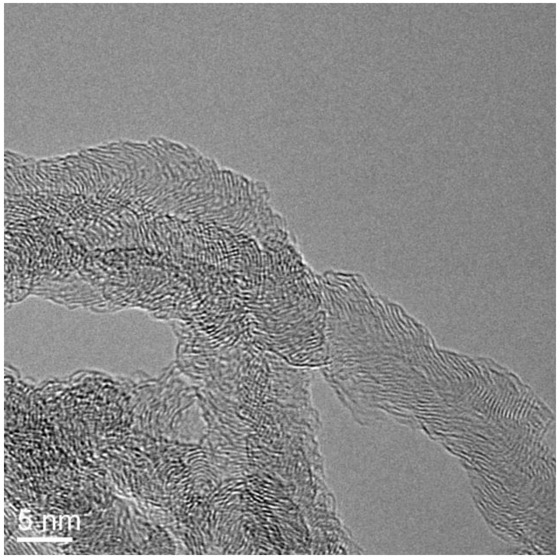
Schematic picture of MgO refractory composed of MgO, Graphite and MgO-CNF

Not submitted

CNF for Ceramic Conductivity

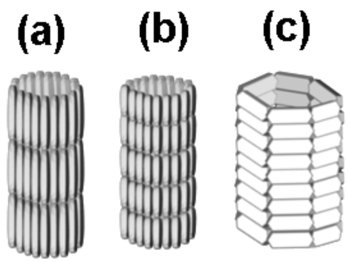






·KNF−MgO−004のSEMとTEM写真:
Herringbone CNF/MgO

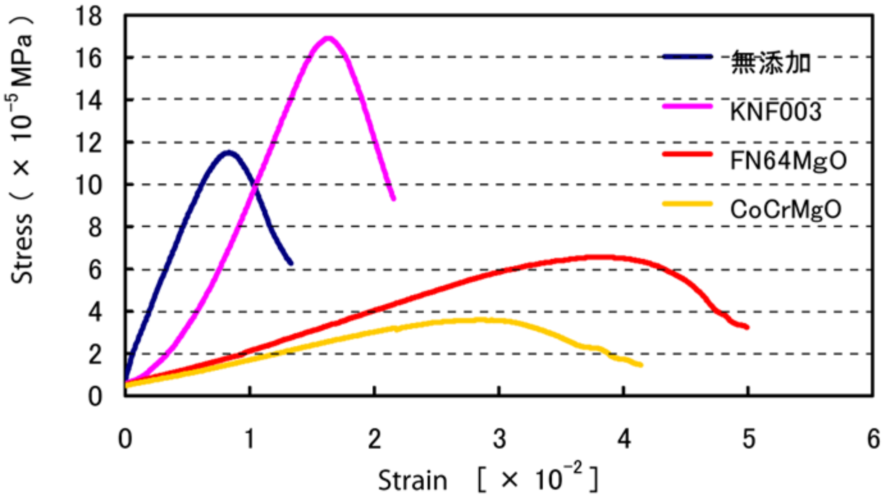
Strength evaluation of CNF-MgO added MgO-C Refractory



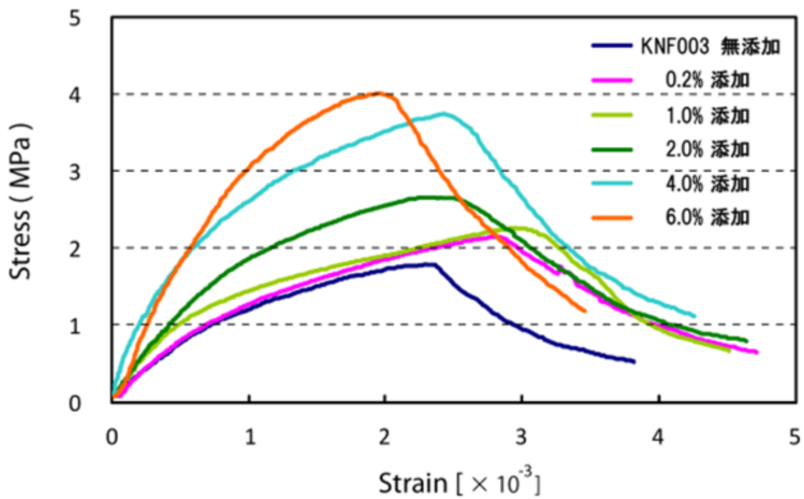
Structural Models of CNFs

CNF preparation conditions

Catalyst		Component	Ratio	Carbon Source	Yield (times)
KNF003	(a)	Fe/Mo/MgO	2/24/100 (mol)	CH_4	0.87
FeNiMgO	(b)	Fe/Ni/MgO	48/32/20 (mol)	CO	19.5
CoCrMgO	(c)	Co/Cr/MgO	6/2/2 (wt.)	C_2H_4	19.5

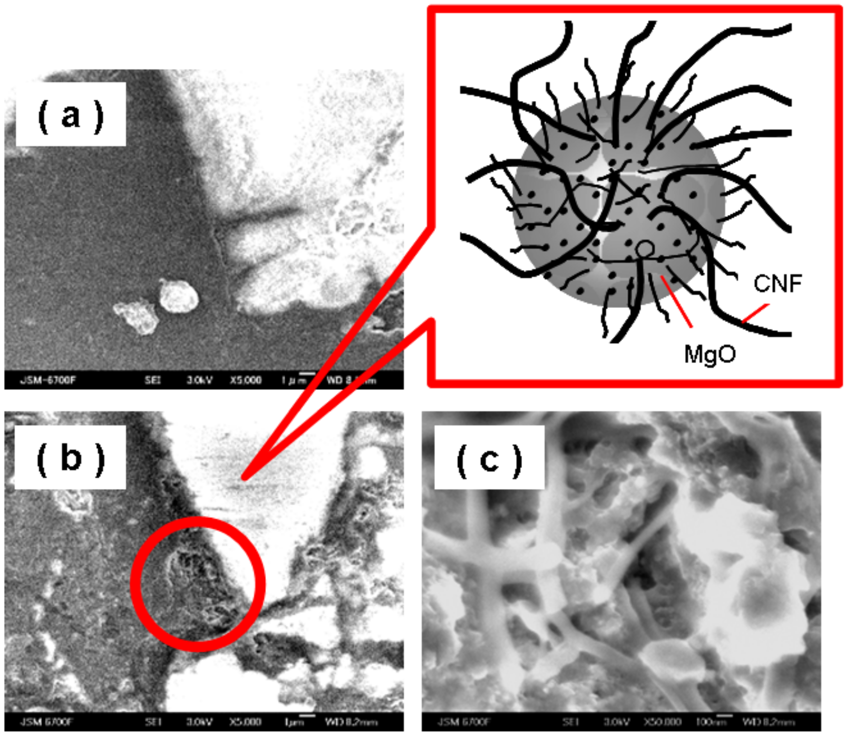


Strain-stress curves of CNF-MgO composite added refractories



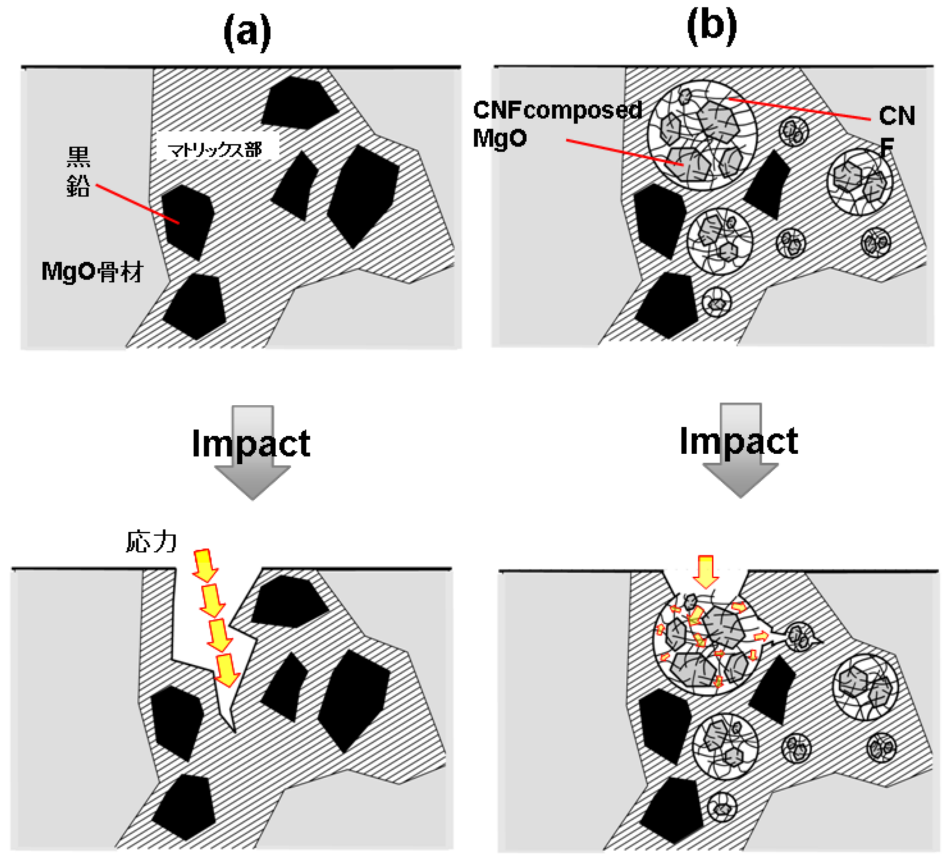
Effect of addition amounts of CNF-MgO composites (Graphite：15%)

SEM images of KNF003-composed refractory



KNF003 composed MgO added MgO-C refractory
(a) None (× 5000)、(b) KNF003 (× 5000)、(c) KNF003 (× 50000)

Crack propagation prevention mechanism



CNF composed MgO added refractory
(a) No CNF-MgO、(b) CNF-MgO added

Conclusions

- Best Structure Must Be Selected For Each Objective and Prepared.
  - Preparation step (Selective and Controlled Synthesis)
  - Modifications
- Carbon Nanofibers Can Be
  - A Promising Candidate
  - As A Unique Component
- Composite Structure Must Be Always Designed.

New Carbonaceous Materials Technology

New feasible technology to solve urgent energy and environmental problems which fusion conventional fuel science, carbon technology and nano-carbon technology.

Fossil Fuel Science & Technology

- Petroleum Chemistry, Technology
- Coal & Biomass Sciences
- Catalyst, Mining

Conventional Carbon Technology

- Carbonaceous Materials Sciences
- Carbon Technology
- Carbon alloy science
- Activated carbon science

Nano Carbon Technology

- Nano structural concept
- Nano technologic method

Why New Carbon Technology through the fusion of Conventional and Nano Carbon Technologies ?

- **Innovation of performances of carbon materials.**
- **Consumption of fossil fuels grows by 2~3 times up to 2050.**
  - **High utilizations of fossil fuels and biproducts,**
  - **Decreasing environmental burdens**

Lab Staffs

- ✓ Isao Mochida: Professor of special appointment
- ✓ Seong-Ho Yoon: Professor
- ✓ Jin Miyawaki: Assistant Professor
- ✓ Satoko Mitoma: Researcher of Alliance
- ✓ 1 Guest Professor
- ✓ 3 Post-doctorates
- ✓ 1 Researcher for Analyses
- ✓ 9 Doctor course students
- ✓ 5 Mater course students
- ✓ 3 Secretary

Staffs for Nano-studies
- Faculties
- 1 Post-doctorate
- 3 Doctor course students

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Thank you for attentions!