



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

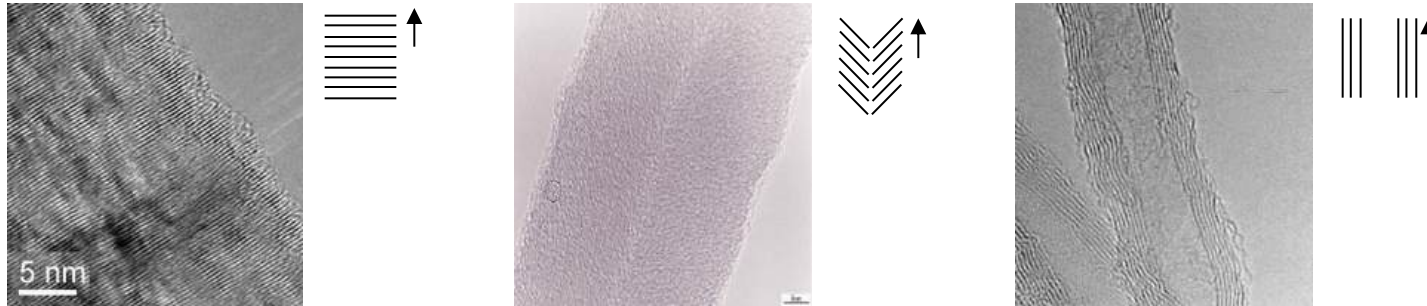
Relatively low price
Patent problems
Mass-production
Various applications
Large diameter



Structural variety of CNFs

Typical classification of CNF Structure

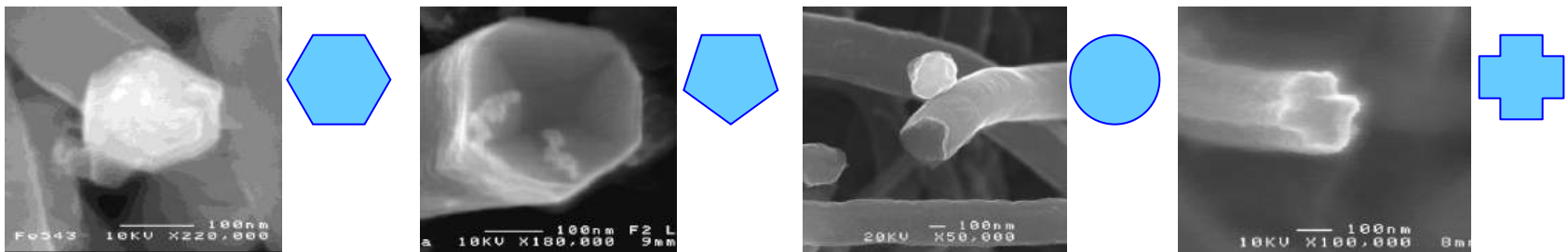
- graphene ((002) layers) alignment to the fiber axis, TEM observation



< 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



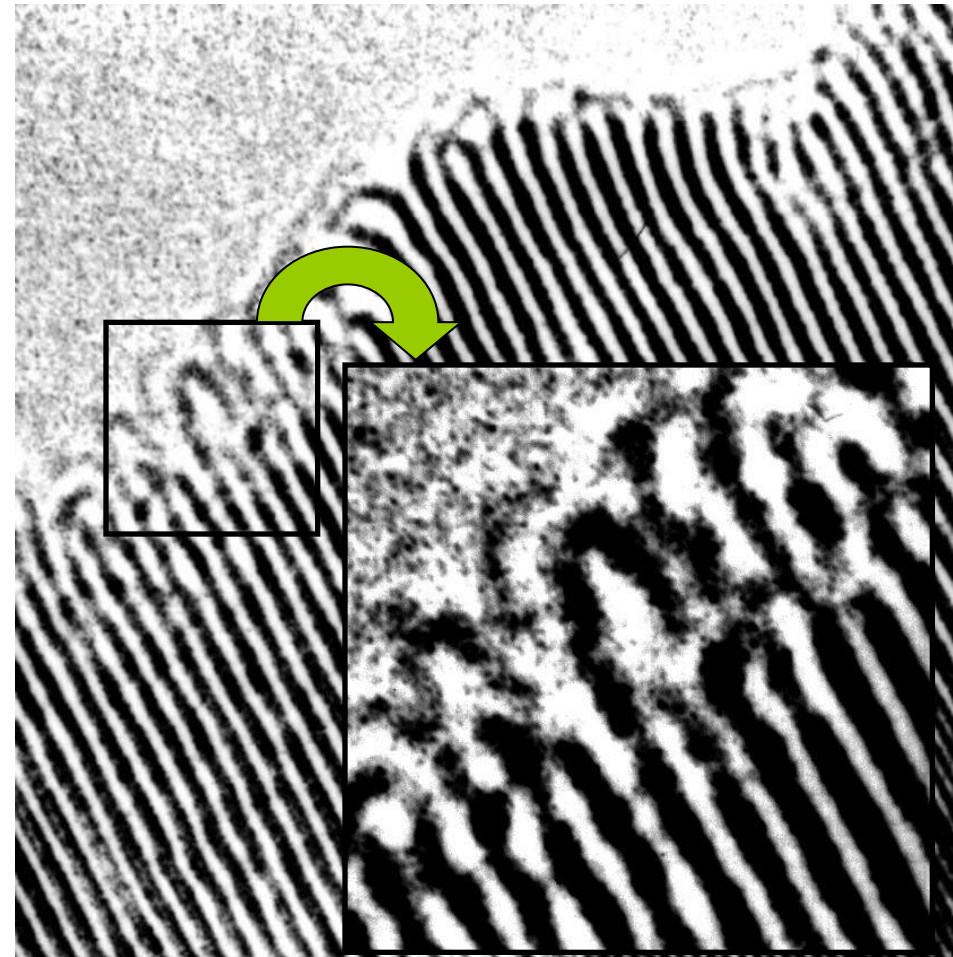
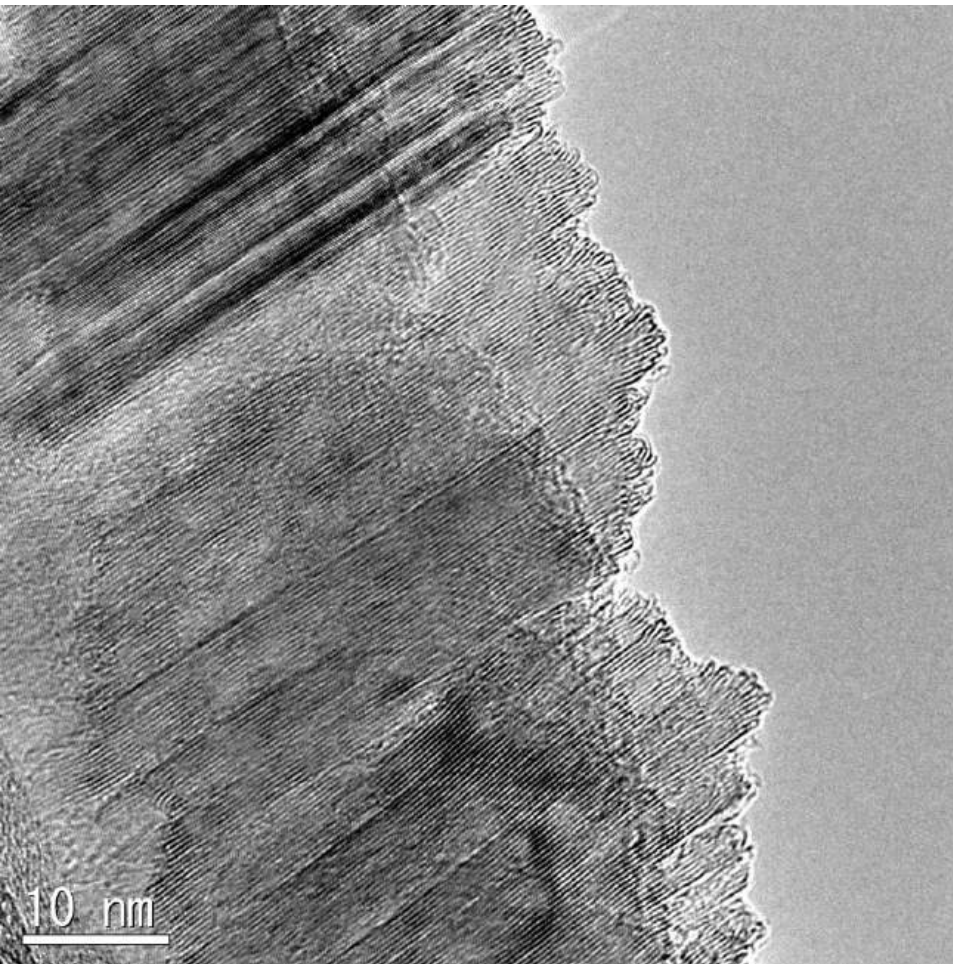
Polygonal

Circle

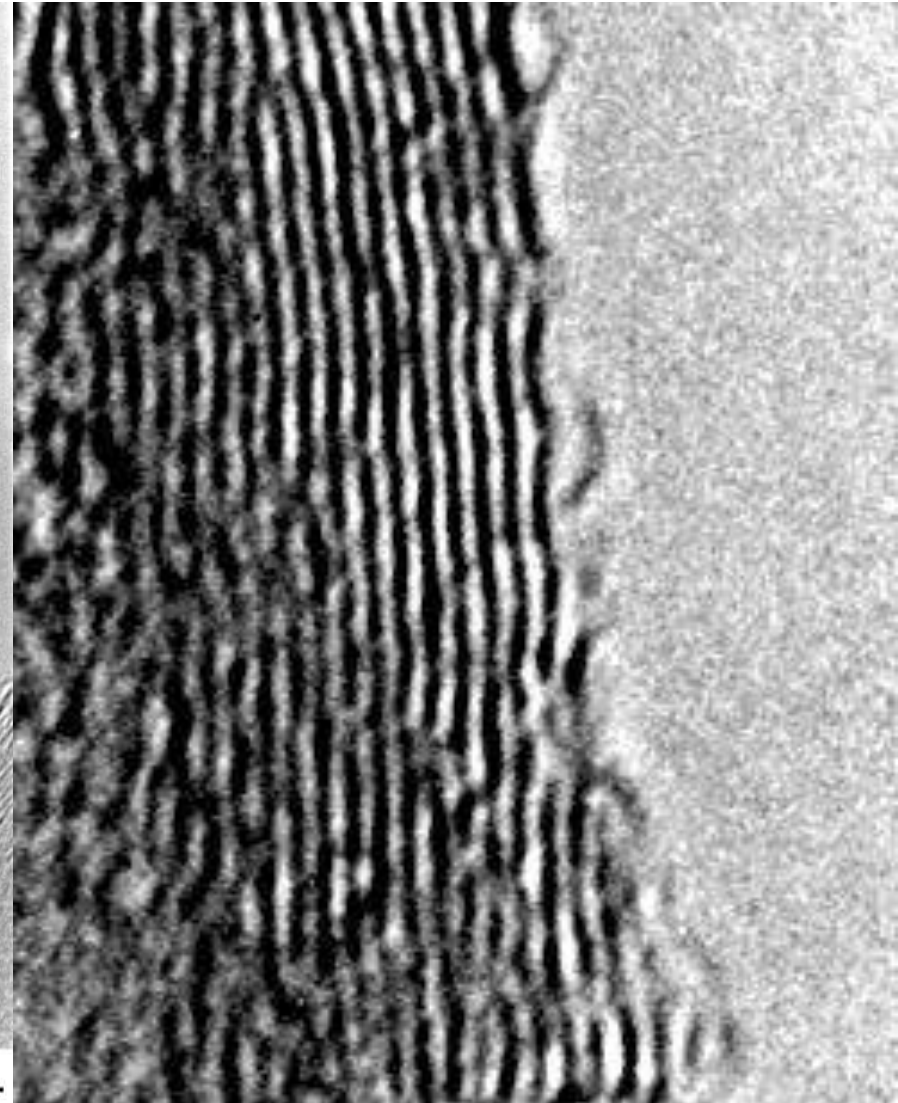
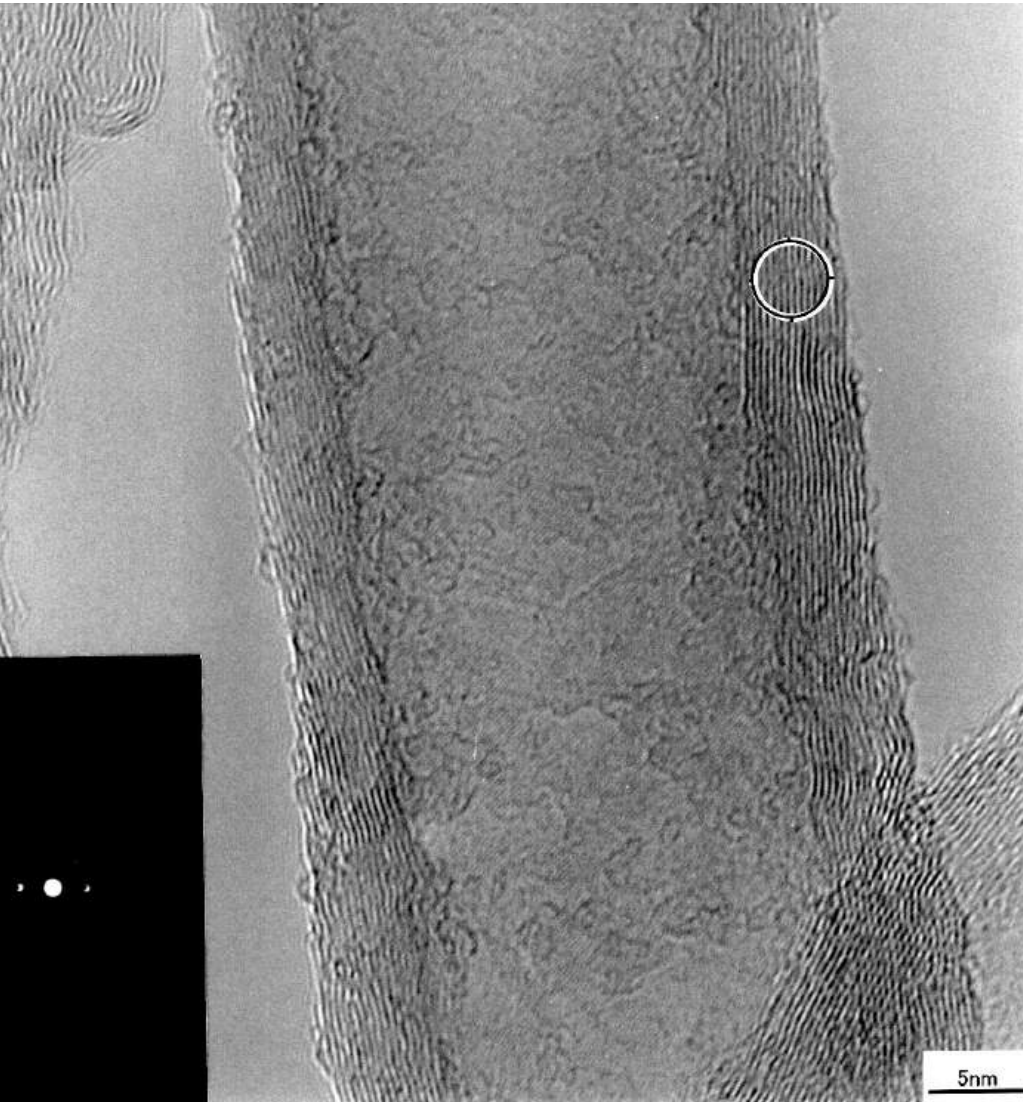
Cross

Different Surface Characteristics

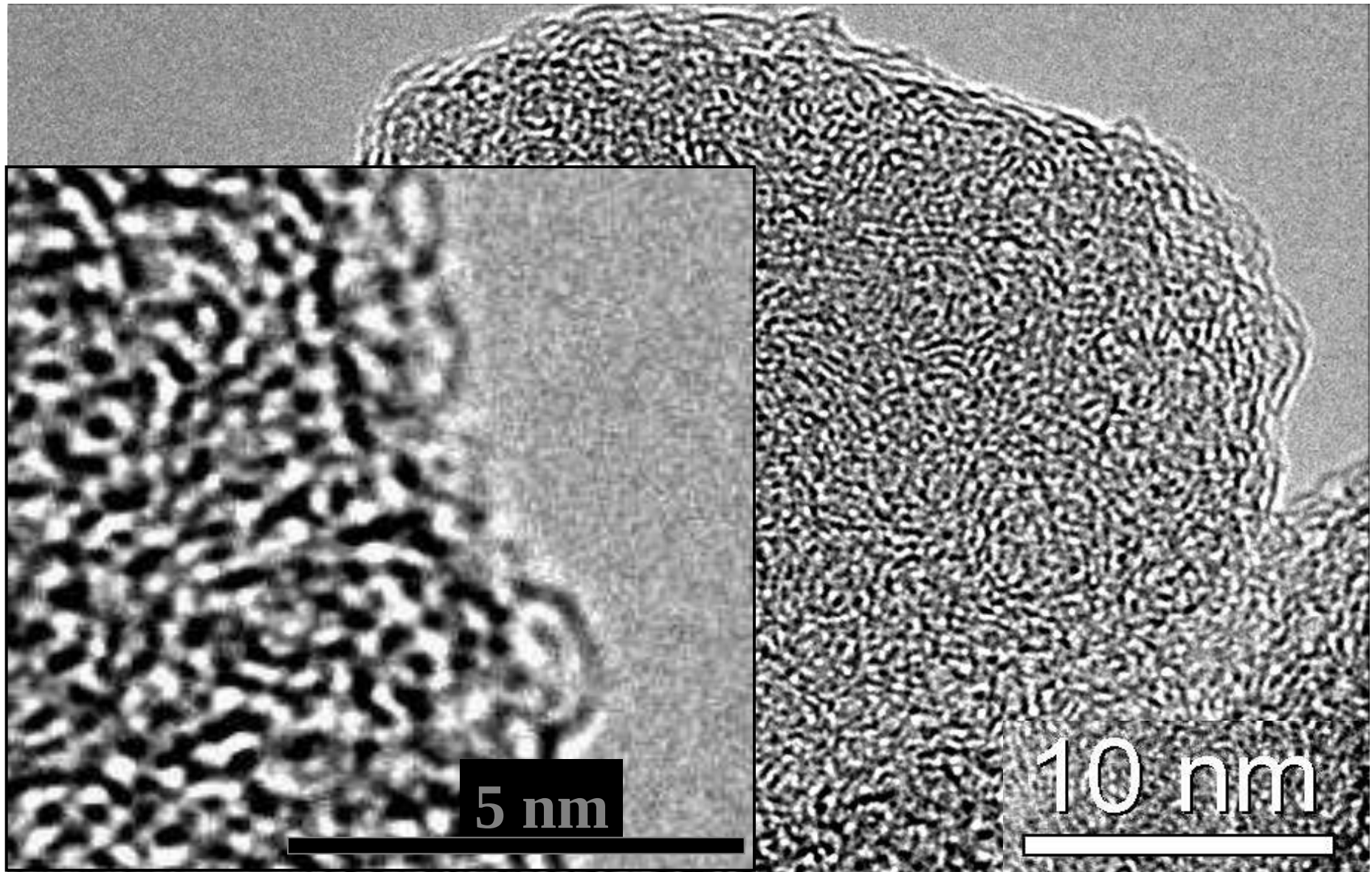
Surface of Platelet CNF



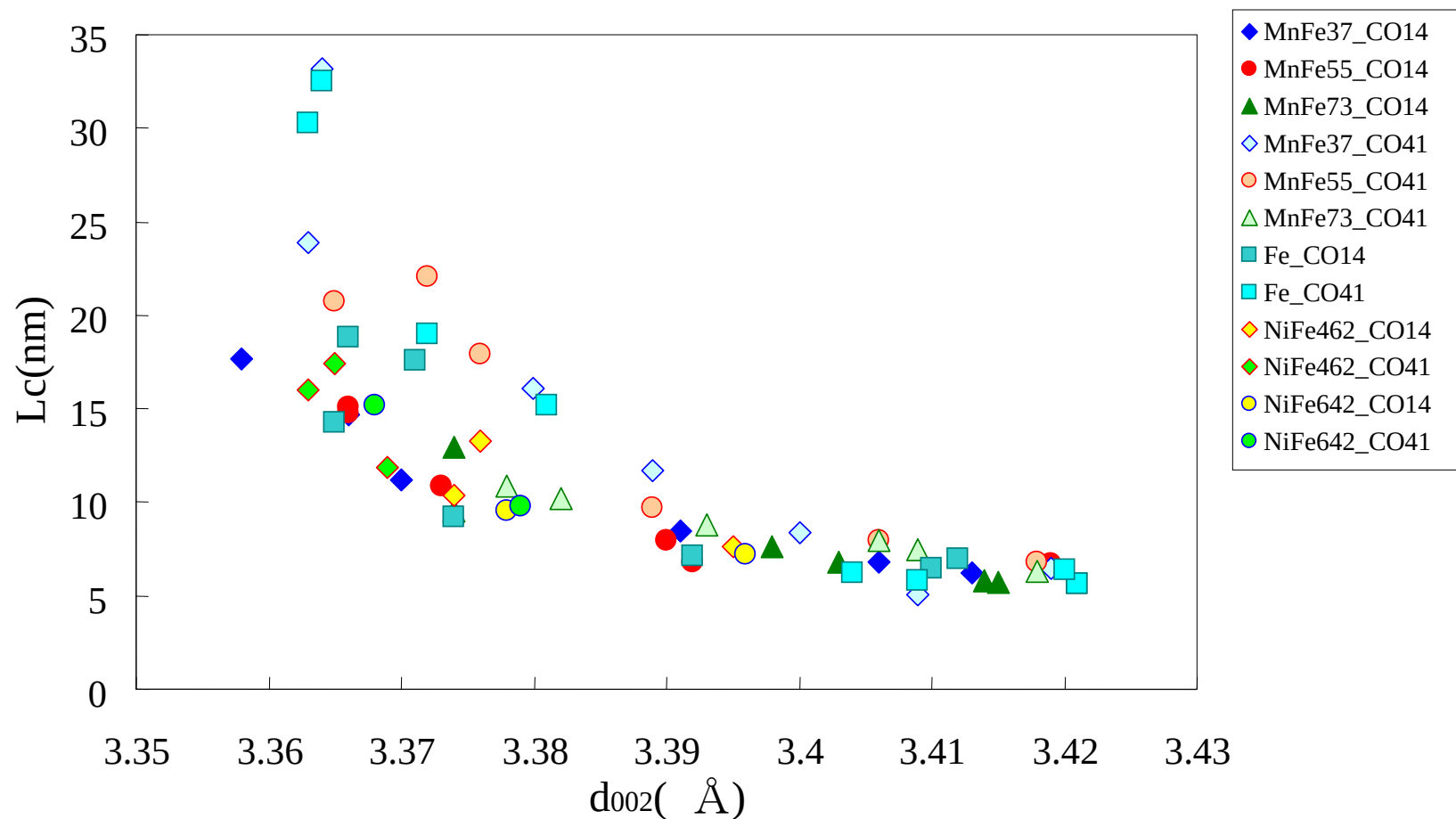
Surface of Platelet CNT



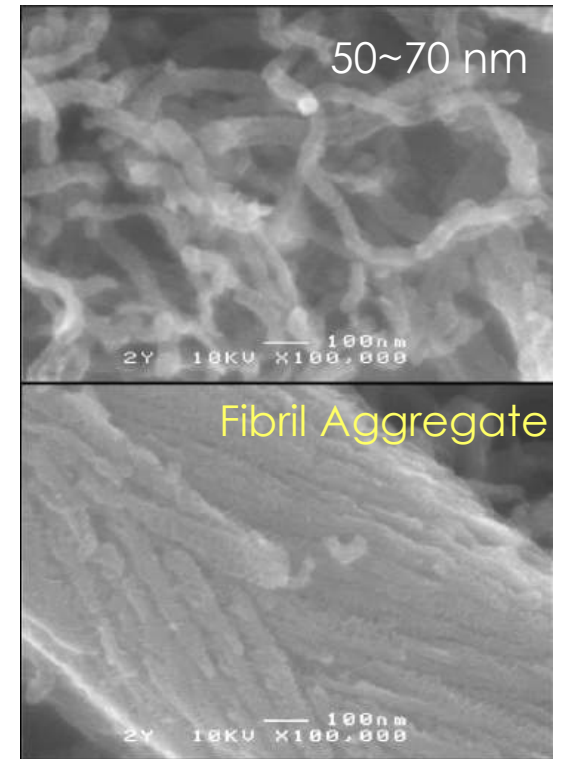
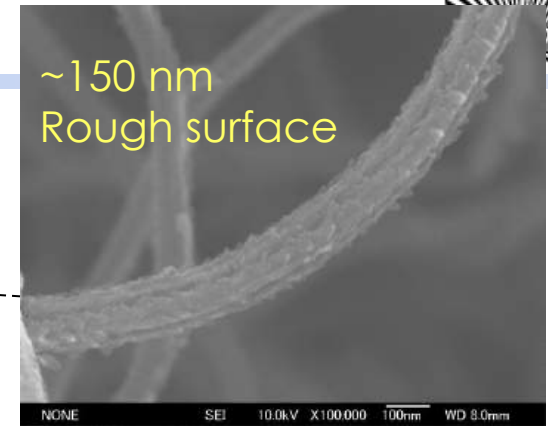
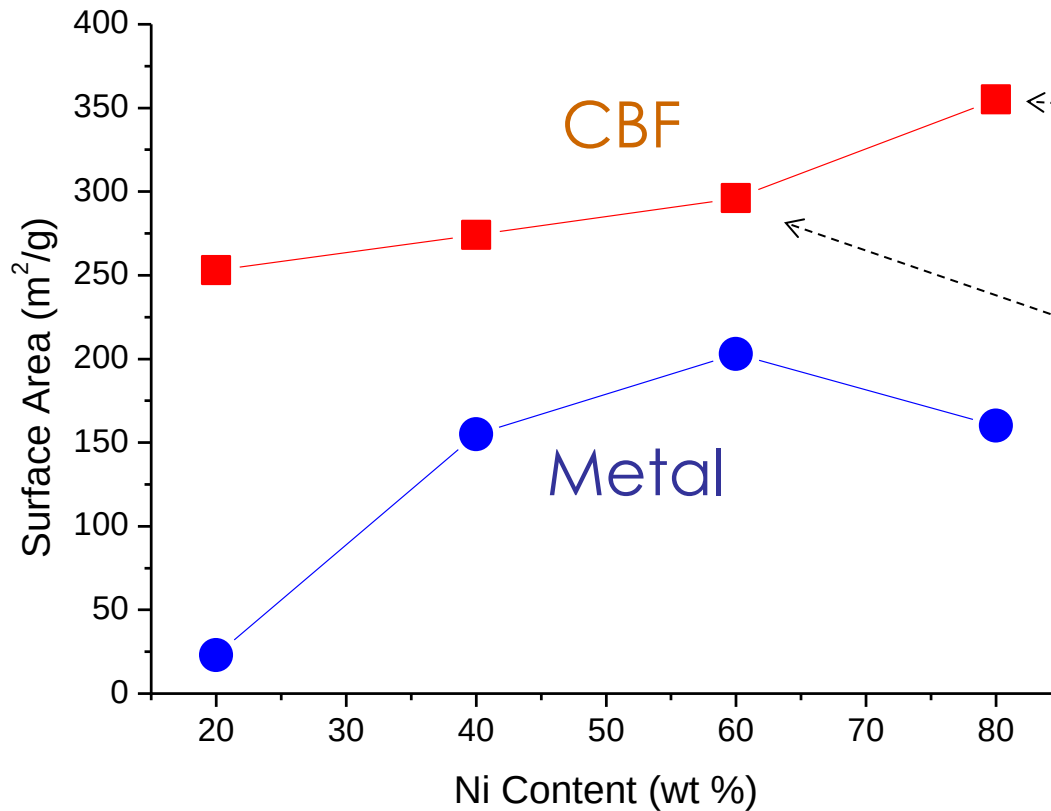
Surface of carbon blacks



Control of Graphitic Properties of TCNFs



Control of surface area



- CBF fibers 250 ~ 350m²/g, Metal fibers 20 ~ 200 m²/g
- CBF fibers shows 2~10 times higher SA than Metal fibers.
- SEM of CBF fibers with SA around 300 m²/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**

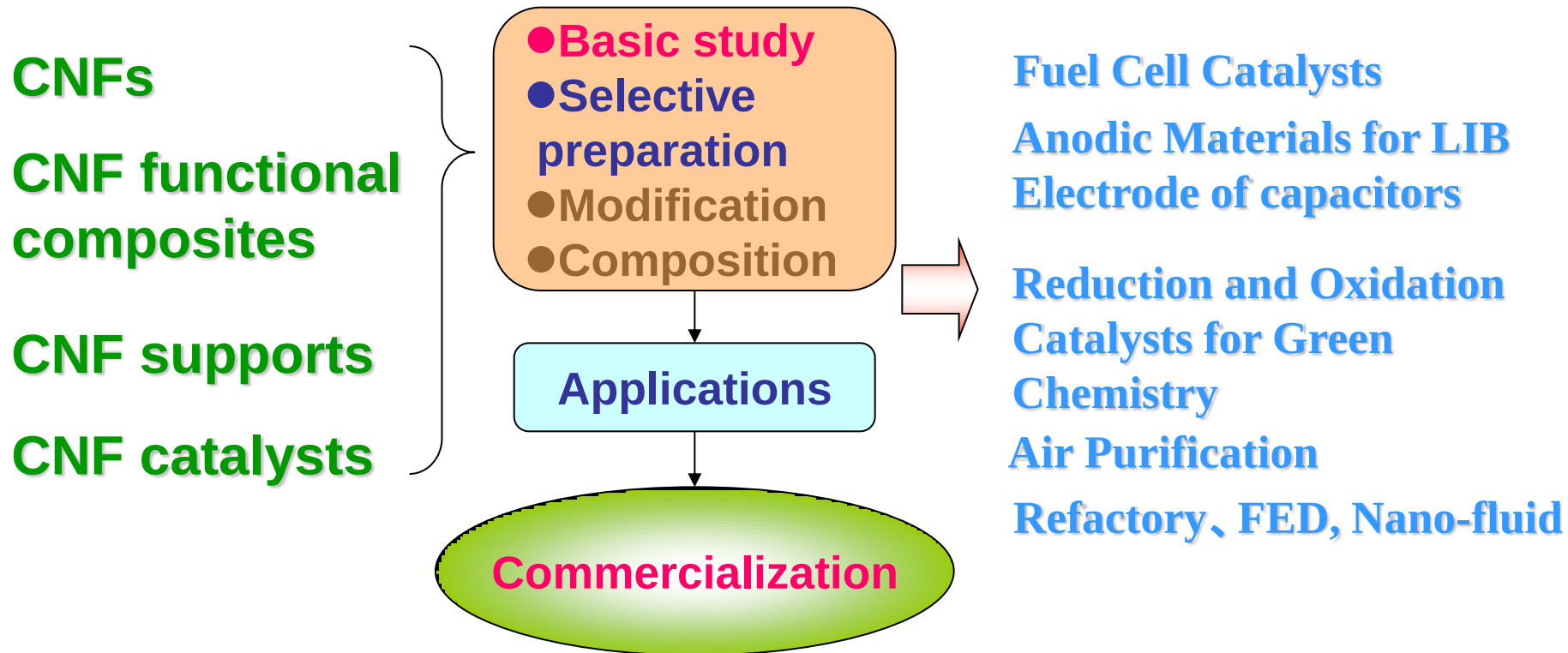


Objective of this study



Backgrounds of Objectives:

Functional revolution of CNFs Based on the Carbon Nanotechnology





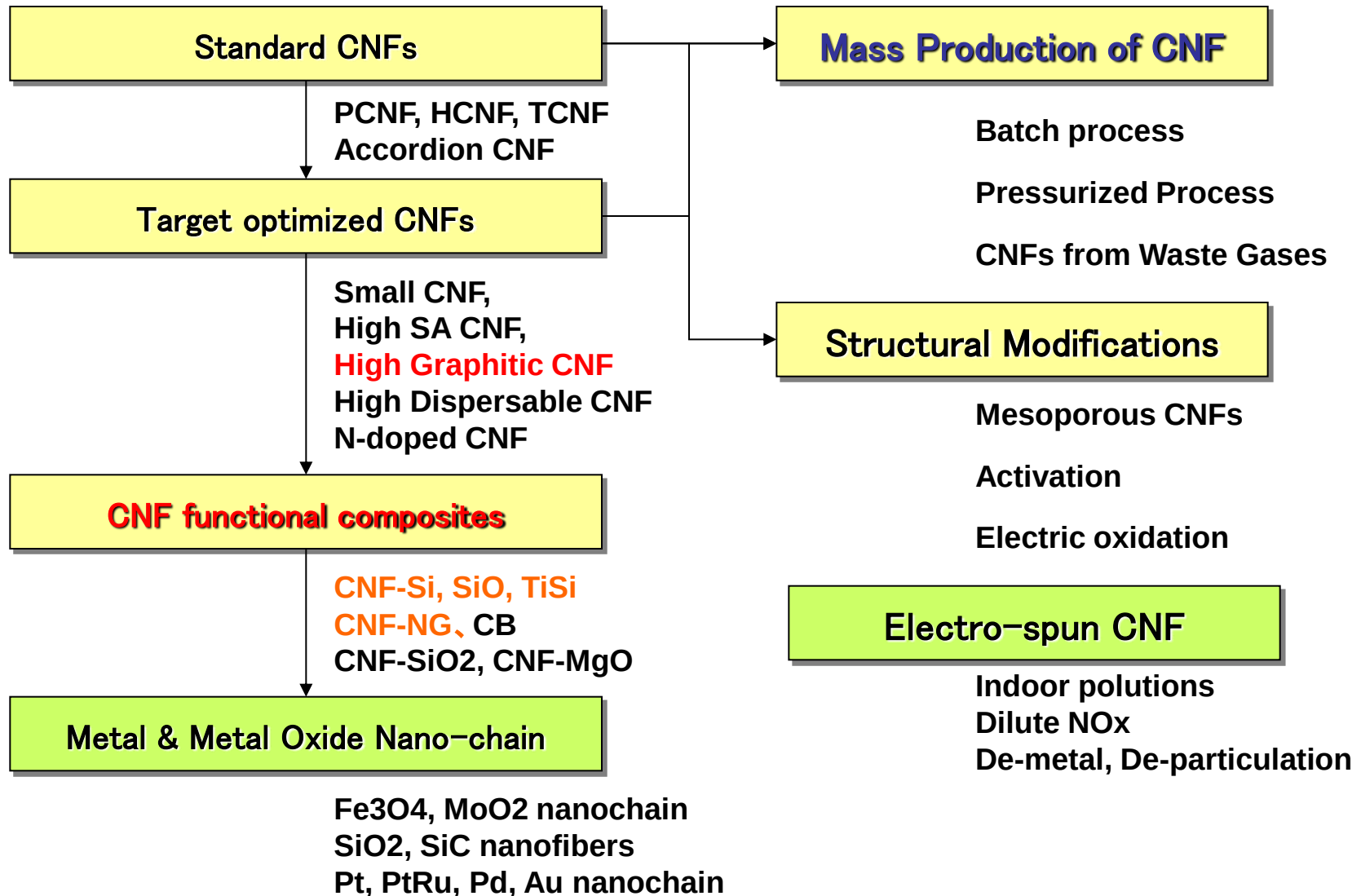
Synthesis of CNF

CNFs

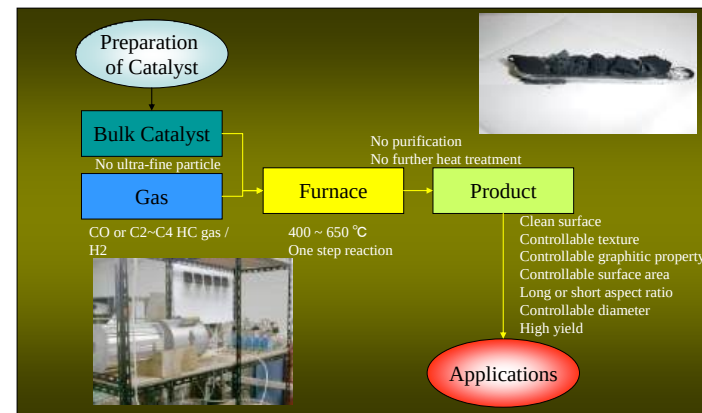
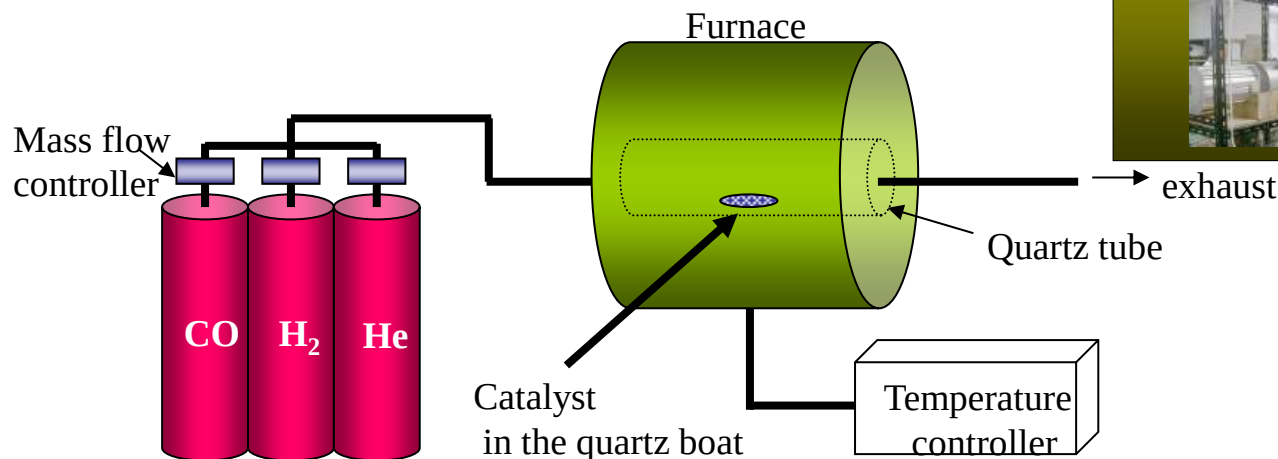
CNFs related syntheses



Selective Preparation of CNFs



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 : H₂/He(1/9, 200sccm//4.5 cm diameter tubular furnace, 2h

Reaction : CO/H₂ (4/1 & 1/4v/v%), 200 sccm// 4.5 cm diameter tubular furnace

Reaction Time & temperature : 1 h, 540 ~ 675 °C



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

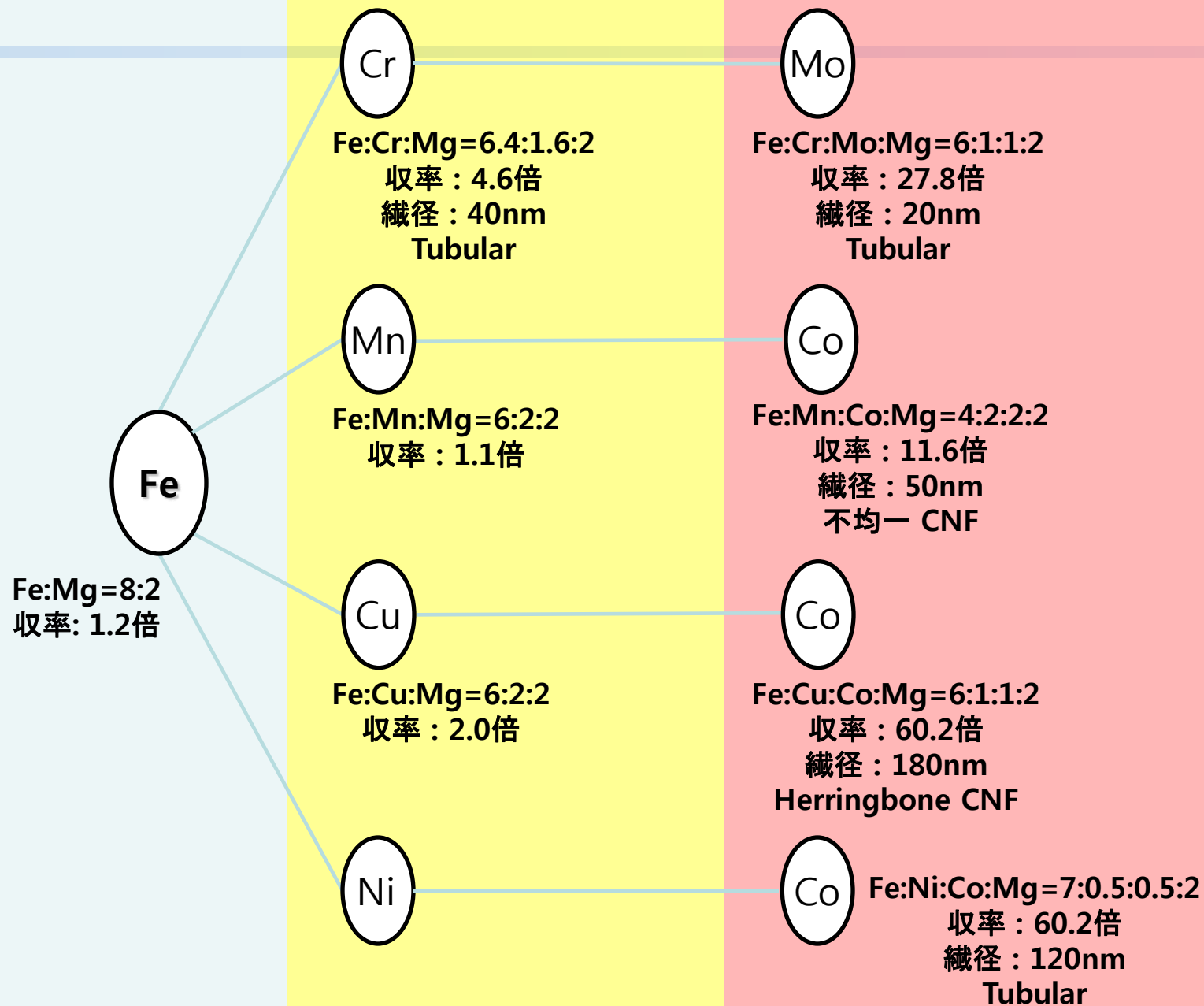
Functions of Second or Third Metals ?



Main Catalyst

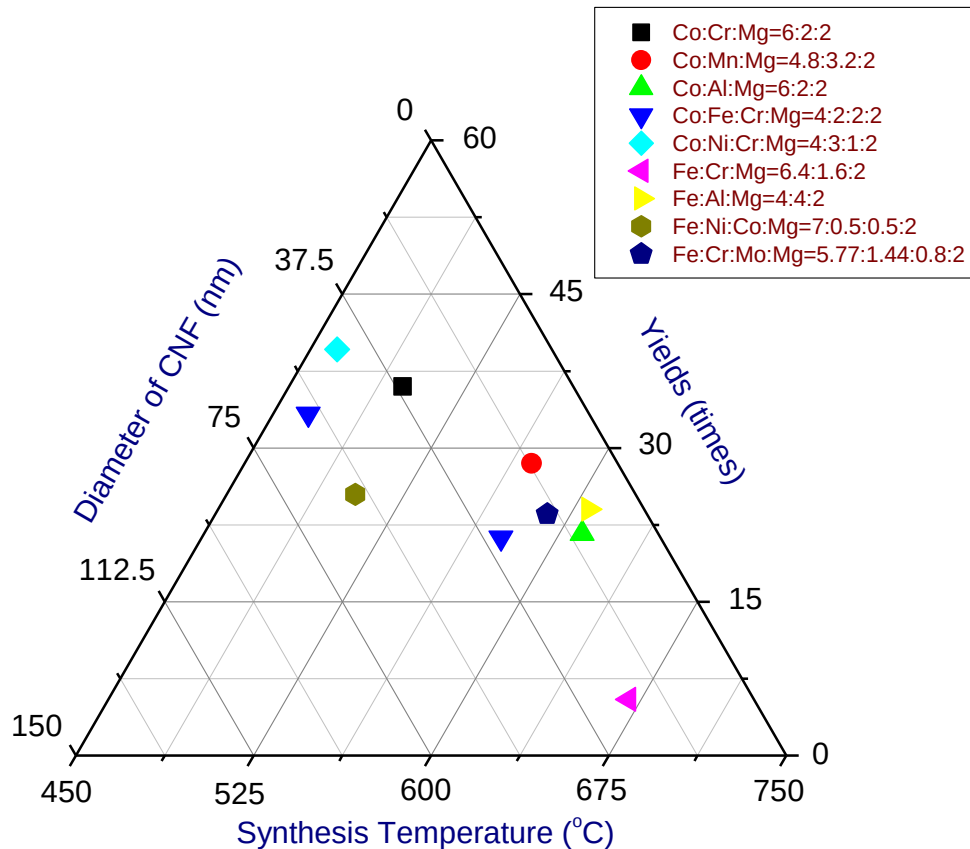
2nd Catalyst

3rd Catalyst





Tri Metallic Catalysts



研究結果

収率, 繊維径, 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

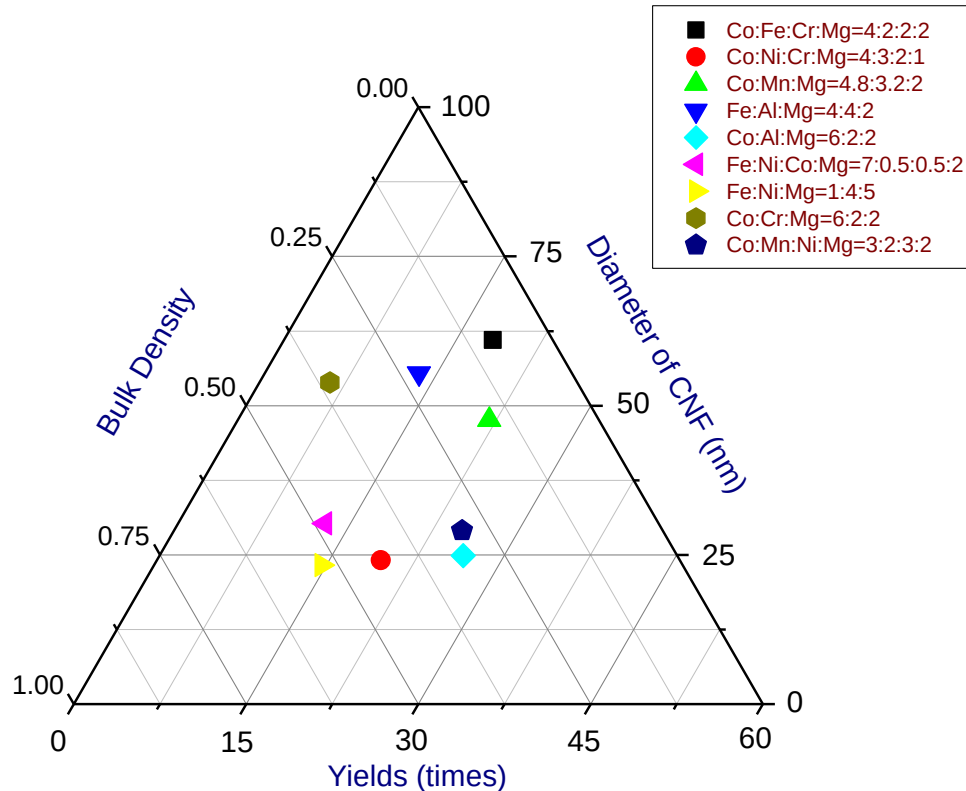
- Cr 及び Al 補助触媒皆合成温度が高いほど触媒収率が増加する傾向を見せて Tubular 構造の繊維が合成される。
- Cr 補助触媒の場合には触媒収率が非常に低いが一方向見掛け密度が非常に低い繊維が合成される。
- Cr 及び Mo 補助触媒を一緒に使う場合には 30 倍以上の非常に高い触媒収率を得ることができる。

3. FeNiCoMg 触媒

- 最大繊維径 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°C임.
(Co:Ni:Cr:Mg=4:3:1:2, Fe:Ni:Mg=1:4:5 촉매는 600°C에서 합성한 결과임)

□ 연구결과

경제的に有利なC₃H₈ 가스を利用して C₂H₄ 가스 より
り少し高い温度で CNF를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 가스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.

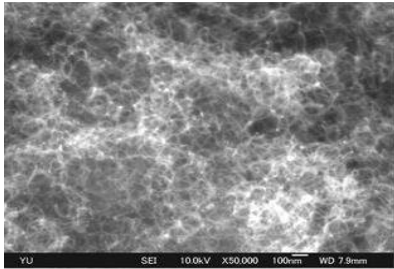
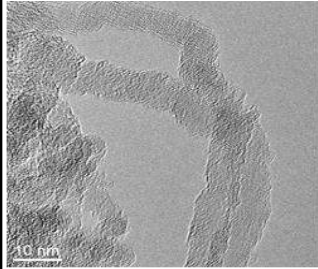
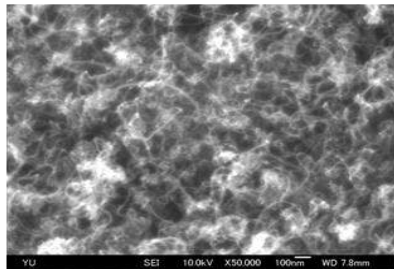
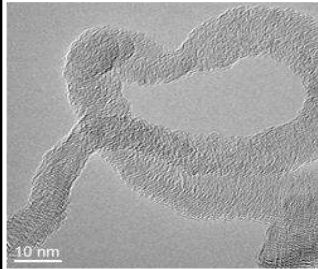
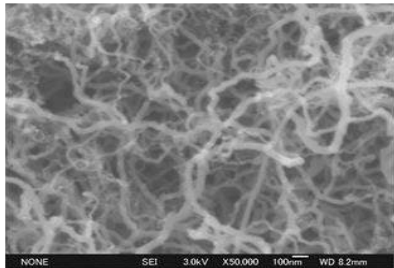
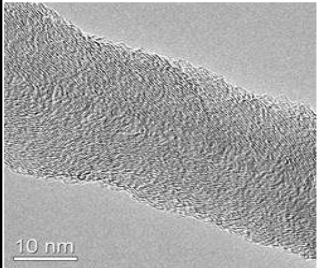
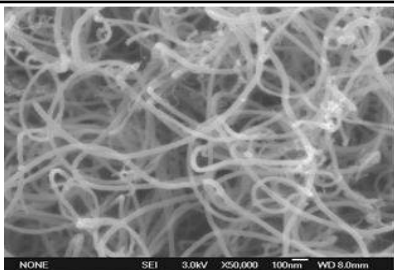
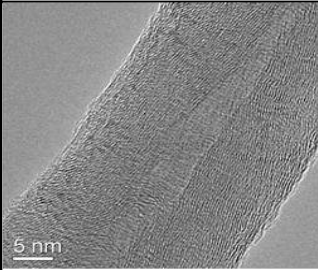


Standard CNFs

Sample #	SEM	TEM	Properties	Applications	Etc.
KNF-SPR Platelet Nano-rod			Platelet high graphit. 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 Herringbone			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 graphit. 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 小繊維径			tubular, hollow 5~15 nm, 4 -7 walls	複合材料、触媒担体、FED	20 g/日

CNF (Small & Middle Diameters)

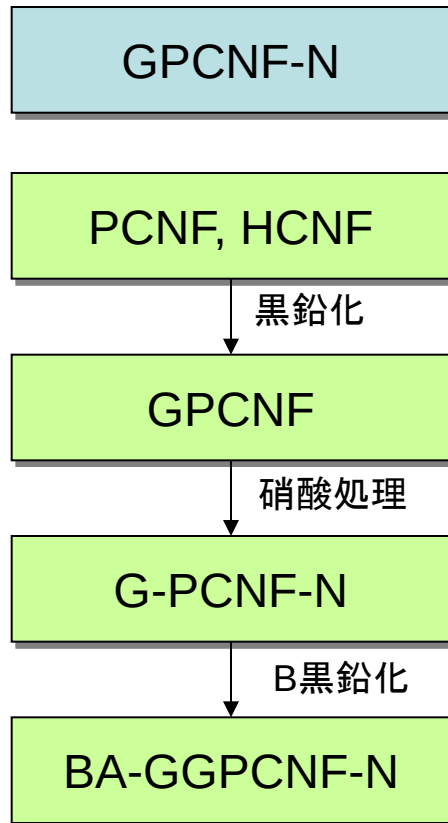


Sample #	SEM	TEM	Properties	Applications	Product
KNF-CM 小繊維径 高分散			Herringbone, hollow 7 ~ 20 nm	複合材料、吸着 剤、 触媒担体、FED	20-30 g/日
KNF-CC 小繊維径			Herringbone 7 ~ 15 nm	複合材料、吸着 剤、 触媒担体、FED	15-20 g/日
KNF-NM 中繊維径			Herringbone 10~60 nm (30~40)	複合材料、吸着 剤、 触媒担体	50-70 g/日
KNF-NF 中繊維径 直線性			Herringbone 20 ~ 50 nm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

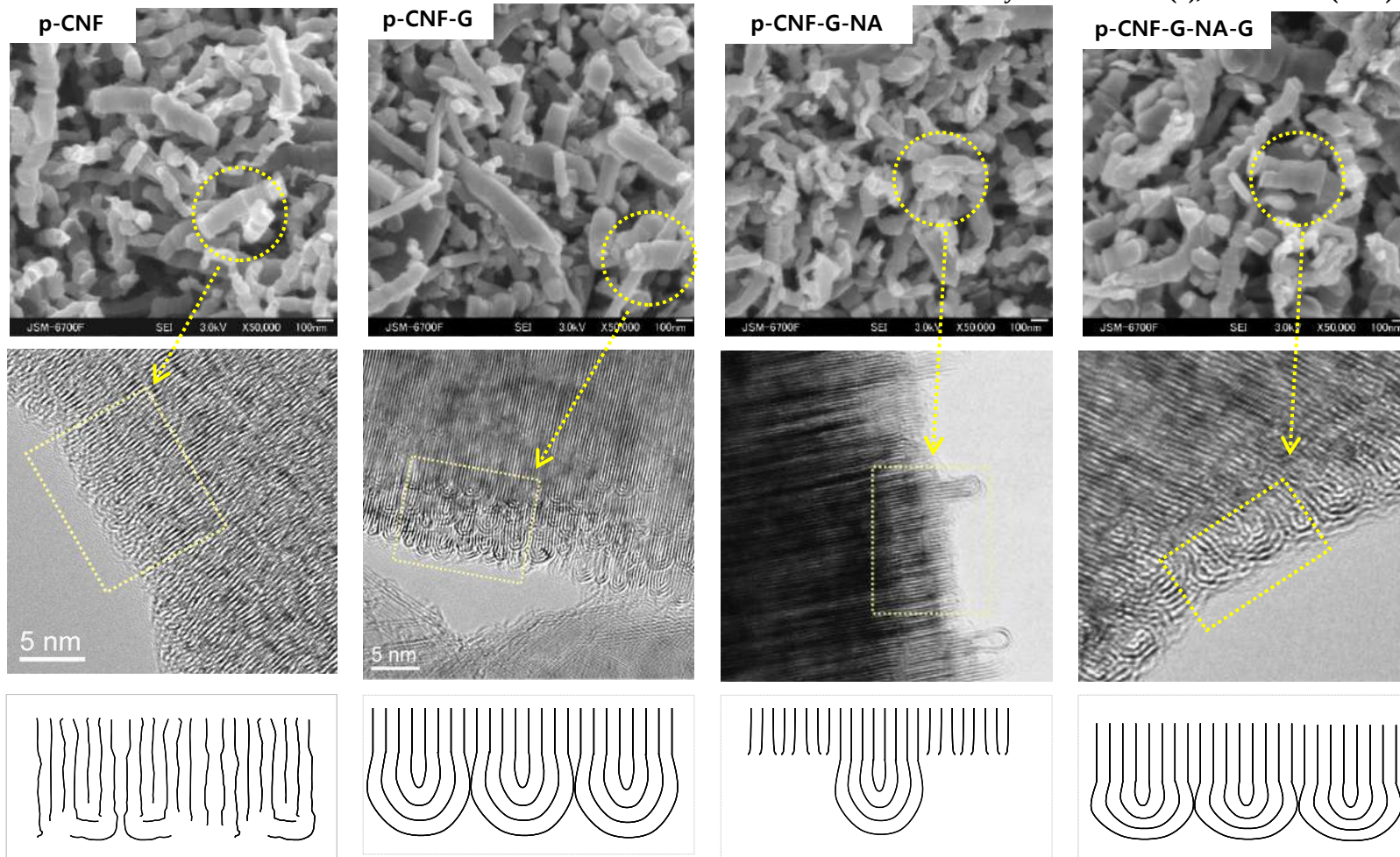


	Preparation conditions	d ₀₀₂ (nm)	L _{c(002)} (nm)
PCNF	Fe catalyst, 620, CO/H ₂ : 4/1	0.3365	72
G-PCNF	2800°C heat treatment of PCNF	0.3364	83
G-PCNF-N	30% HNO ₃ treatment of GPCNF for 50°C, 8hs	0.3362	152
GG-PCNF-N	2800°C heat treatment of GPCNFN	0.3362	106
BA-G-PCNF	Boric acid added heat treatment of PCNF	0.3359	115
BA-GG-PCNF-N	30% HNO ₃ treatment of GPCNF for 50°C, 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% HNO ₃ treatment of GPCNF for 50°C, 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**

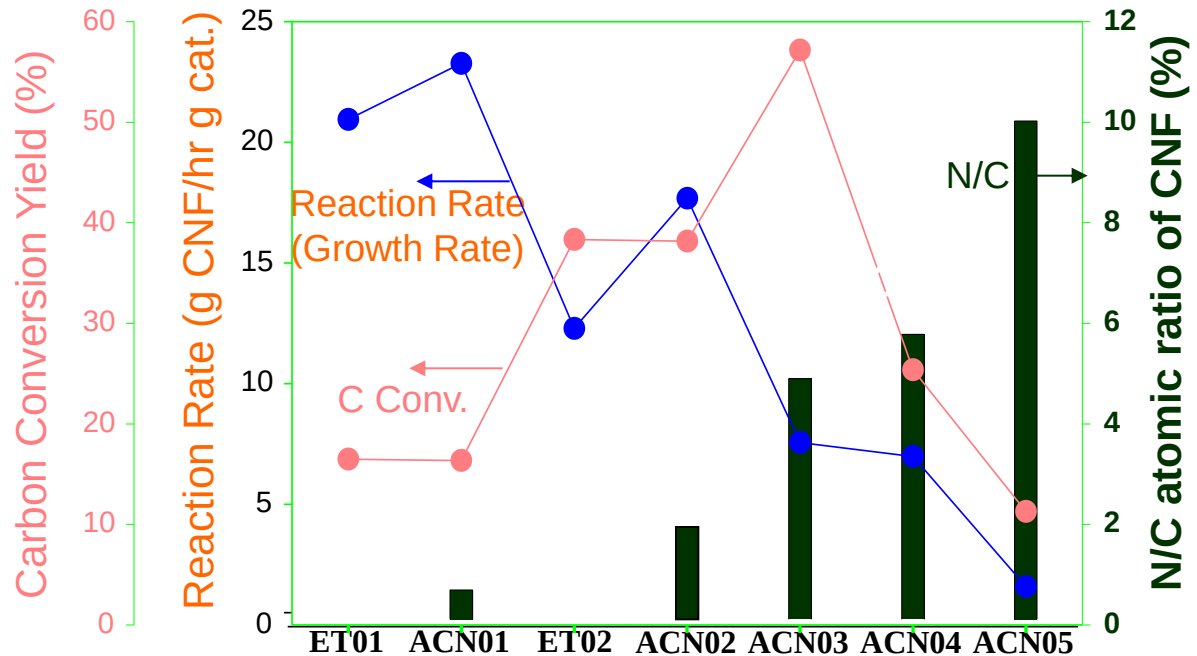


N-doped CNFs

N-Source
: Acetonitrile



Reaction Temp.
530°C



Ethylene		160	160	40	40	0	0	0	Total 200 ml/m
Hydrogen	ml/m (g)	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

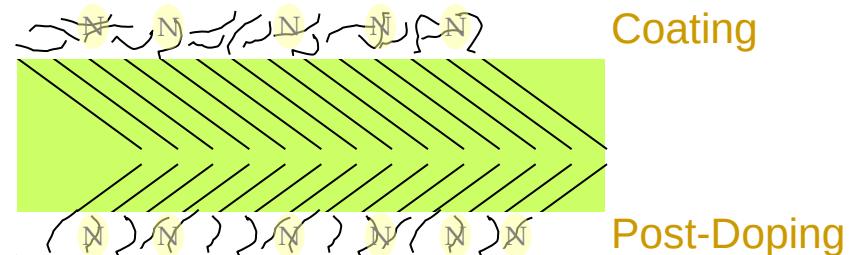
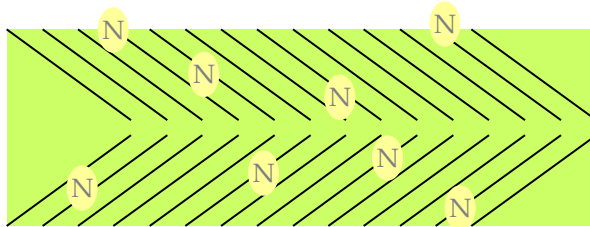
A. Direct Synthesis of Carbon Nanofibers with Nitrogen (the method of this study)

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

- Using Carbon Sources Containing Corresponding Heteroatoms
- Mixing General Carbon Sources with a Nitrogen Source (NH_3)

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

Direct Synthesis





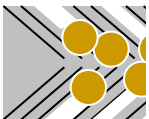
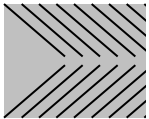
Nano-Chains

Synthesis of Magnetite Nanoparticle-Chain

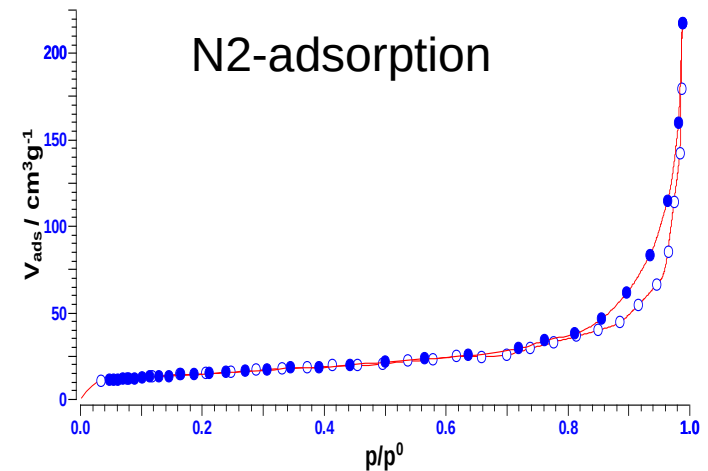
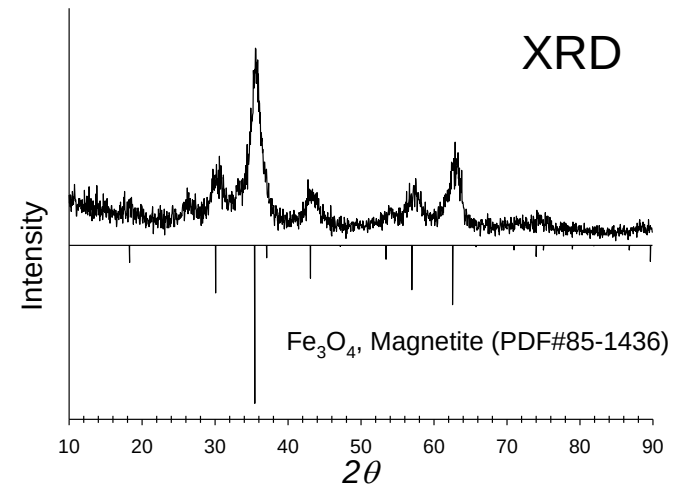
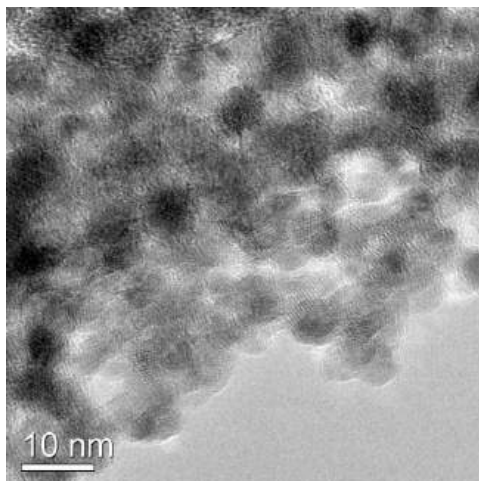
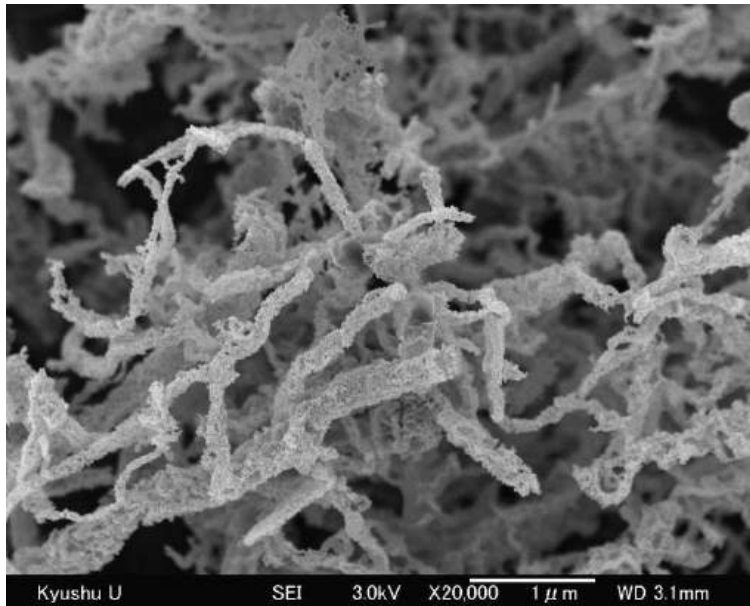
Ref.) S.Y. Lim, et al. *Carbon 2006: International Conference on Carbon, Robert Gordon College, Scotland (2006)*

- Syn

Ca



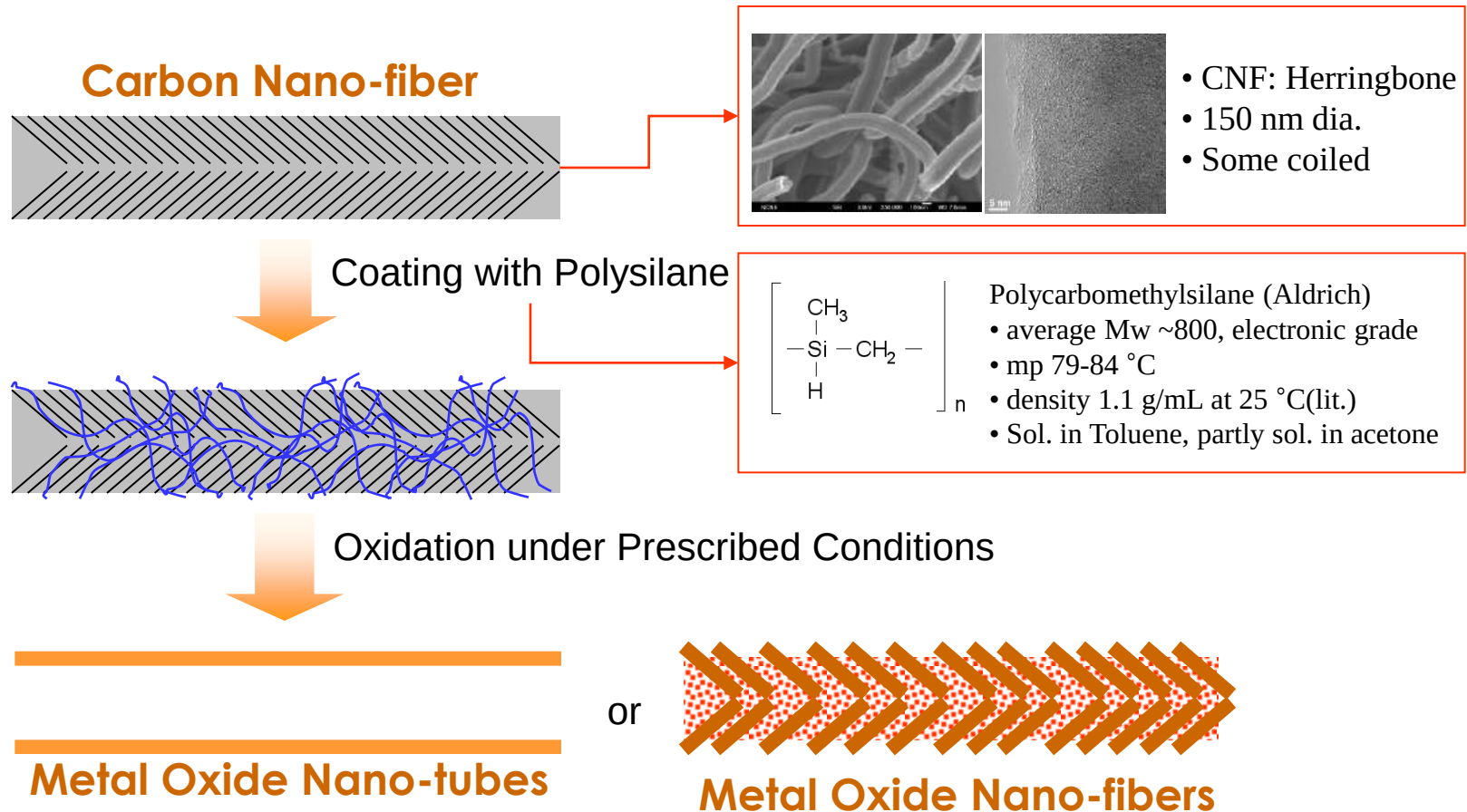
Metal



Schematic Procedure of SiO₂ NF



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



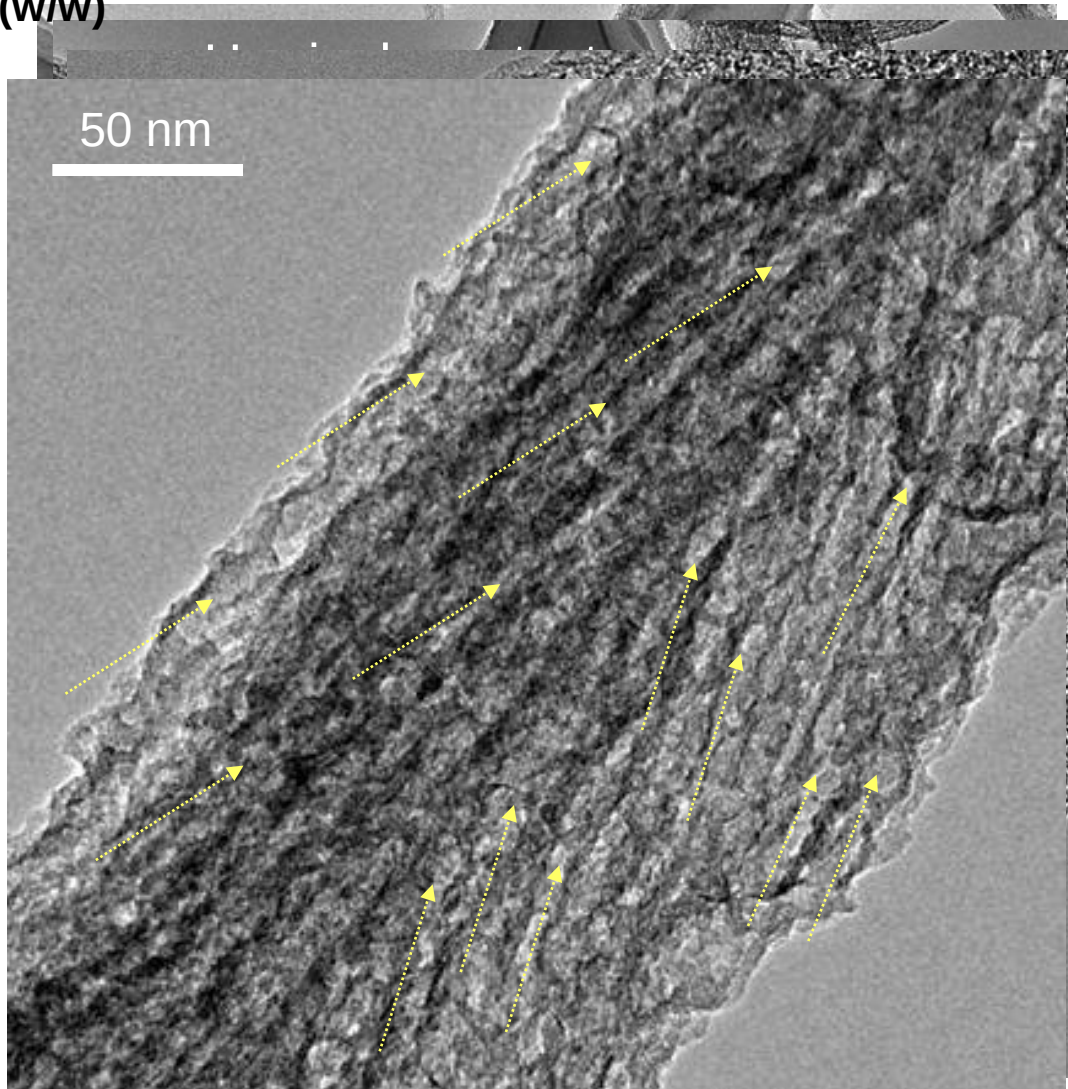
Highly-porous Nano-fibers



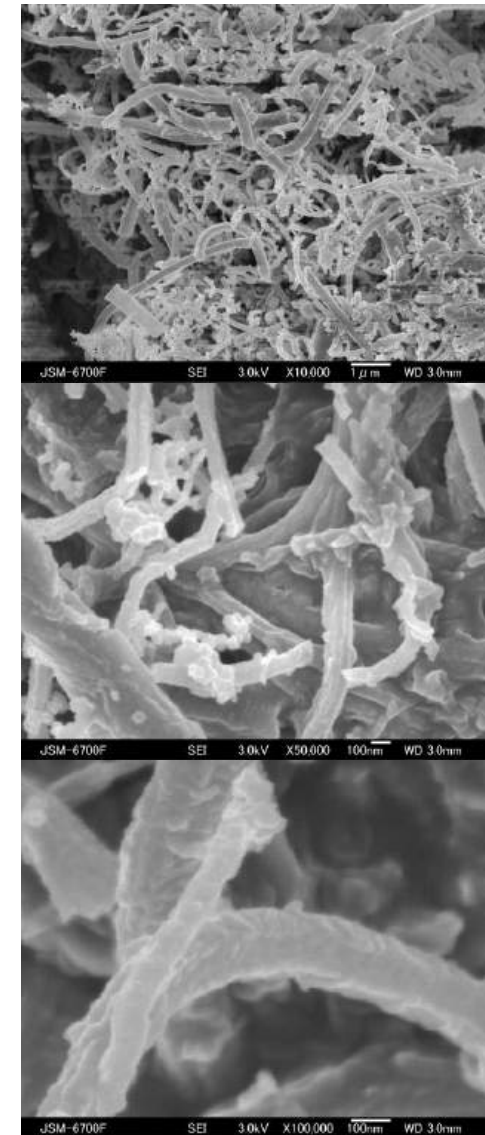
TEM & SEM of SiO_x NFs

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

TEM of SiO_x-NF



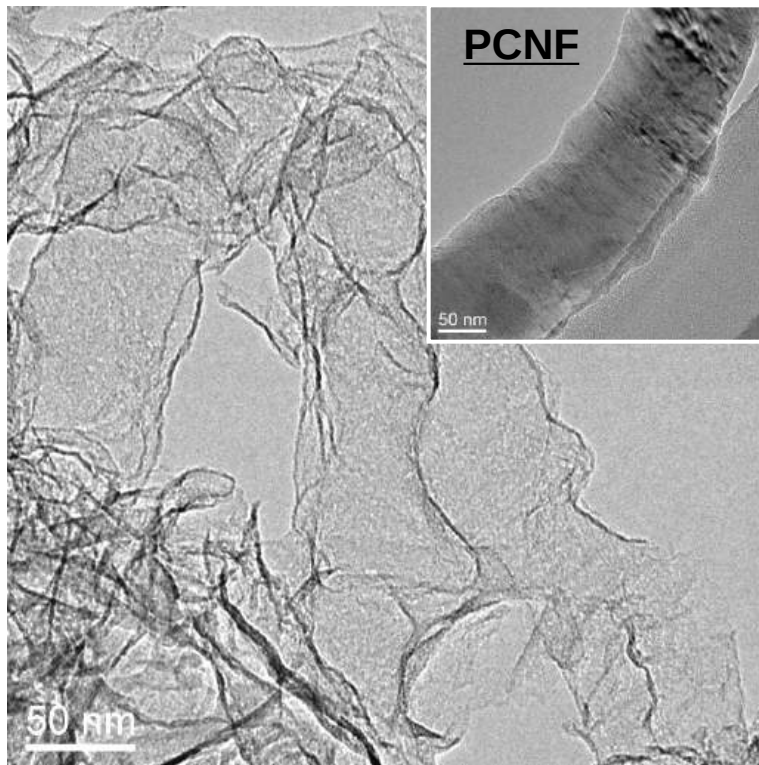
SEM of SiO_x-NF



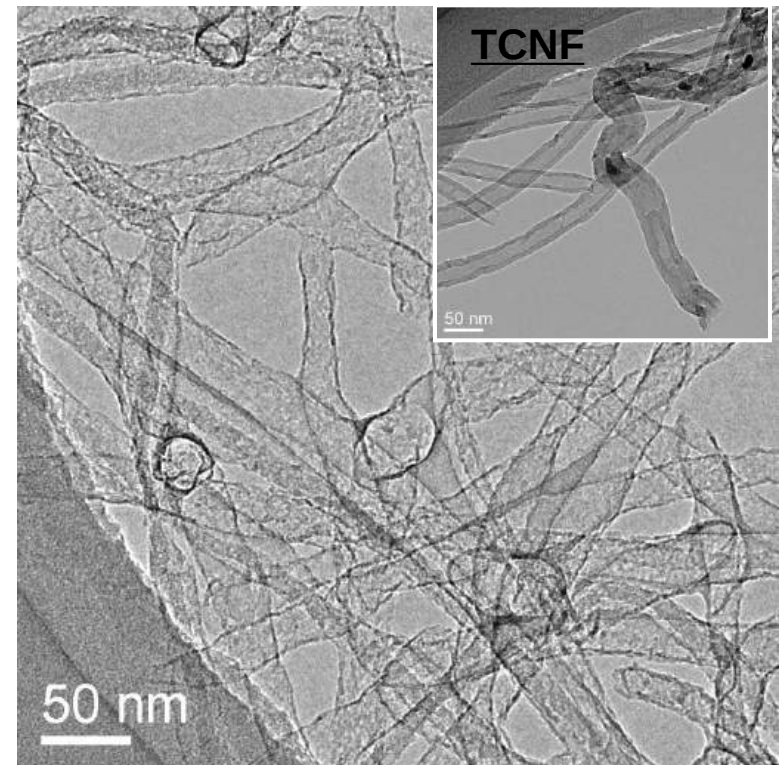
Various SiO_x NFs



TEM of SiO_x-NF using PCNF



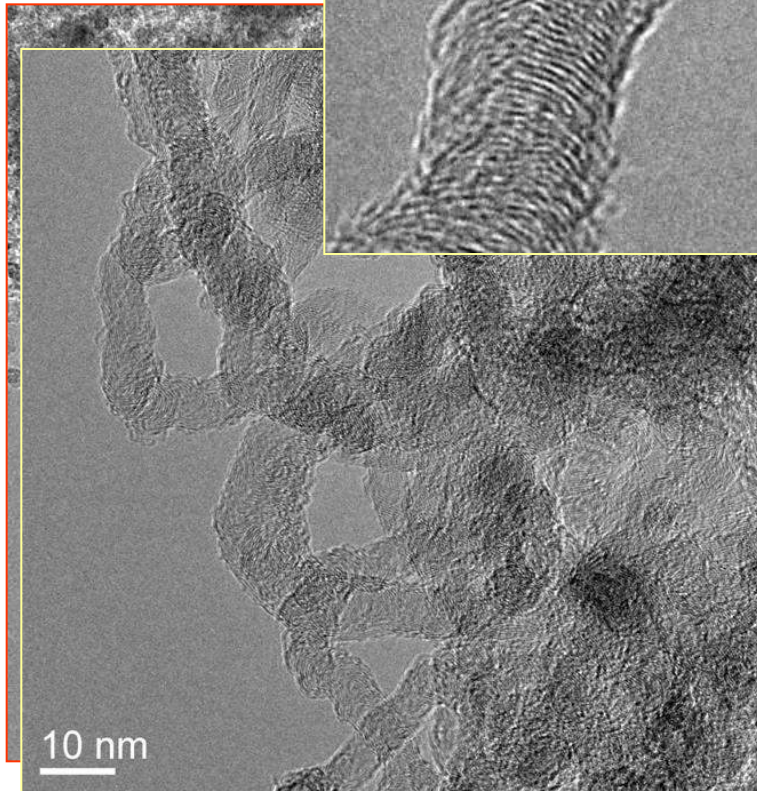
TEM of SiO_x-NF using TCNF



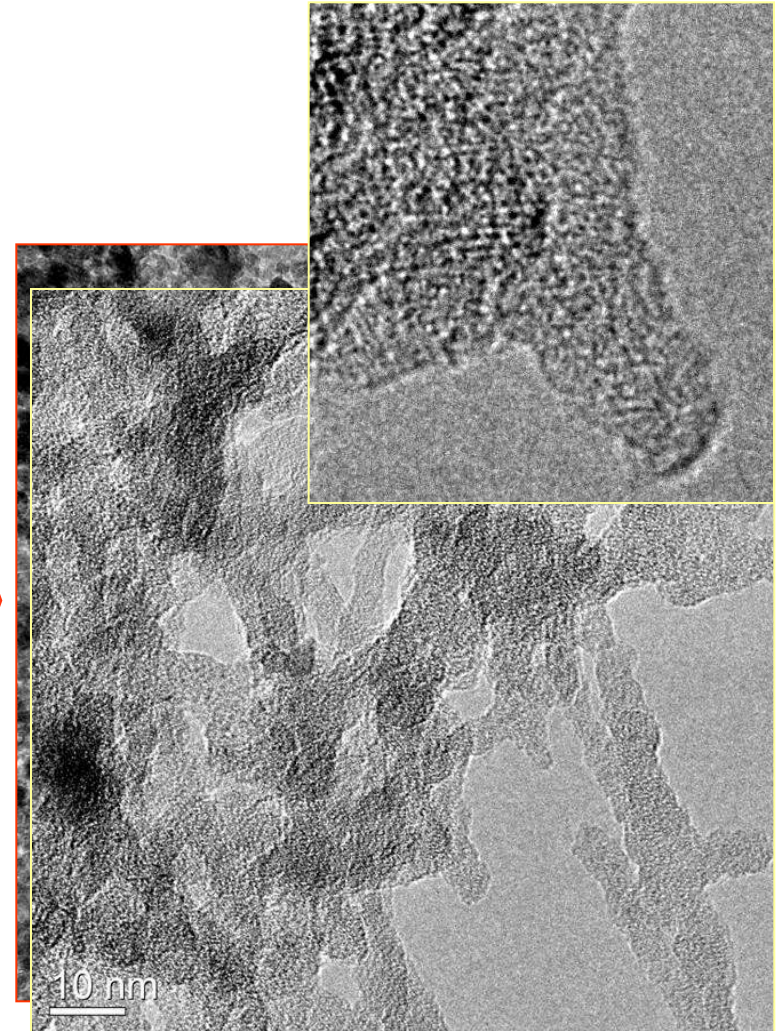
SiO_x NF Using Thin CNF

- **Thin CNF (~20 nm dia.)**

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



Thin CNF



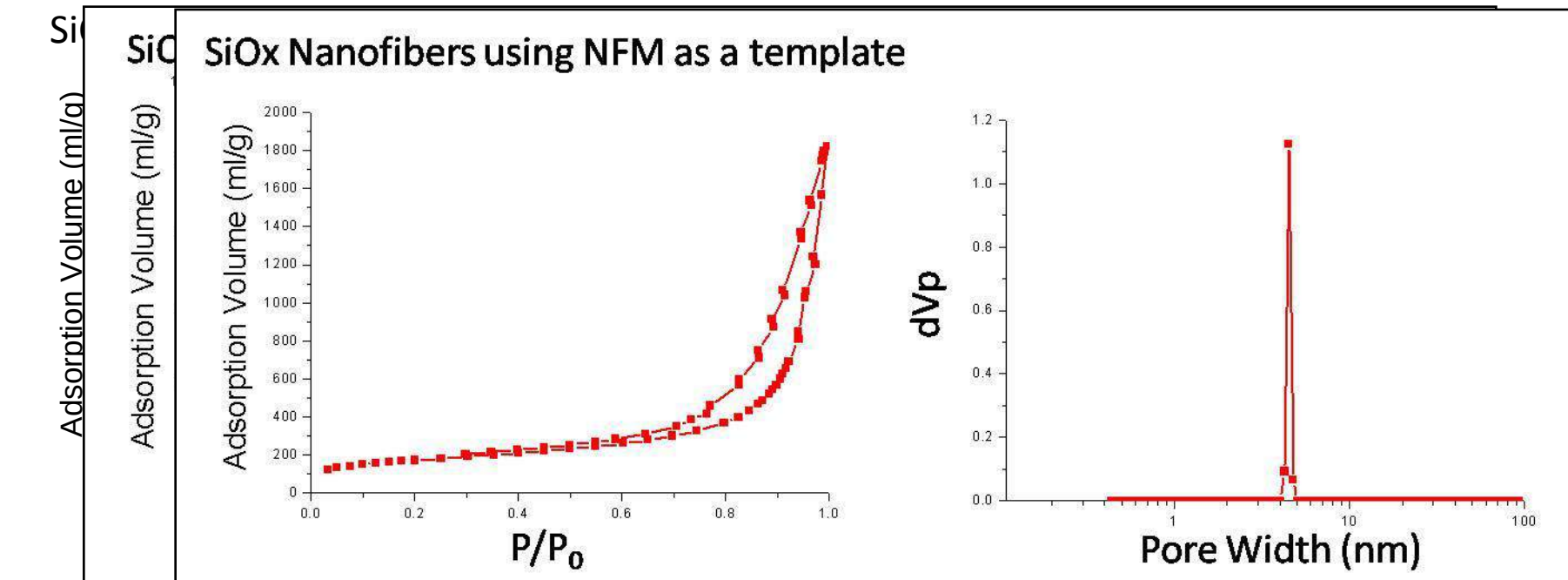
Corresponding SiO_x-NF

SA and PSD of SiO_x NFs

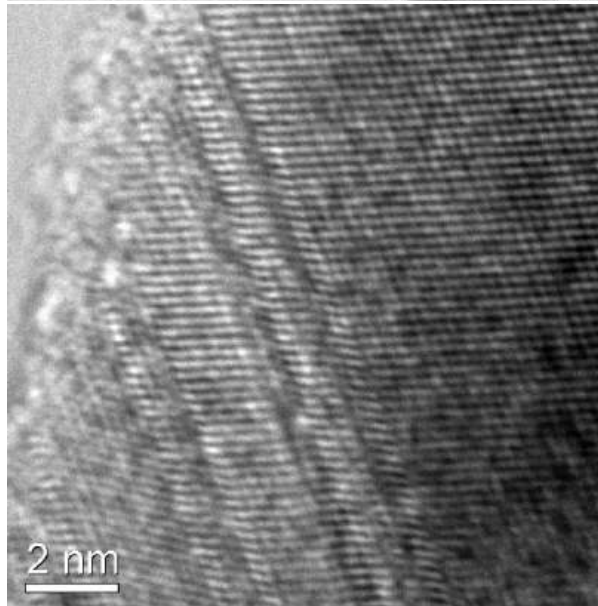
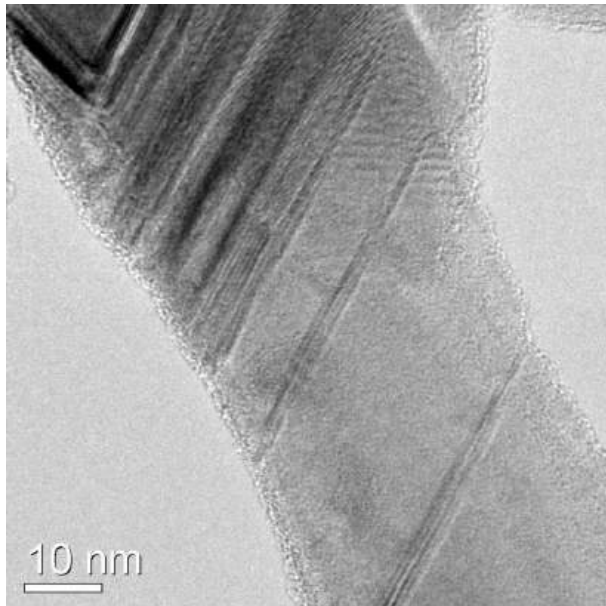
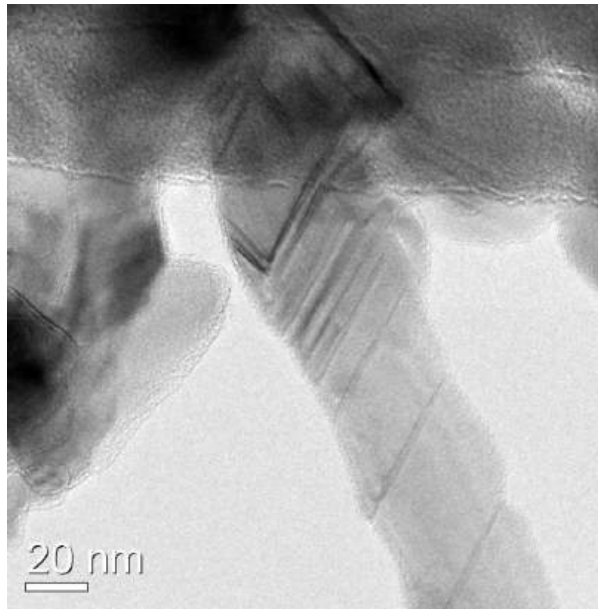
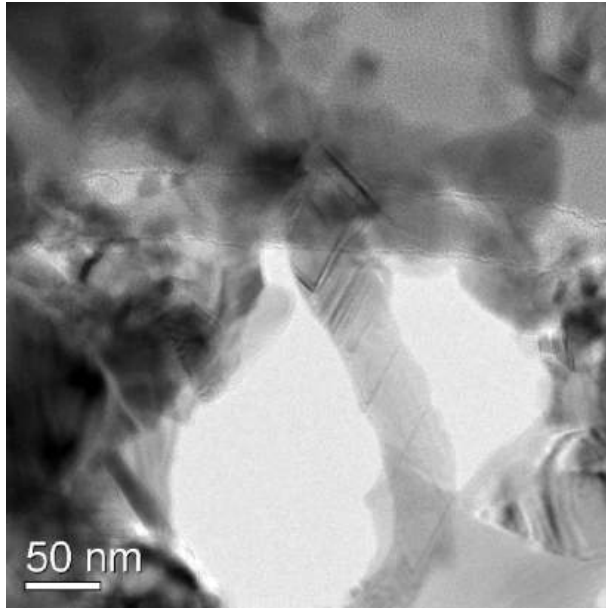


Surface Area and Pore Size Distribution depending on the synthesis template

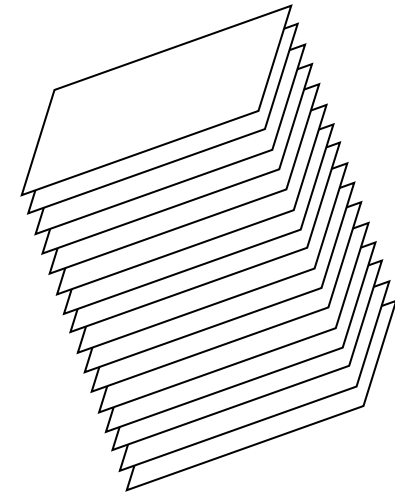
- PS in Toluene
- PS/CNF 1/5 (w/w)



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



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.

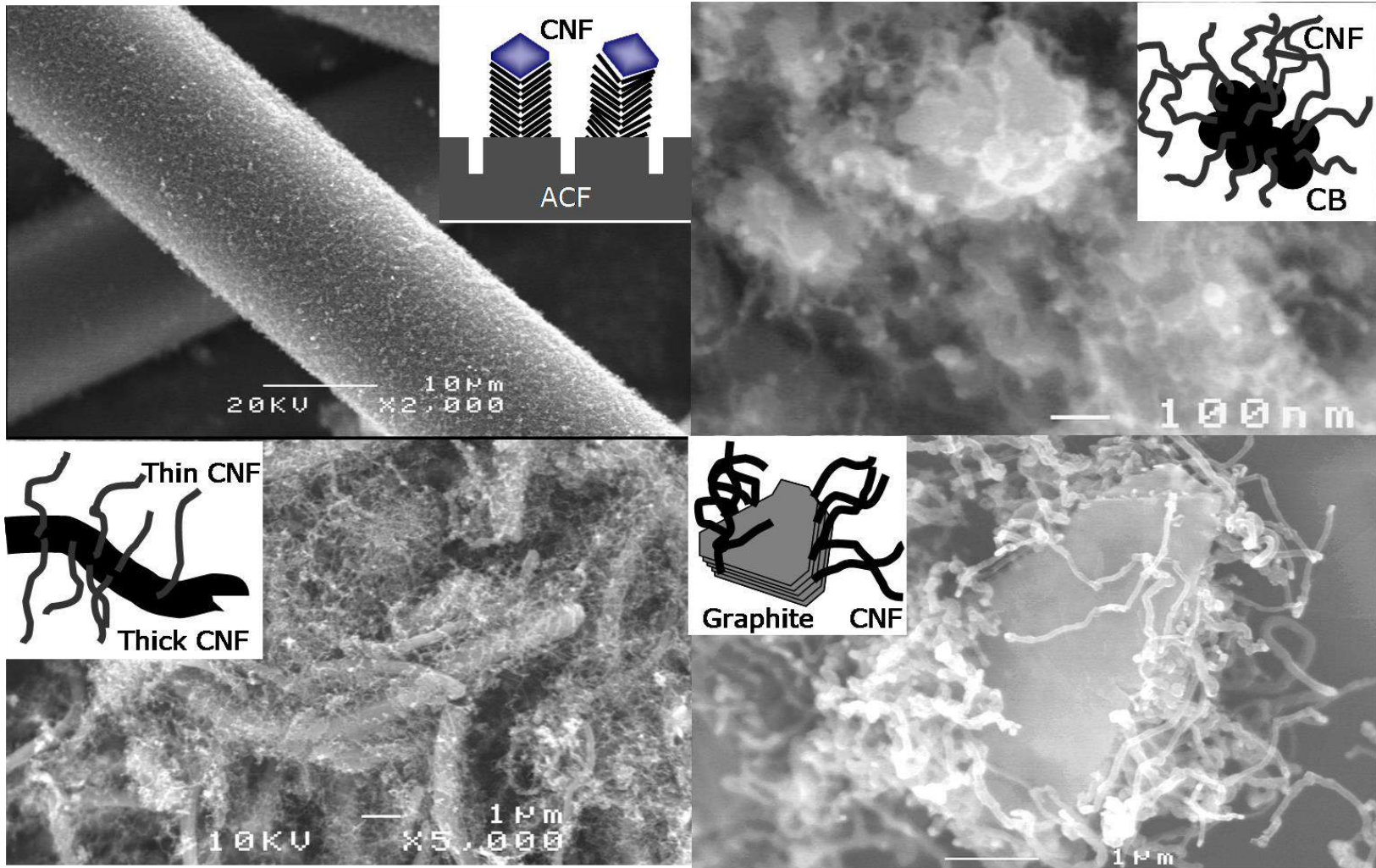
CNF
複合化

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

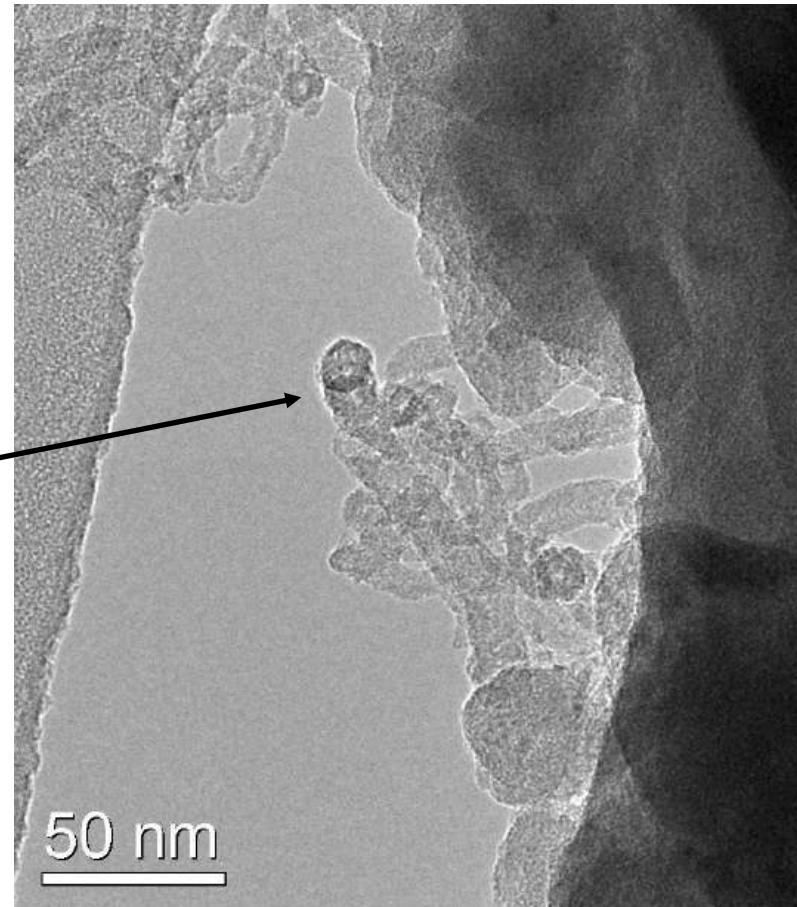
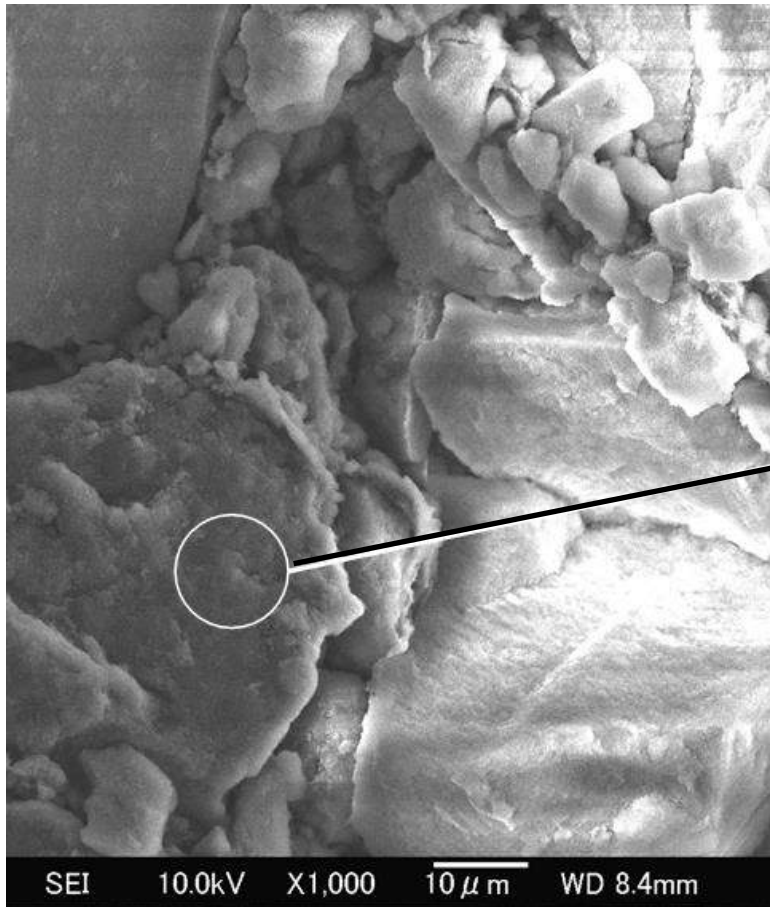


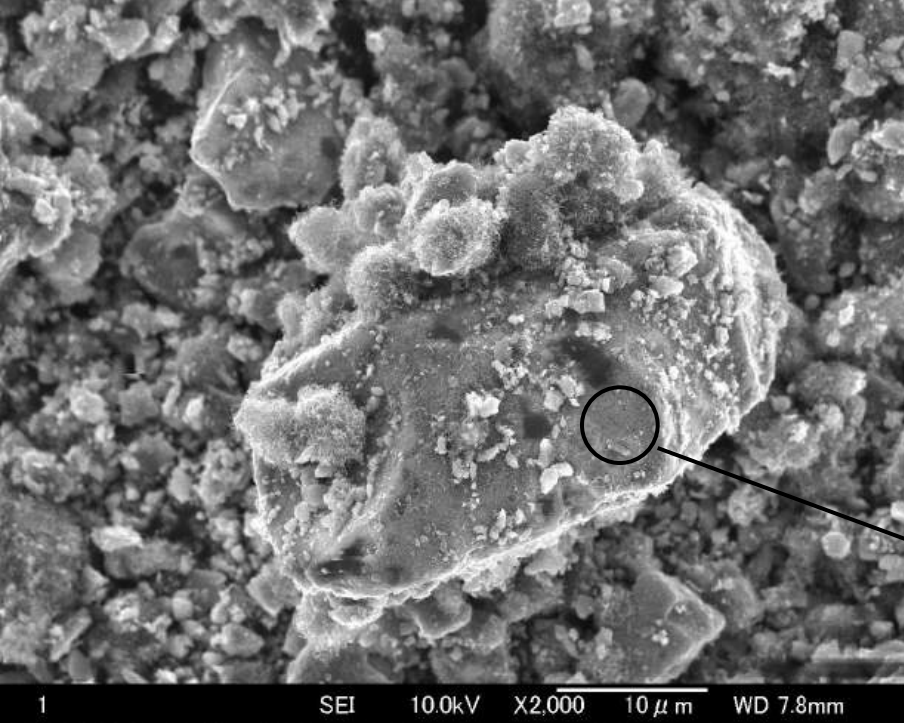
Silica – CNF Composites

Additive to Tire

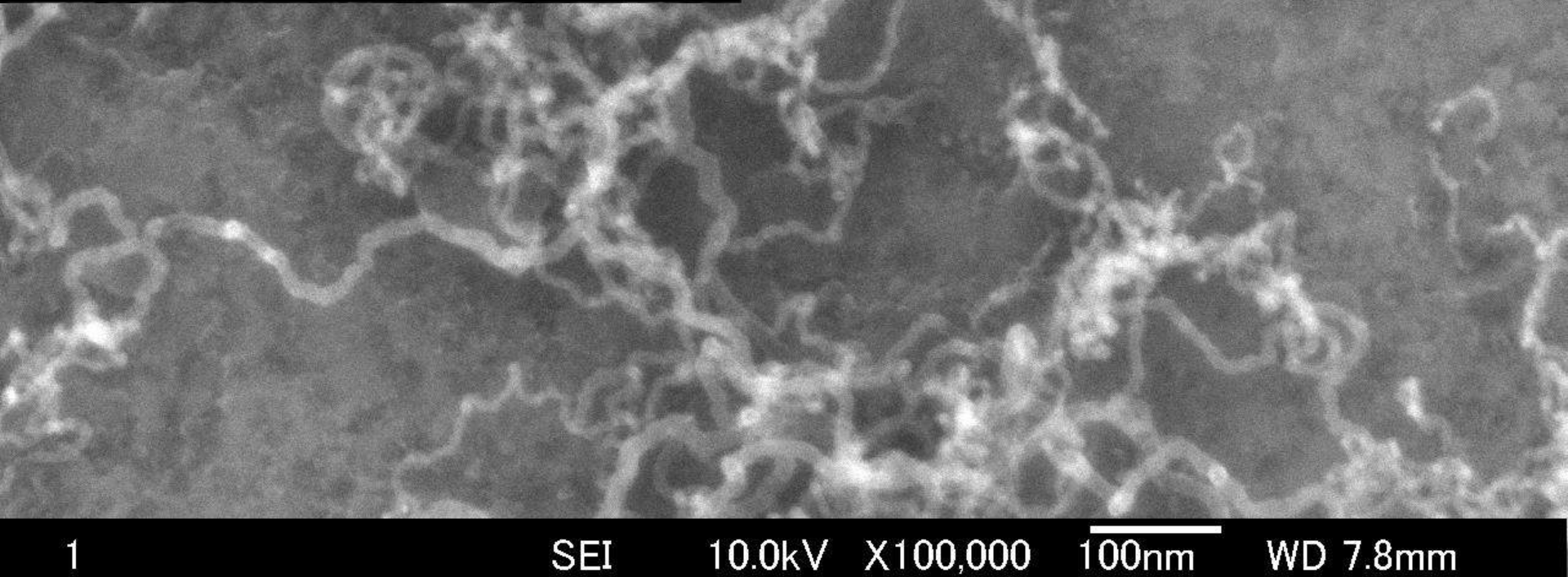
Bad compatibility to rubber

➤ CNF-silica composite to solve – Improvement of compatibility





SiO-CNF

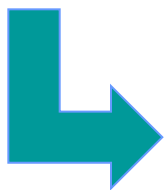


Mass Production of CNFs



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

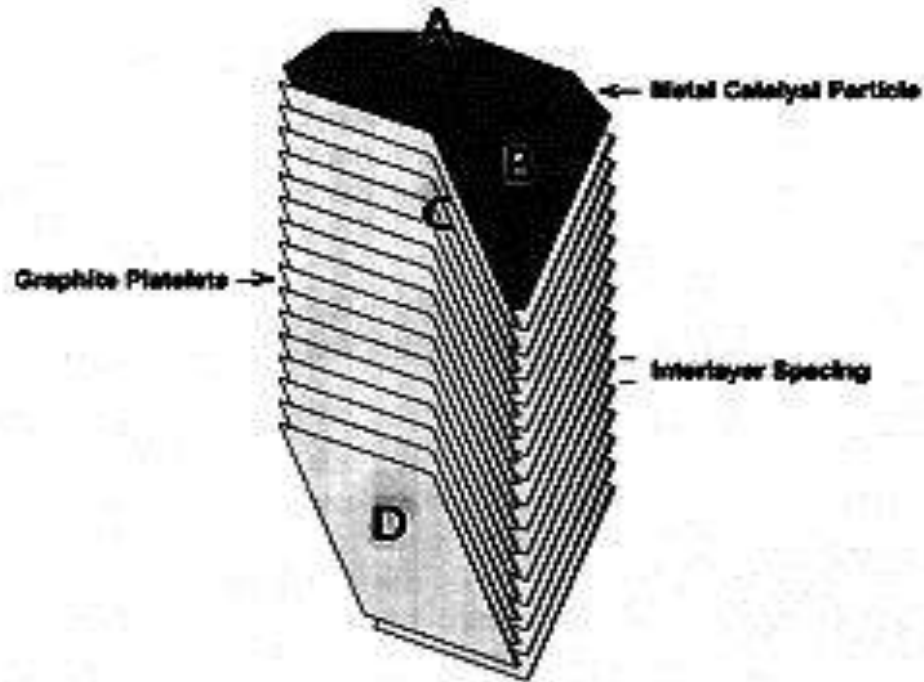
Old structural models of CNFs



(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

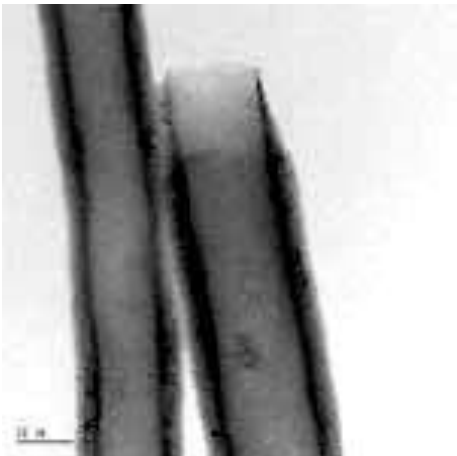
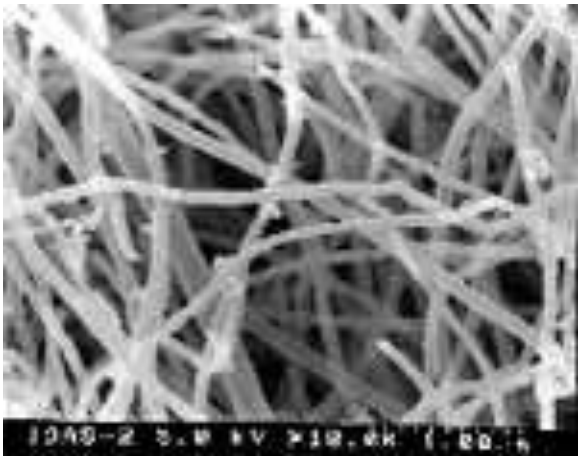
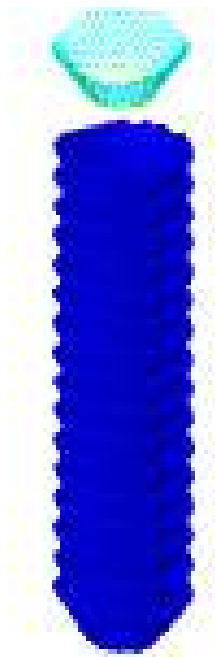
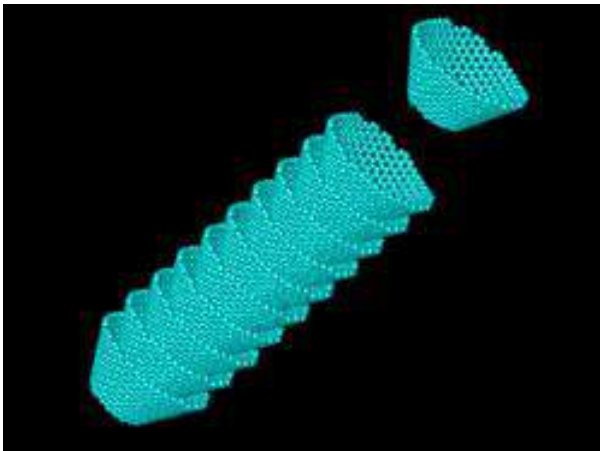
Chemical Physics Letters, Volume 343, Issues 3-4, 3 August 2001, Pages 241-250

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

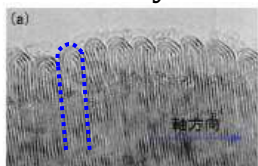
カルベールは超微粒子の金属触媒を核として炭化水素を気相成長させる事によって得られるカーボンナノチューブです。



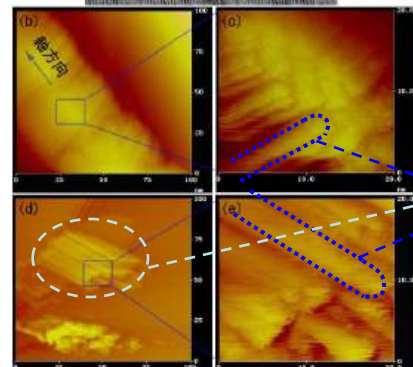
Primary Structures of Various CNFs



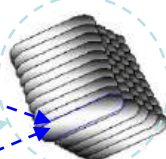
Assembly of carbon nano-rods



軸方向

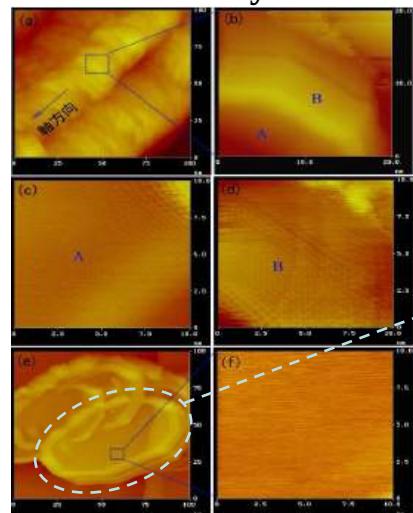


(f)

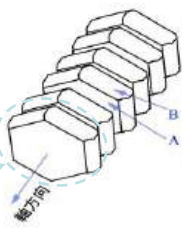


ナノ繊維素集積型模型

Assembly of carbon nano-plates



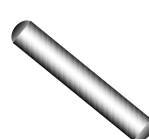
(g)



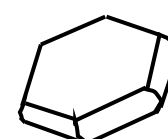
Platelet集積型模型

	Platelet CNF		Herringbone CNF		Tubular CNF	
As prepared						
Graphitized						

Carbon nano-rod

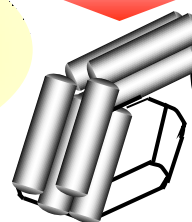


Carbon nano-plate



CNF is composed of carbon Nano-rod and nano-plate.

Quantitative ratios and Arrangement of primary structures should determine Structure, graphitizability, and Most of physical properties of Resultant carbon nanofibers



Platelet CNF

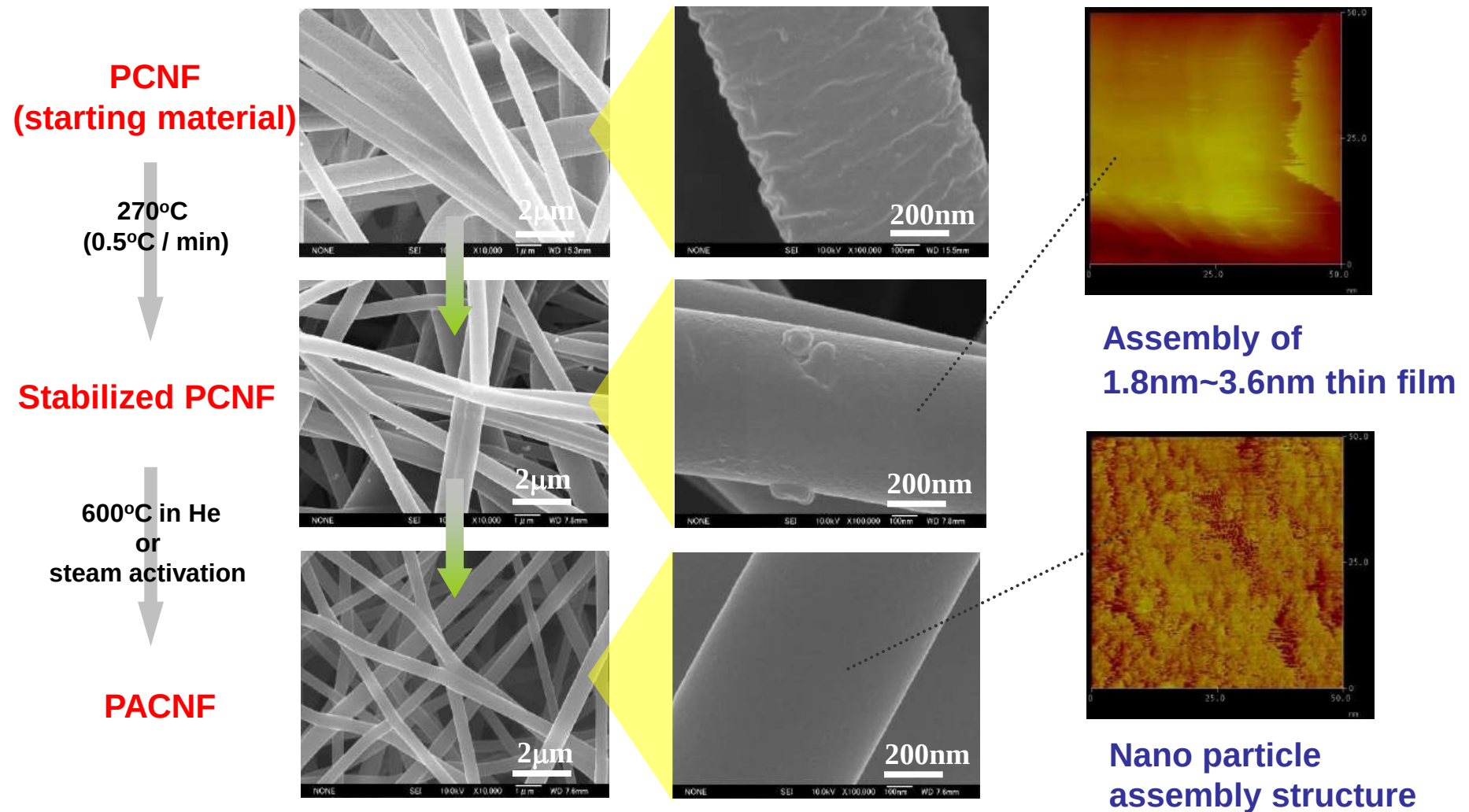
Herringbone CNF

Tubular CNF

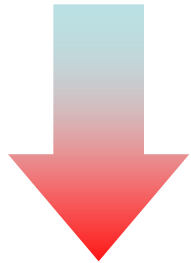
⇒ Various structures and surfaces of CNFs are determined by the arrangements of primary structural units



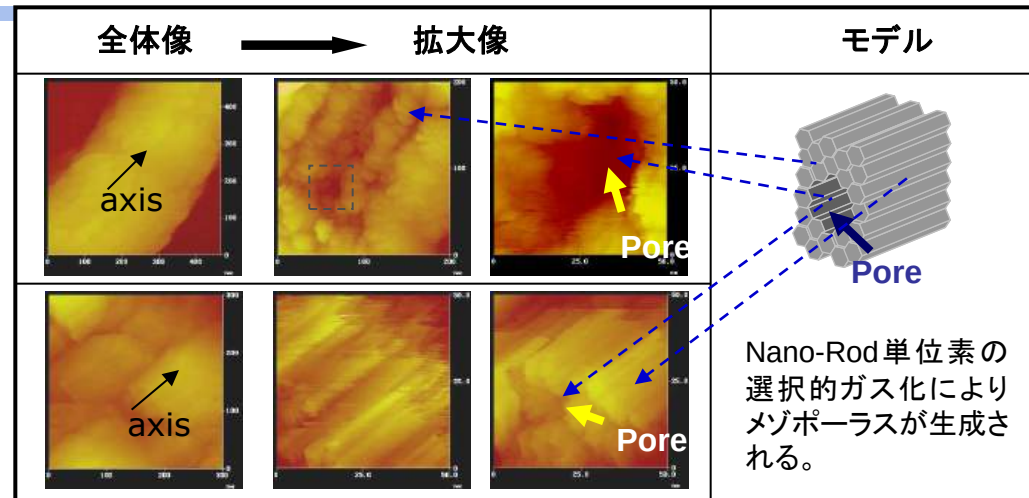
SEM of PCNF, stabilized PCNF and PACNF



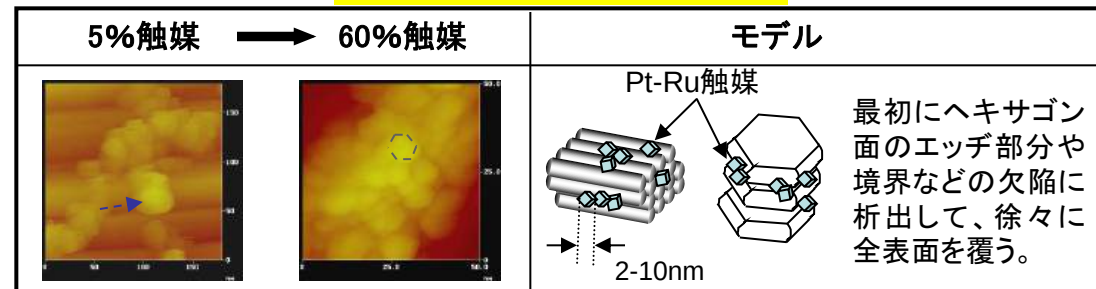
Mesoporous CNFs



CNFの高触媒機能化
(ナノ構造単位を利用した
機能化処理)

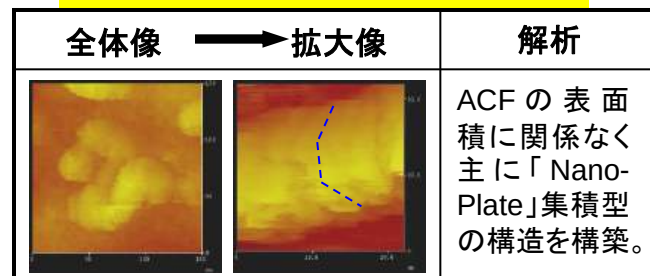


CNFへのPt-Ru触媒担持

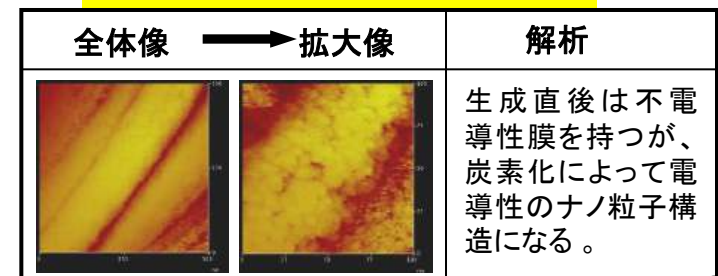


新しいチャレンジ
(新CNF構造の発見、新合
成方法の開発)

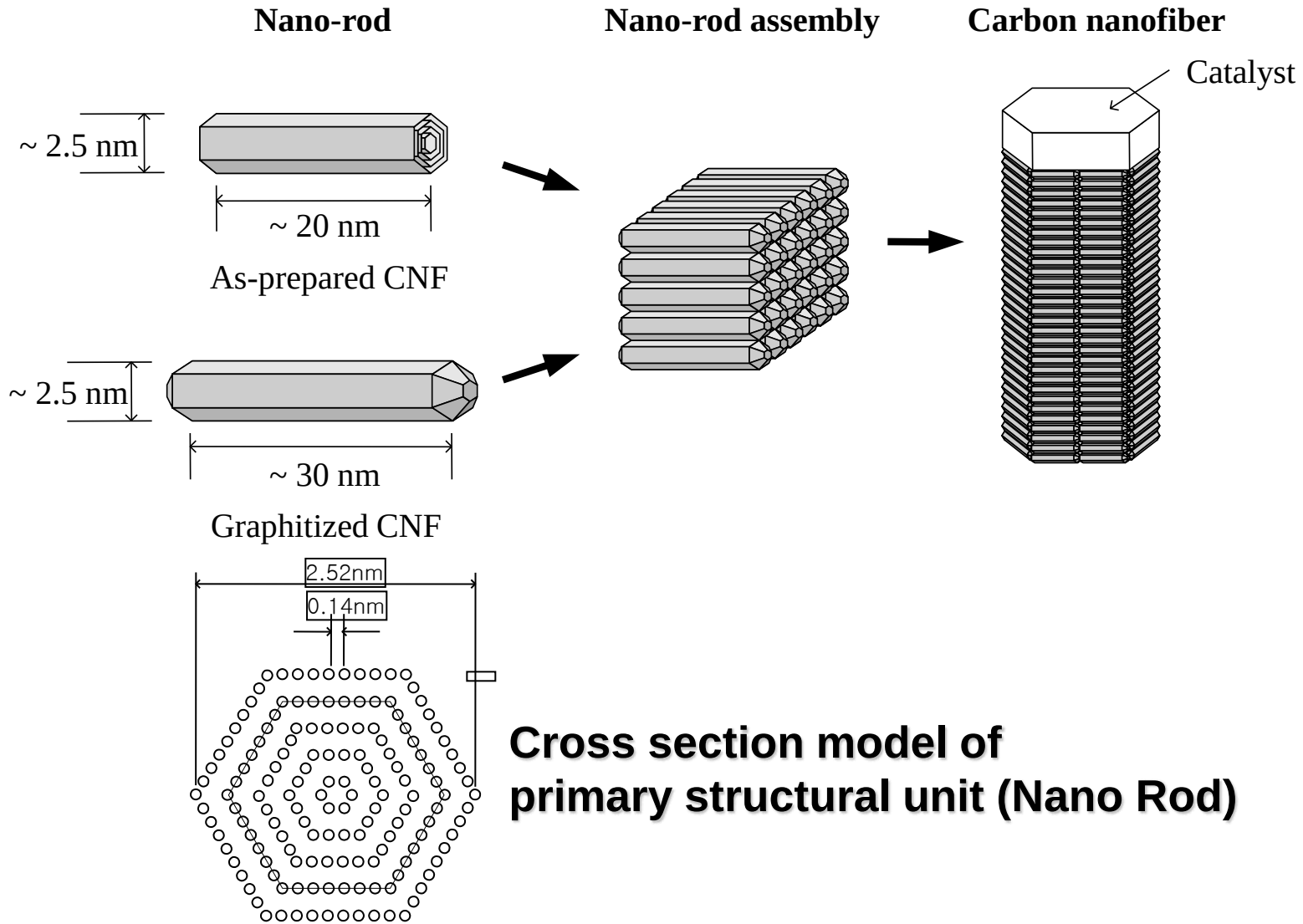
ACF上に成長させたCNF構造



新チャレンジPAN系CNF構造



Structural Model of TCNF





Separation of structural unit (Nano-platelet)

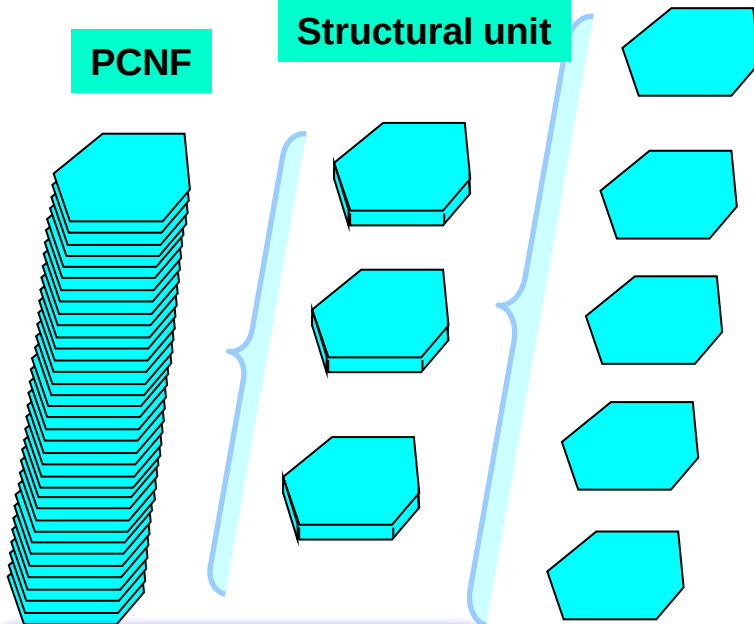
Introduction

The relationship between PCNFs and graphene

Graphene

PCNF

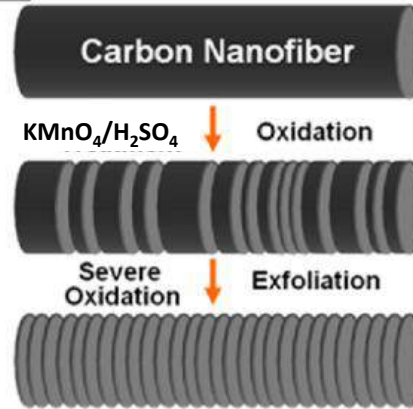
Structural unit



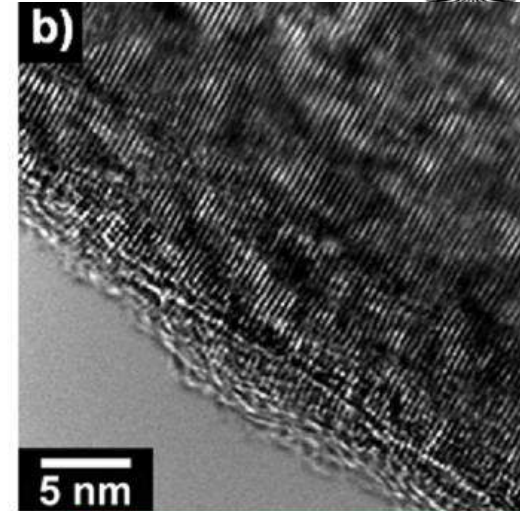
Objective

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

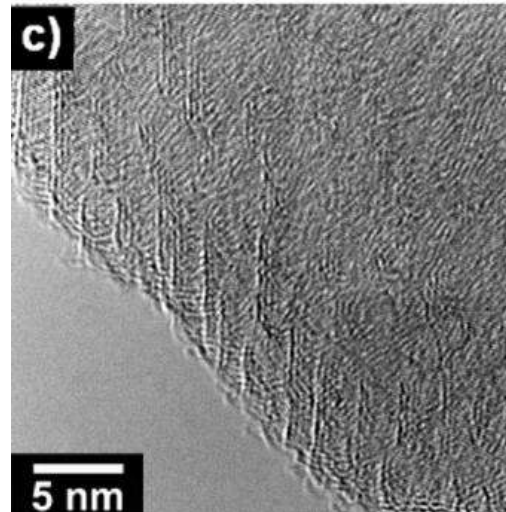
a)



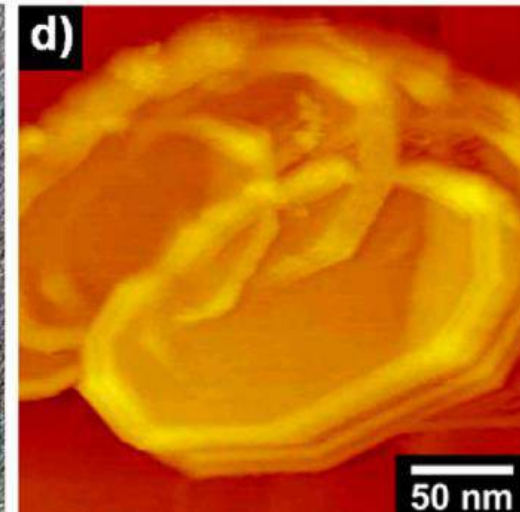
b)



c)



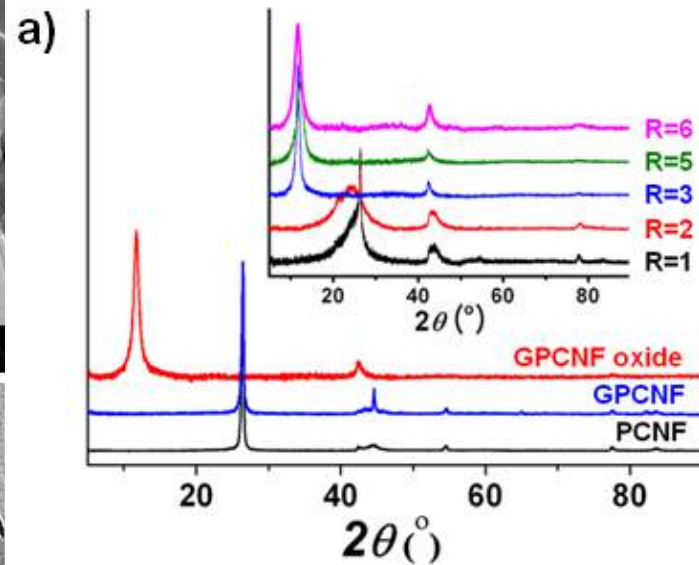
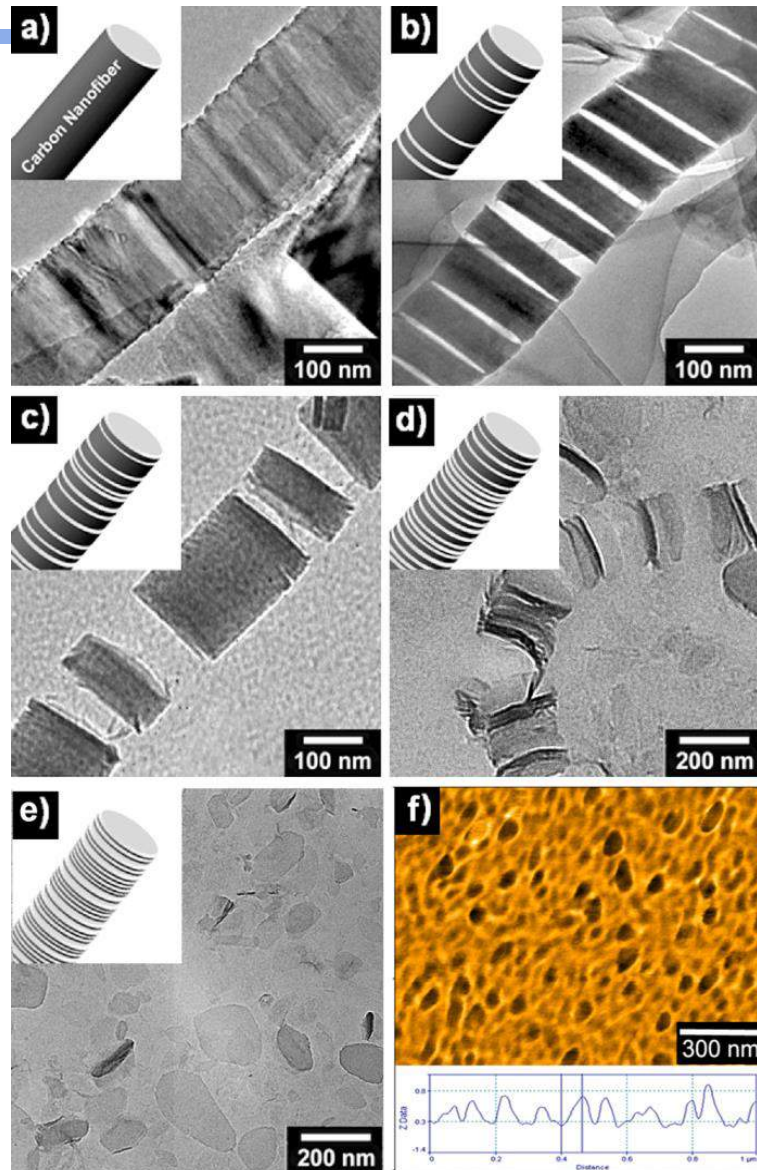
d)



ACS Nano, 2011, 5 (8), pp 6254–6261

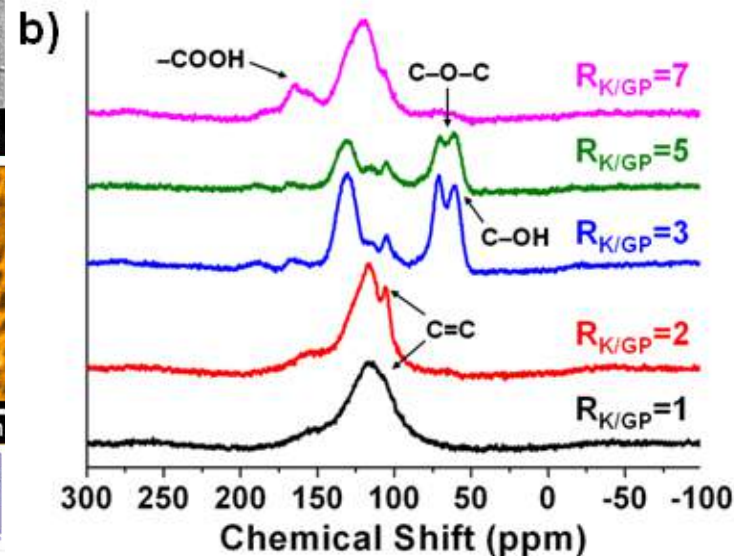


Separation of structural units from GPCNFs



(1)

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

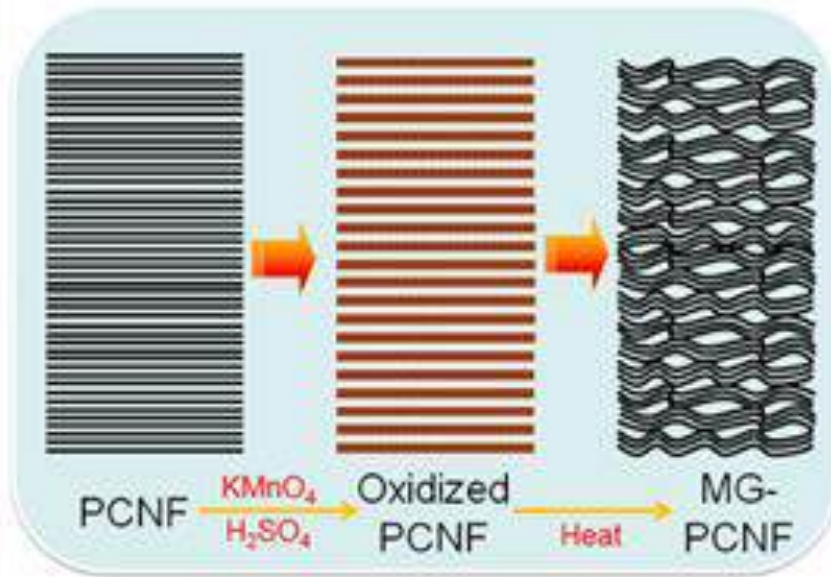


(2)

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

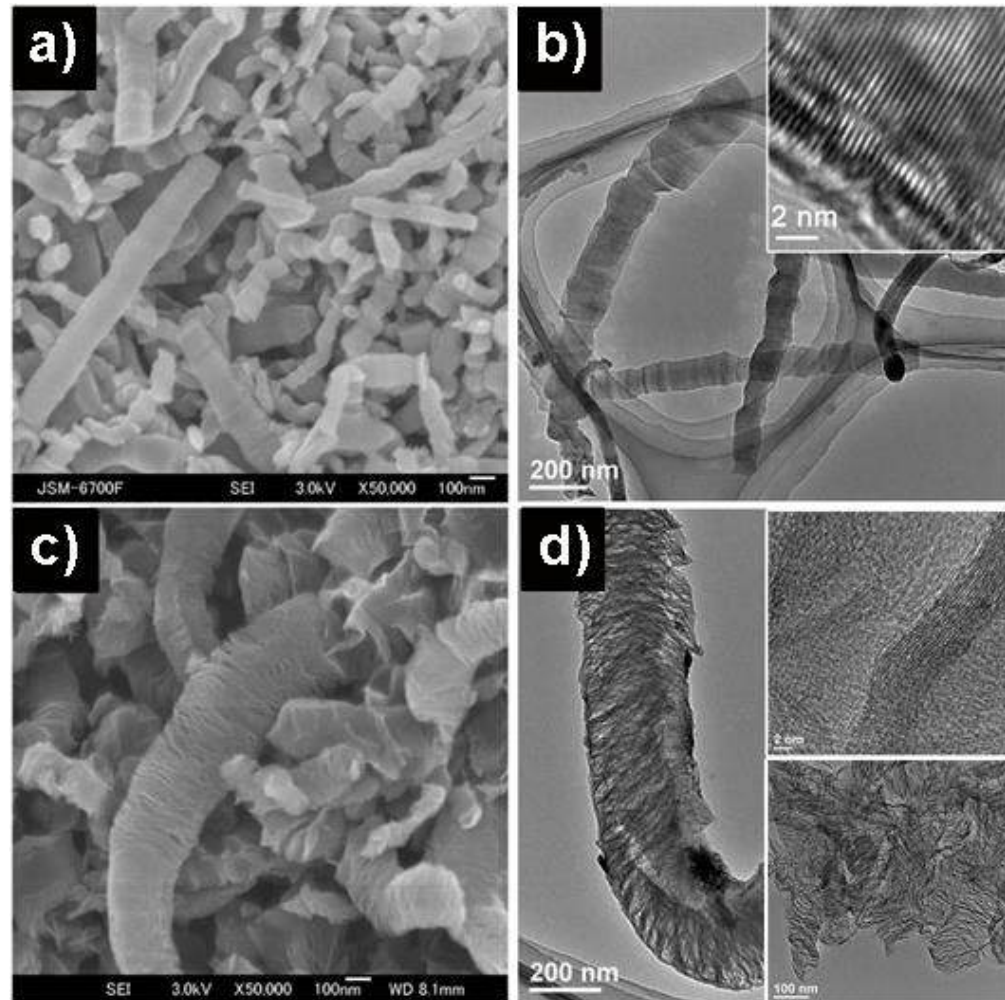
Development and control of mesopores in PCNFs

Introduction

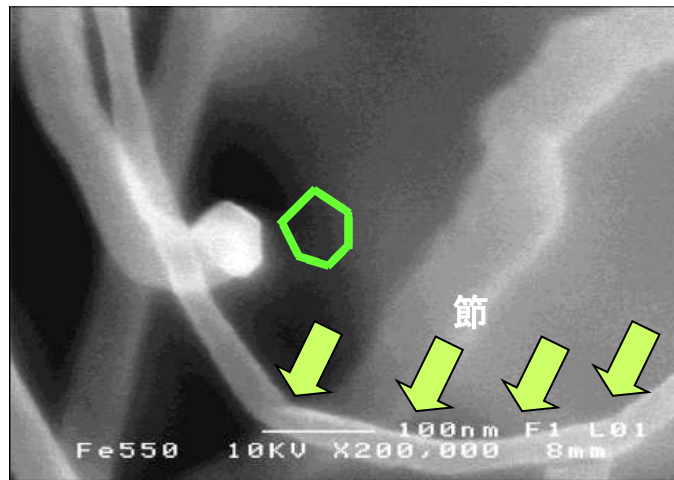
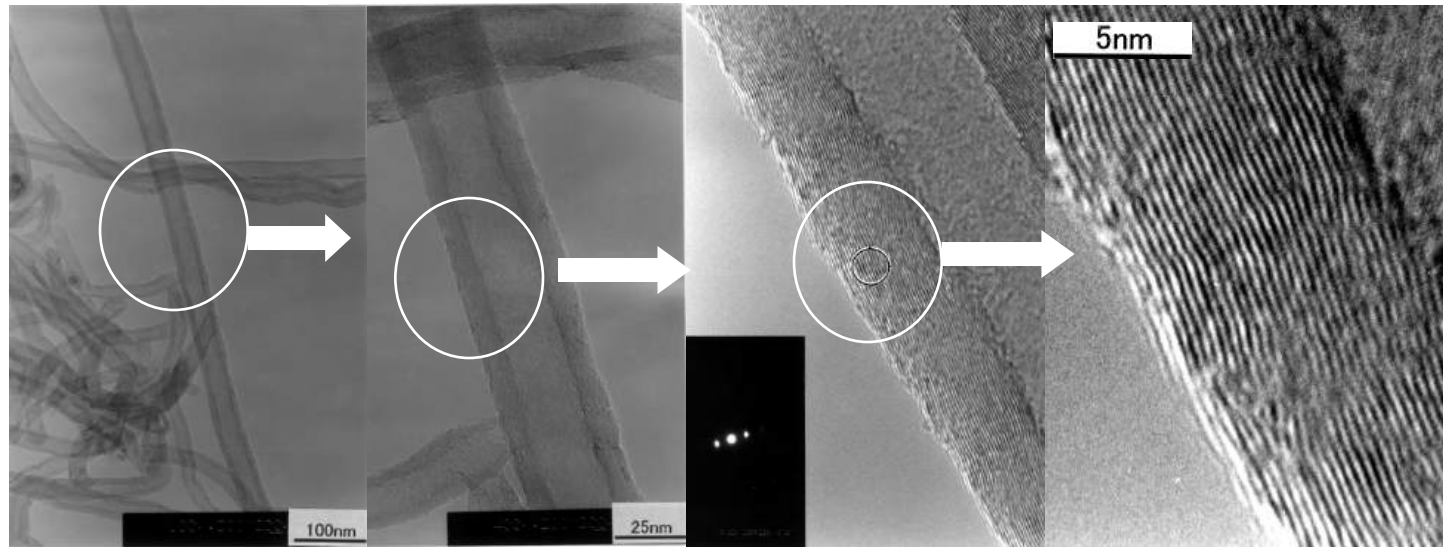


Objective

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



Structural Defects of TCNFs



Heat treatment	$d_{002}(\text{\AA})$	$L_{c002}(\text{nm})$	$L_{a110}(\text{nm})$
As-prepared	3.369	9.5	6.5
Graphitic temp. 2000°C	3.387	13.7	6.7
Graphitic temp. 2800°C	3.375	16.2	6.9

	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ーンCNFのように軸と角度を持って並んだ構造

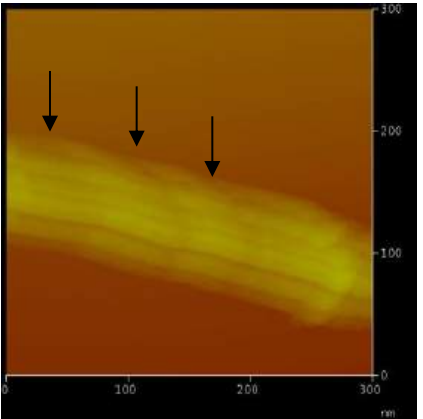
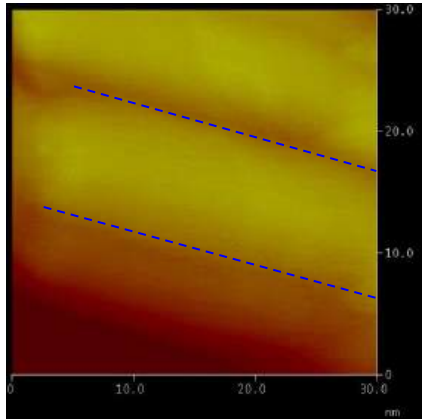
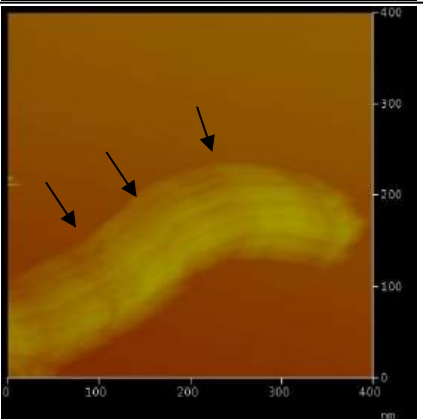
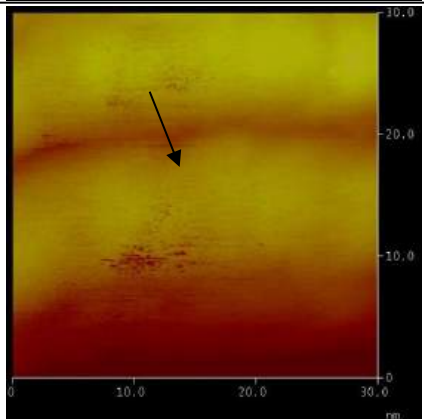
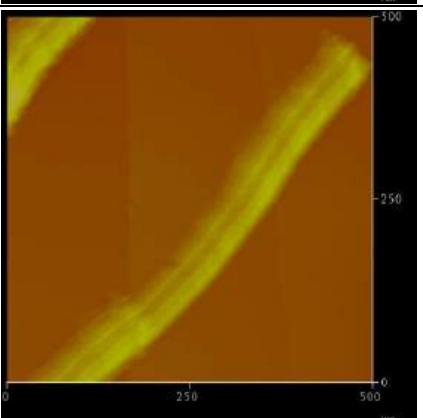
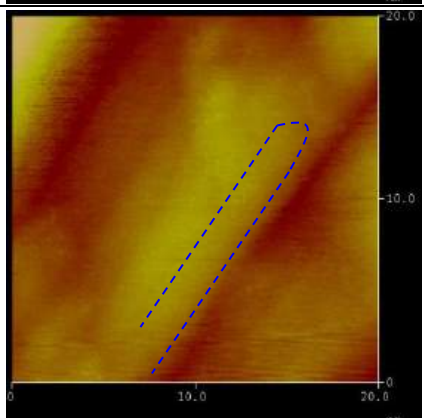
	Large scale	→	Small scale	説明
典型 1				ナノプレットが軸と殆ど平行に並んだ構造
典型 2				ナノプレットがヘリングボンCNFのように軸と角度を持って並んだ構造

KNF-KH2

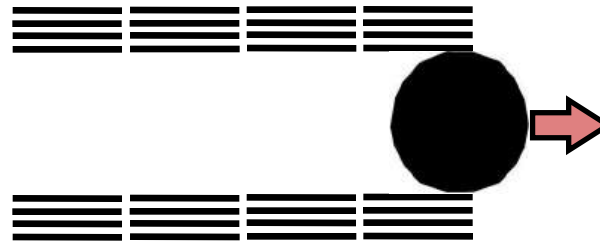
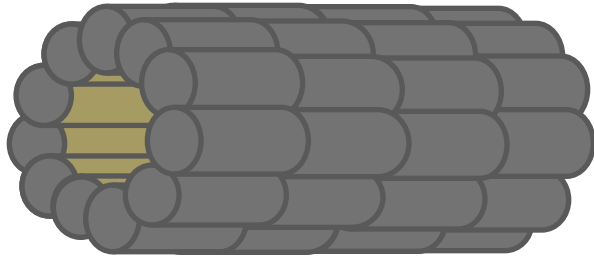


	Large scale	→	Small scale	説明
典型 1				KHF-KH1と類似で、全体的に非直線状で、ナノロッドが軸と平行に並んだ構造
典型 2				全体的に直線状で、ナノロッドが軸と平行に並んだ構造

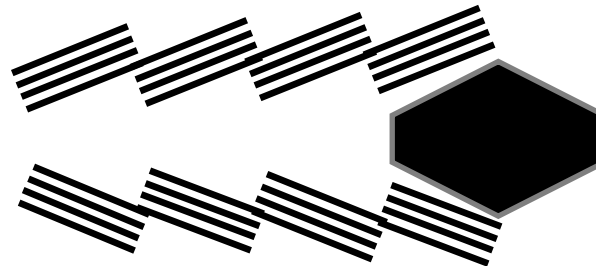
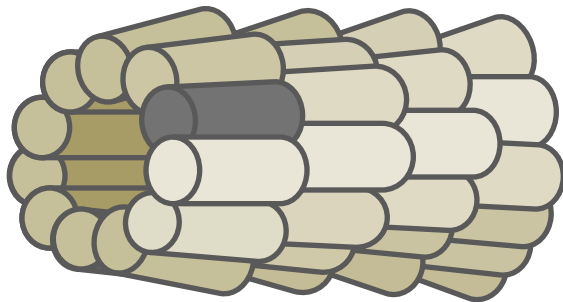
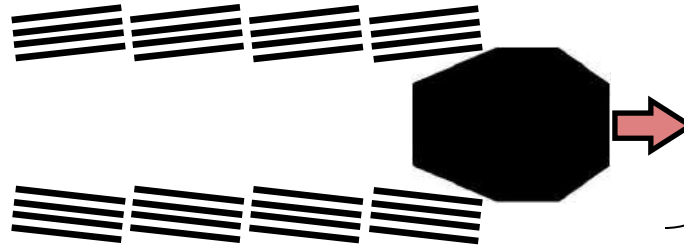
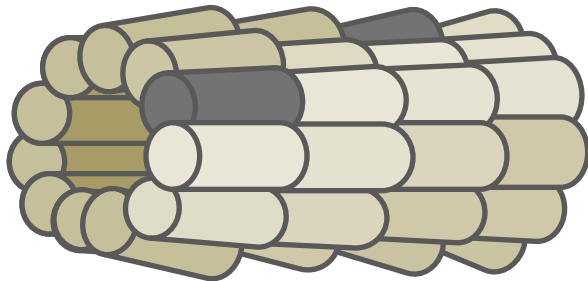


	Large scale	→	Small scale	説明
典型 1				ナノチューブのbundleのようだが、ナノロッドが軸と平行に並んだ構造だとも理解できるかも？ 矢印はロッドの繋ぎ部分だが、正にNature論文でTEMで観察した周期的成長の痕跡
				
				

Schematic Models of TCNF



Usual CNT



Special TCNF
Novel application?



- **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

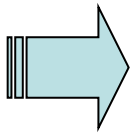


- Anodic Electrode to Hold Reduced Li-ion
Intercalation → Graphite
Surface Electron Transfer into Sealed Void
→ Hard or Low Temperature
Calcined Carbon
- Electron Conductive Material
Anodic Carbon and Cathodes Material
- Expansion Moderator
Holding and Release of Ion Is Accompanied
with Volumetric Charge
Larger Capacity per Volume → Larger
Expansion



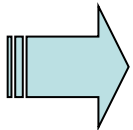
- **Graphite electrode is currently established.**

- 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**

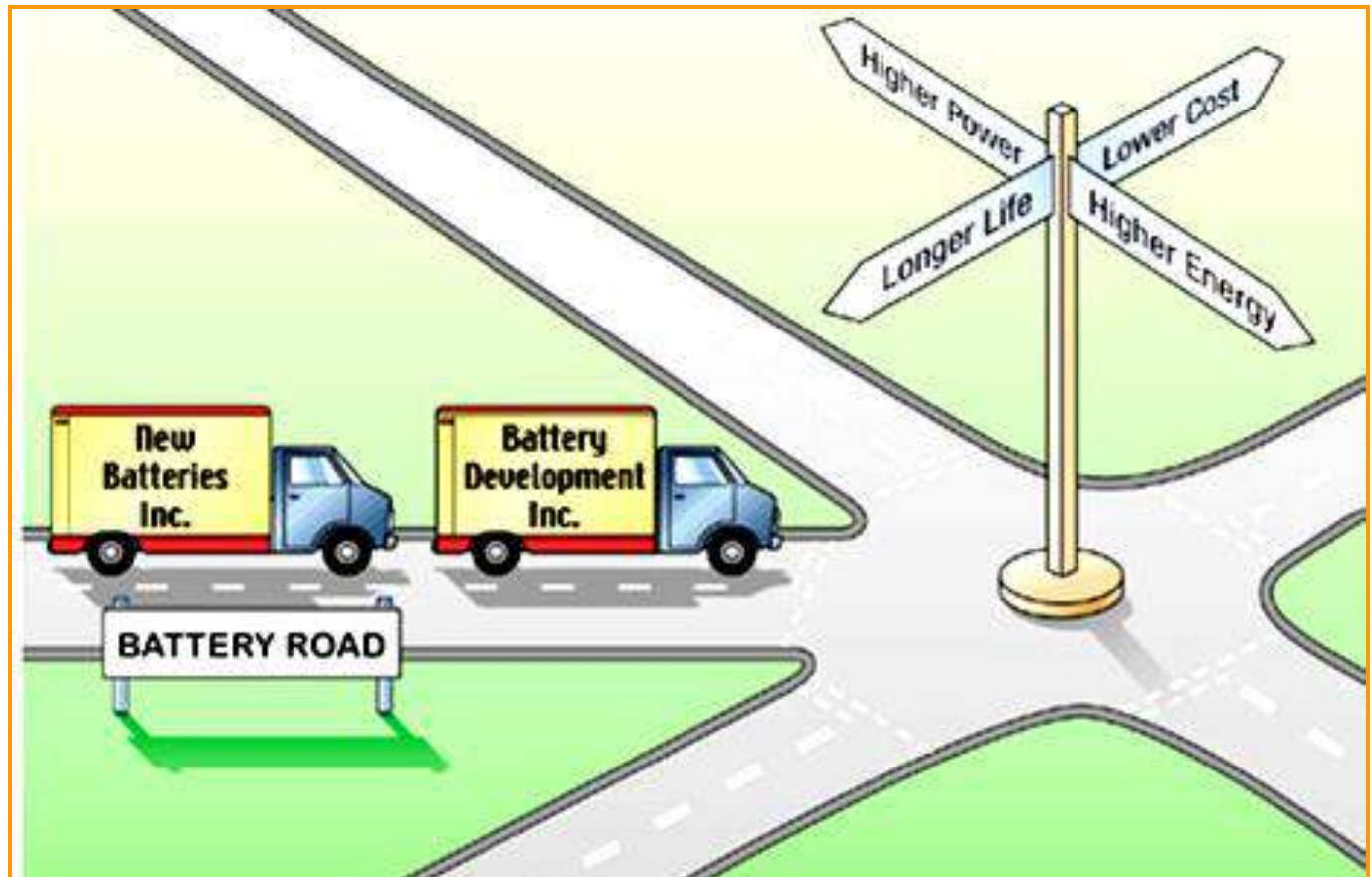
Electrode Materials for Lithium Secondary Battery



Different materials for different applications

A spectacularly reactive cathode

Nature Materials 2, 705–706 (2003)



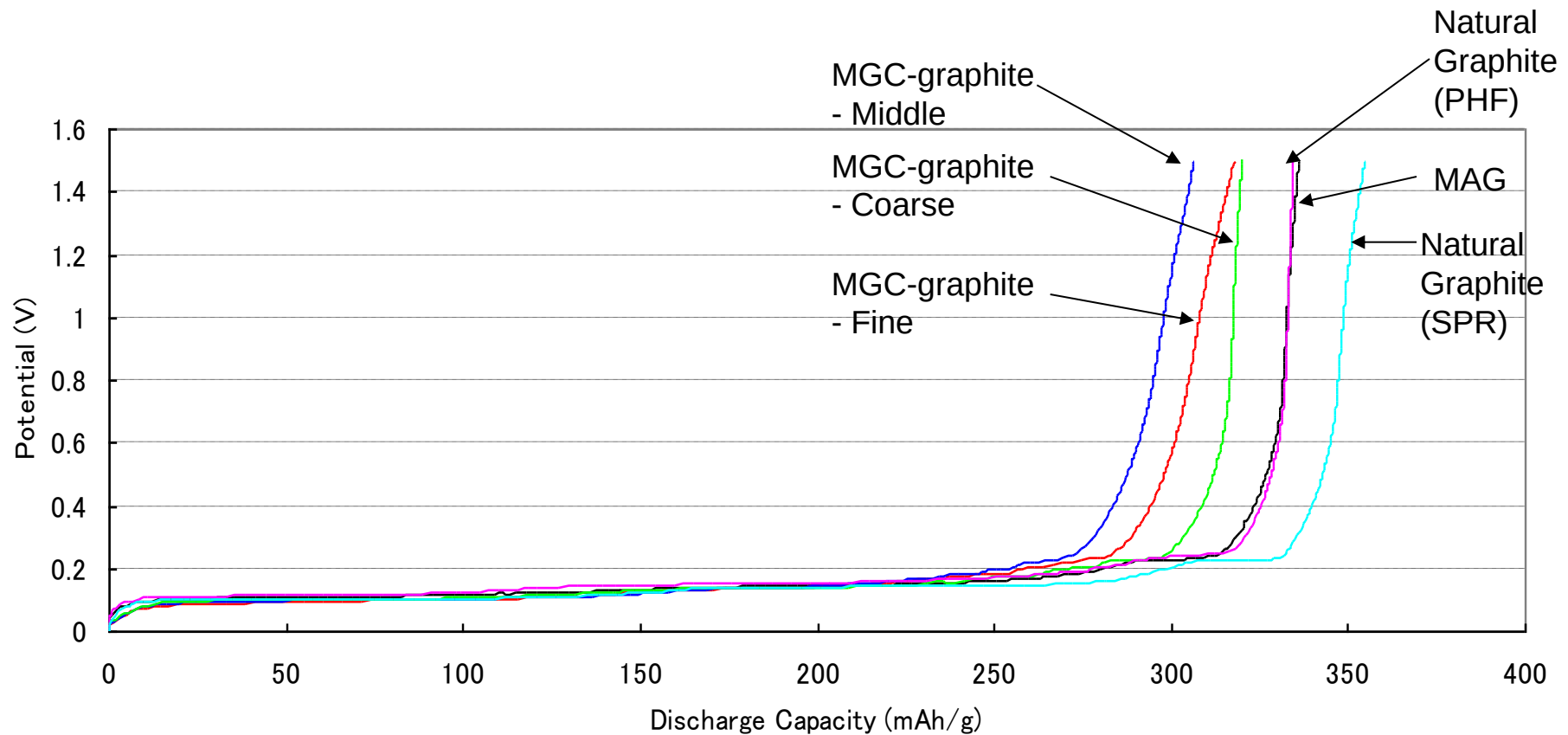


Characteristics of Basic Raw Materials

	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



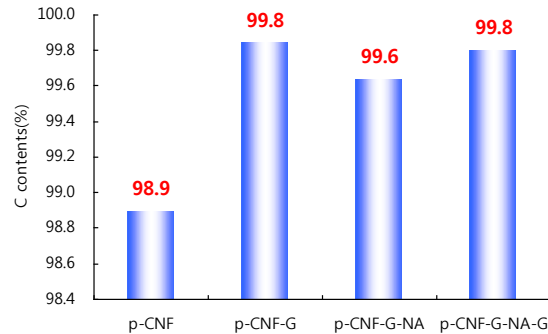
Typical Properties of Synthetic Graphites



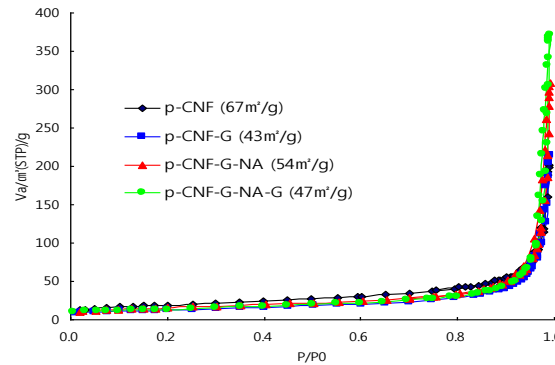


Analysis of physical properties

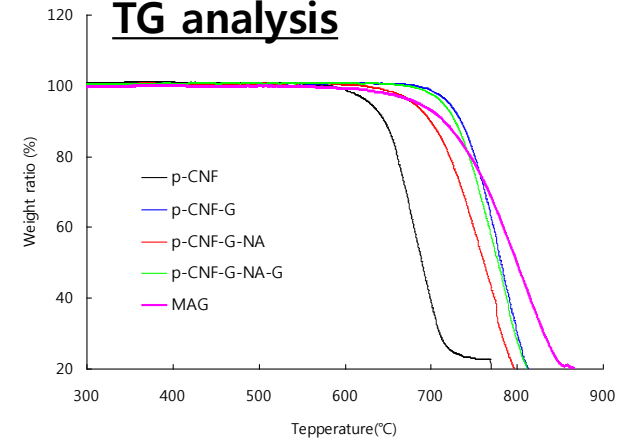
Elemental analysis



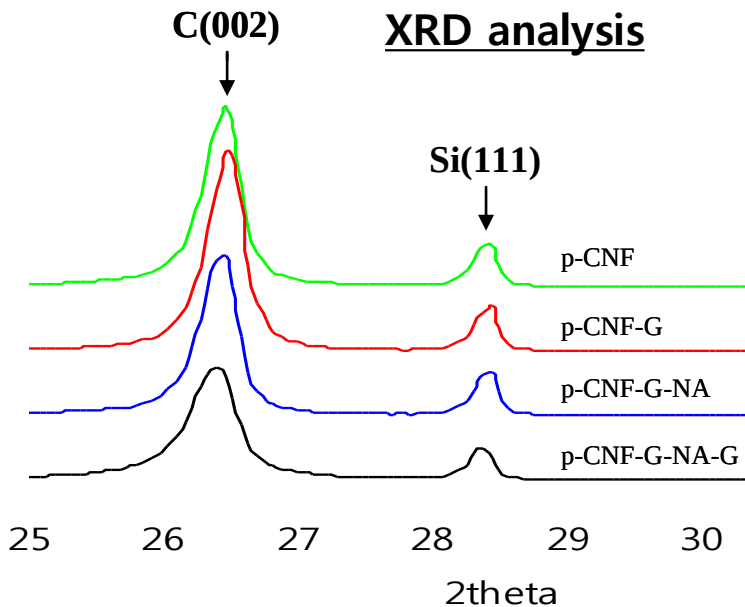
Isotherm curve



TG analysis



XRD analysis

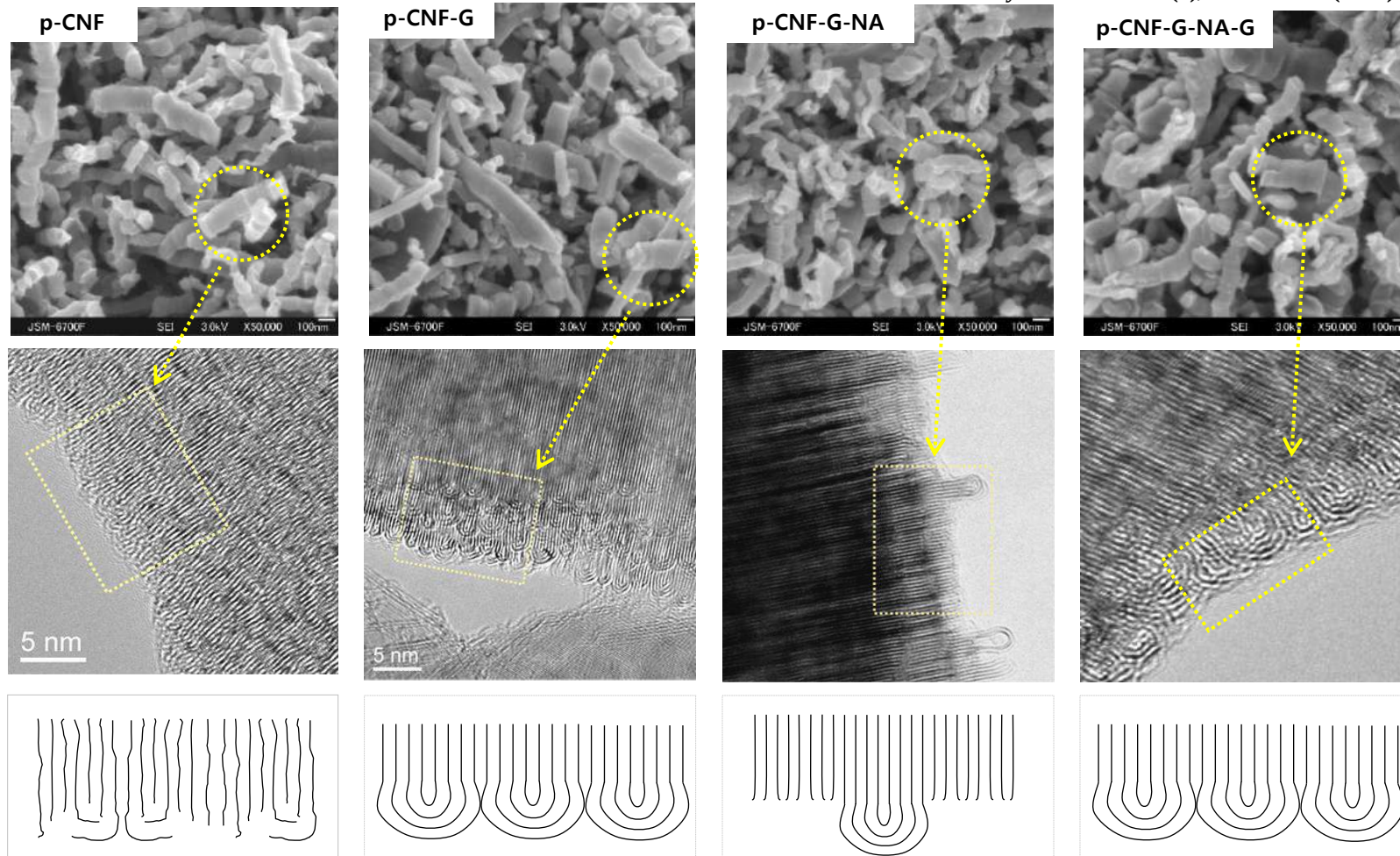


	Elemental Analysis C(%)	Surface area (m²/g)	Oxidation starting Temp.(°C)	XRD Analysis	
				D ₀₀₂ (Å)	Lc ₀₀₂ (nm)
p-CNF	98.9	67	582	3.363	29
p-CNF-G	99.8	43	680	3.365	59
p-CNF-G-NA	99.6	54	628	3.360	>100
p-CNF-G-NA-G	99.8	47	674	3.362	>100
MAG	99.8	< 4	580	3.354	99

Analysis of SEM & TEM Image

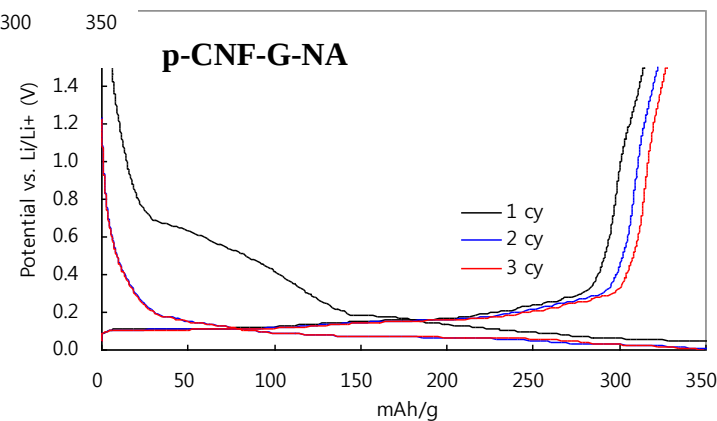
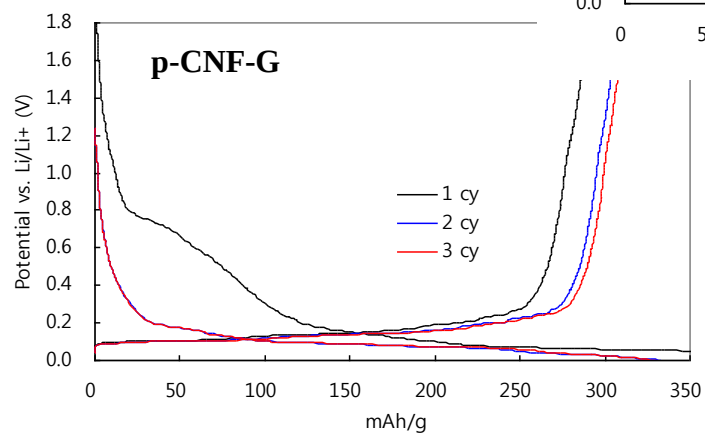
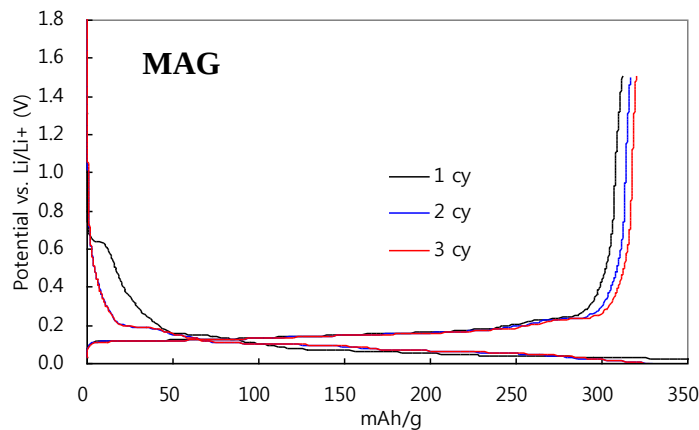
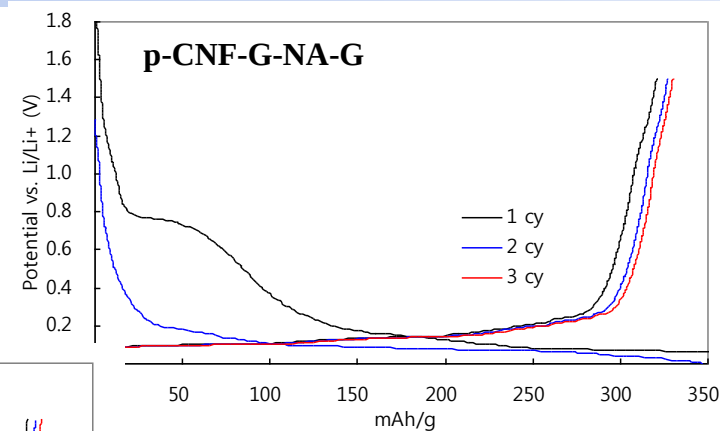
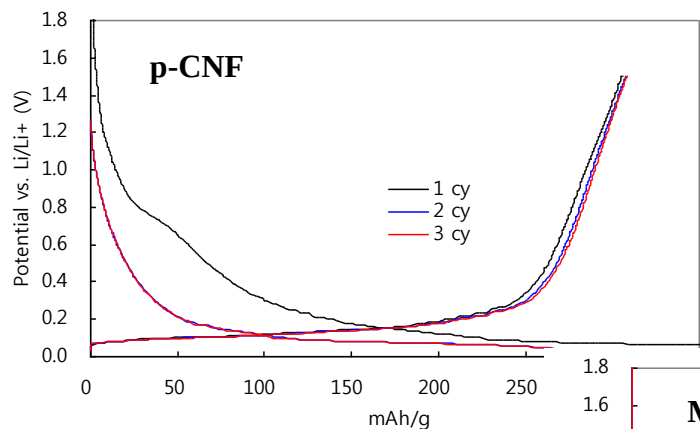


Ref.) S. Lim, et al., *J. Phys. Chem. B* 108 (5), 1533 – 1536 (2004)



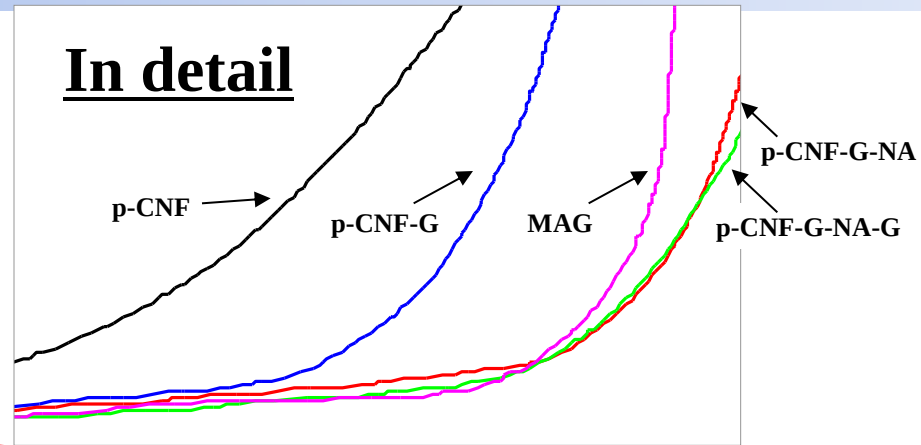
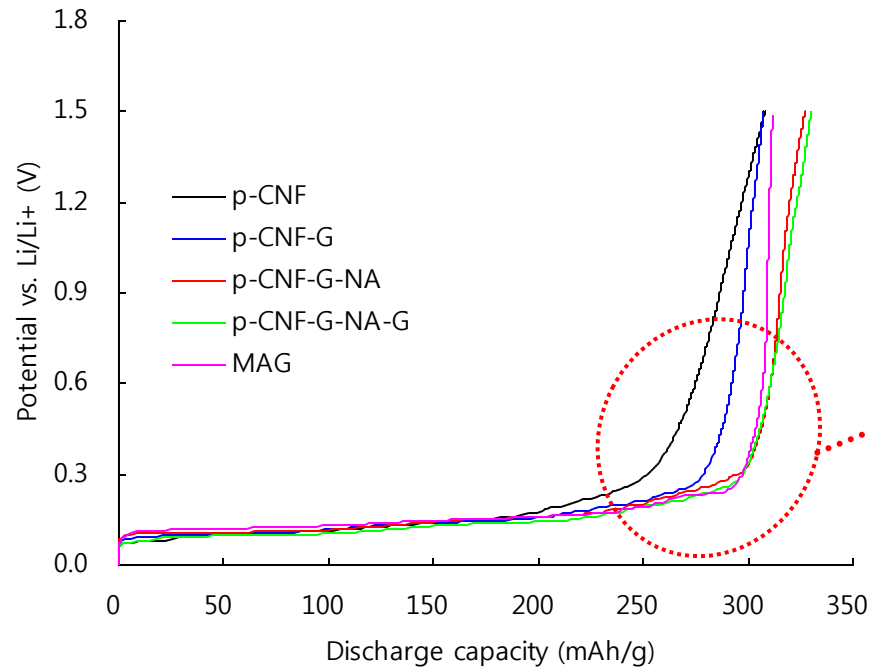
**According to the graphitization degree,
we found some difference at edge plane by TEM analysis**

Electrochemical properties





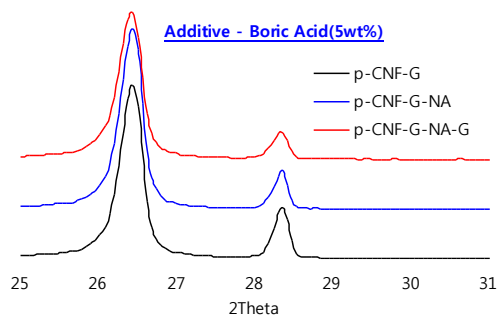
Electrochemical properties



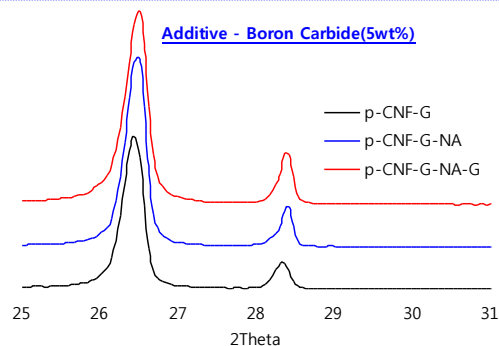
- Discharge capacity depends on graphitization degree .
- p-CNF-G-NA (& -G) showed good electrochemical properties.
- They are almost same with MAG (synthetic graphite)
- But, initial coulombic efficiency is low (52~60%) compared to MAG(over 80%)

	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

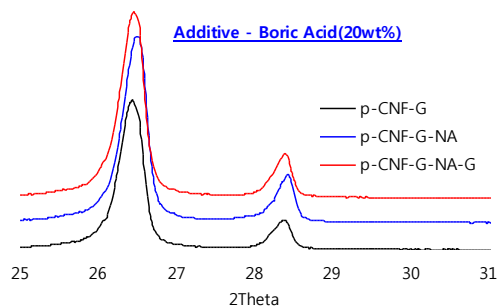
Effects of Boron Additives – XRD analysis



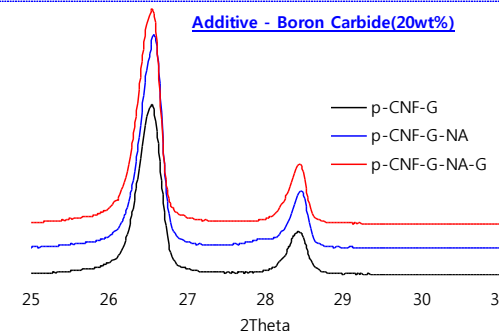
B/A (5wt%)	d002(A)	Lc002 (nm)
p-CNF-G	3.357	> 100
p-CNF-G-NA	3.356	85.4
p-CNF-G-NA-G	3.356	75.4



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

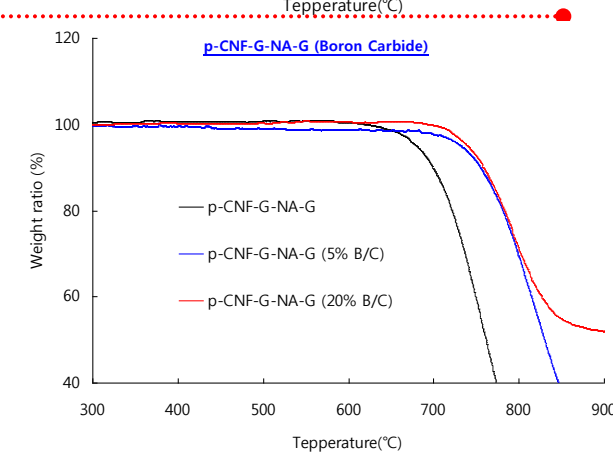
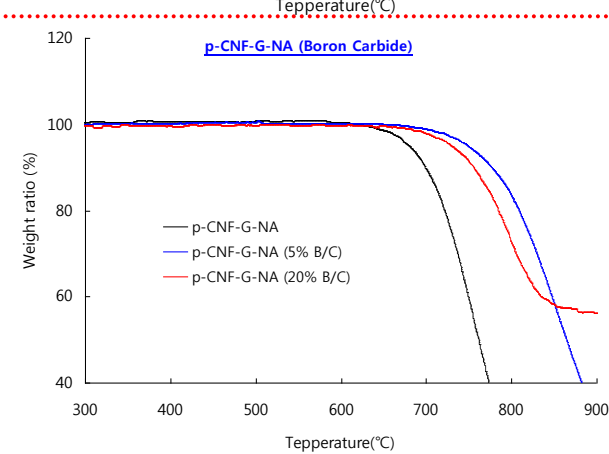
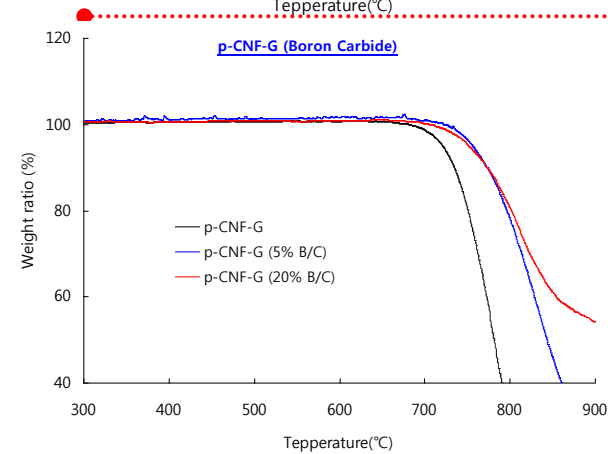
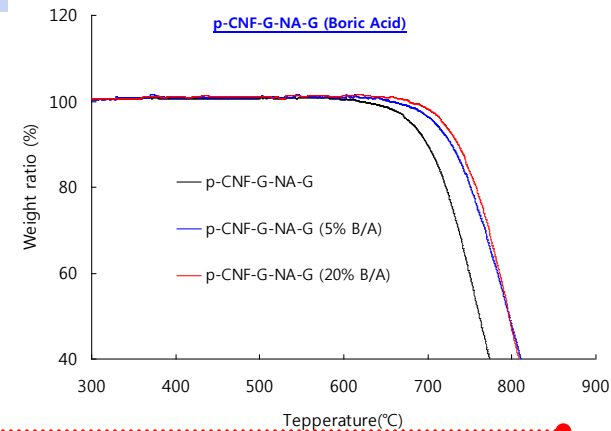
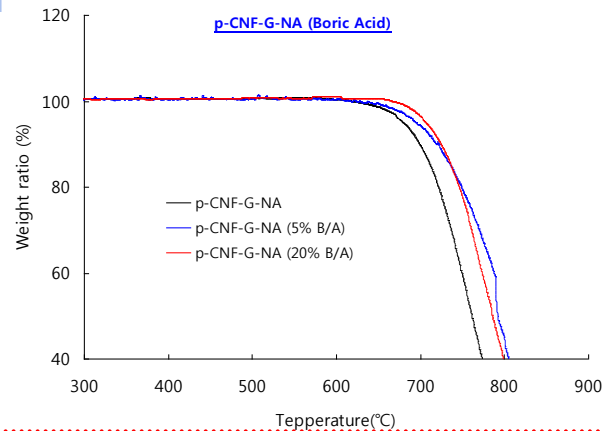
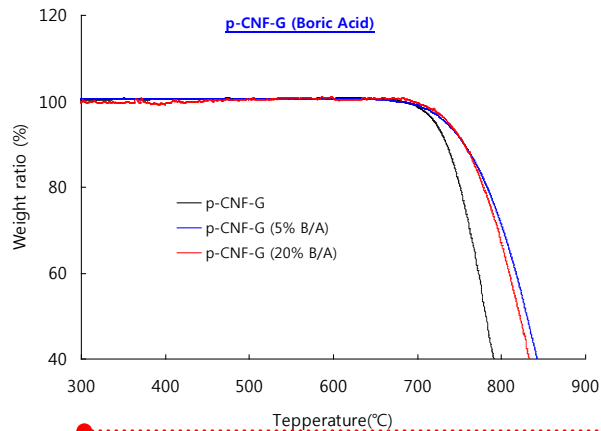
No additive	XRD Analysis	
	D ₀₀₂ (Å)	L _{C002} (nm)
p-CNF	3.363	29
p-CNF-G	3.365	59
p-CNF-G-NA	3.360	>100
p-CNF-G-NA-G	3.362	>100

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

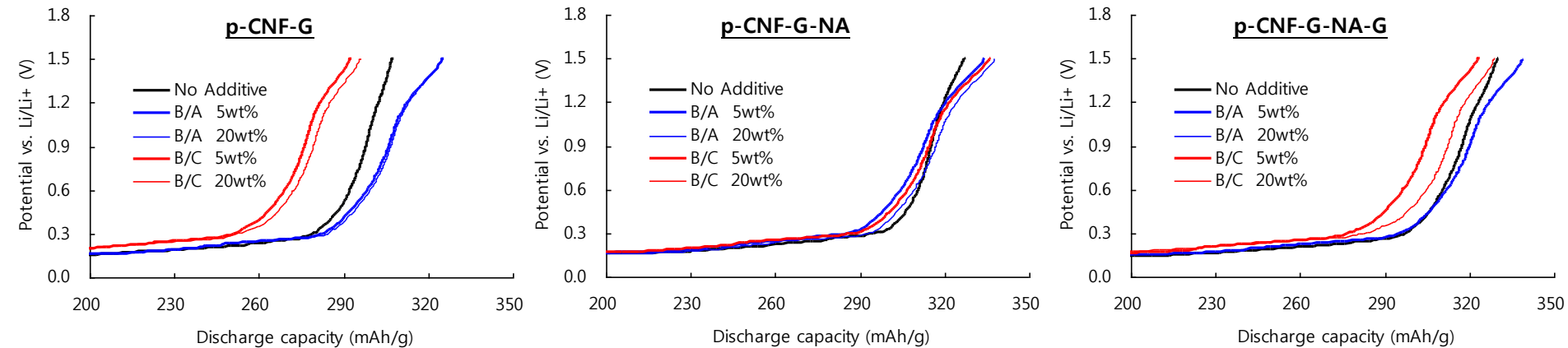


	Oxidation starting temperature (°C)		
	p-CNF-G	p-CNF-G-NA	p-CNF-G-NA-G
No additive	680	628	674
B/A (5wt%)	686	634	661
B/A (20wt%)	697	670	683

	Oxidation starting temperature (°C)		
	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

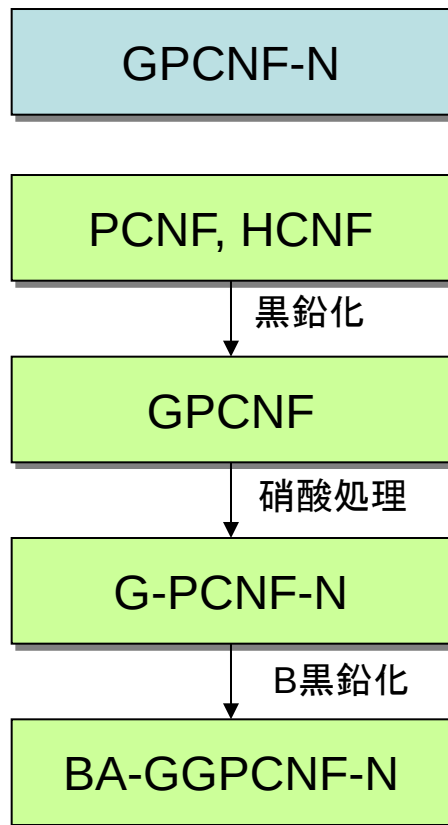


	p-CNF-G				p-CNF-G-NA				p-CNF-G-NA-G			
	Discharge capacity (mAh/g)			Coulombic efficiency (%)	Discharge capacity (mAh/g)			Coulombic efficiency (%)	Discharge capacity (mAh/g)			Coulombic efficiency (%)
	0.25V	0.5V	1.5V		0.25V	0.5V	1.5V		0.25V	0.5V	1.5V	
No additive	268	290	307	58.2	274	308	327	52.5	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

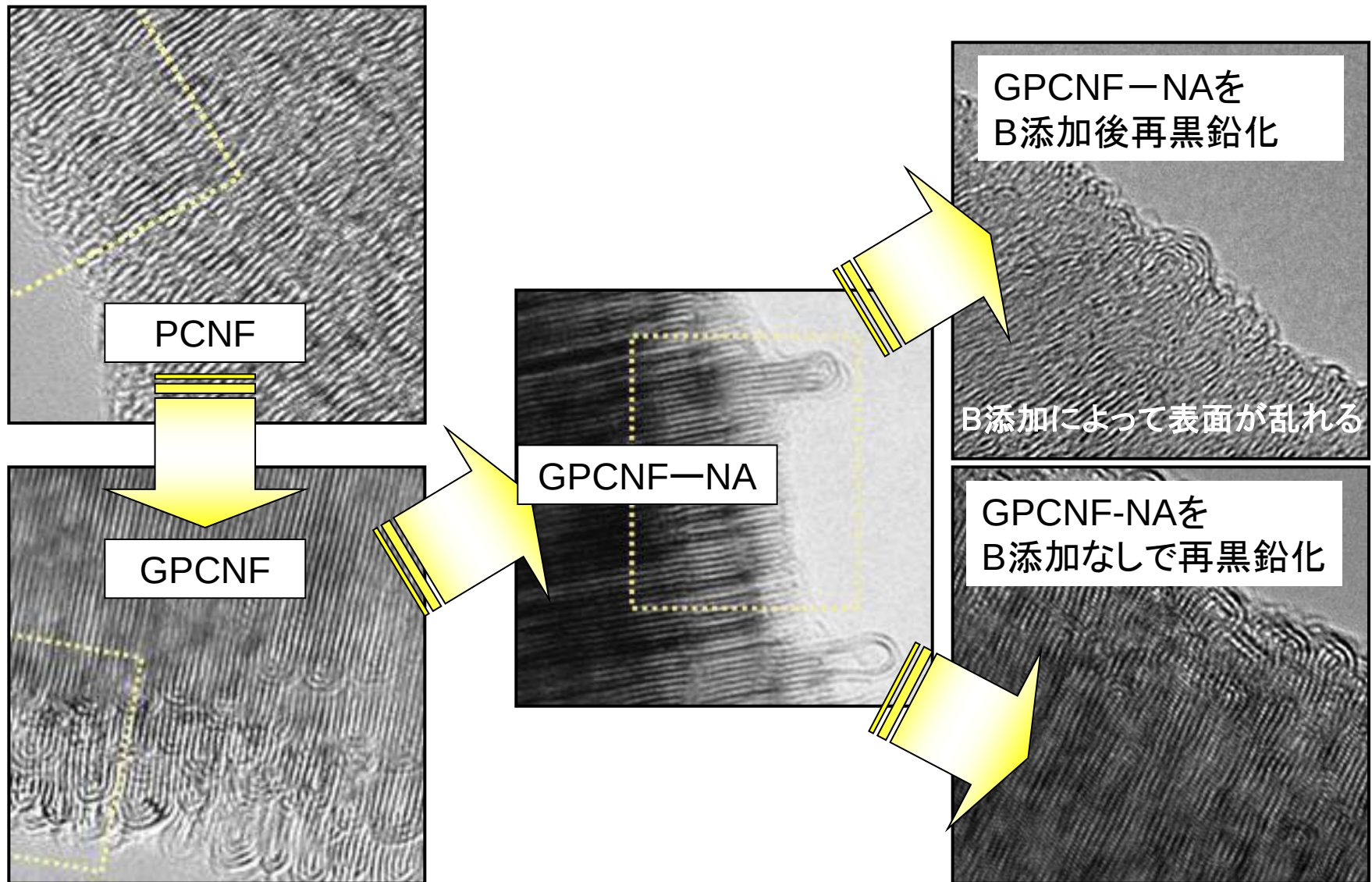


- CNF of similar graphitic properties with Natural Graphite
- CNT usually shows low graphitic properties
- Conductive materials or supports for heterogeneous catalysts

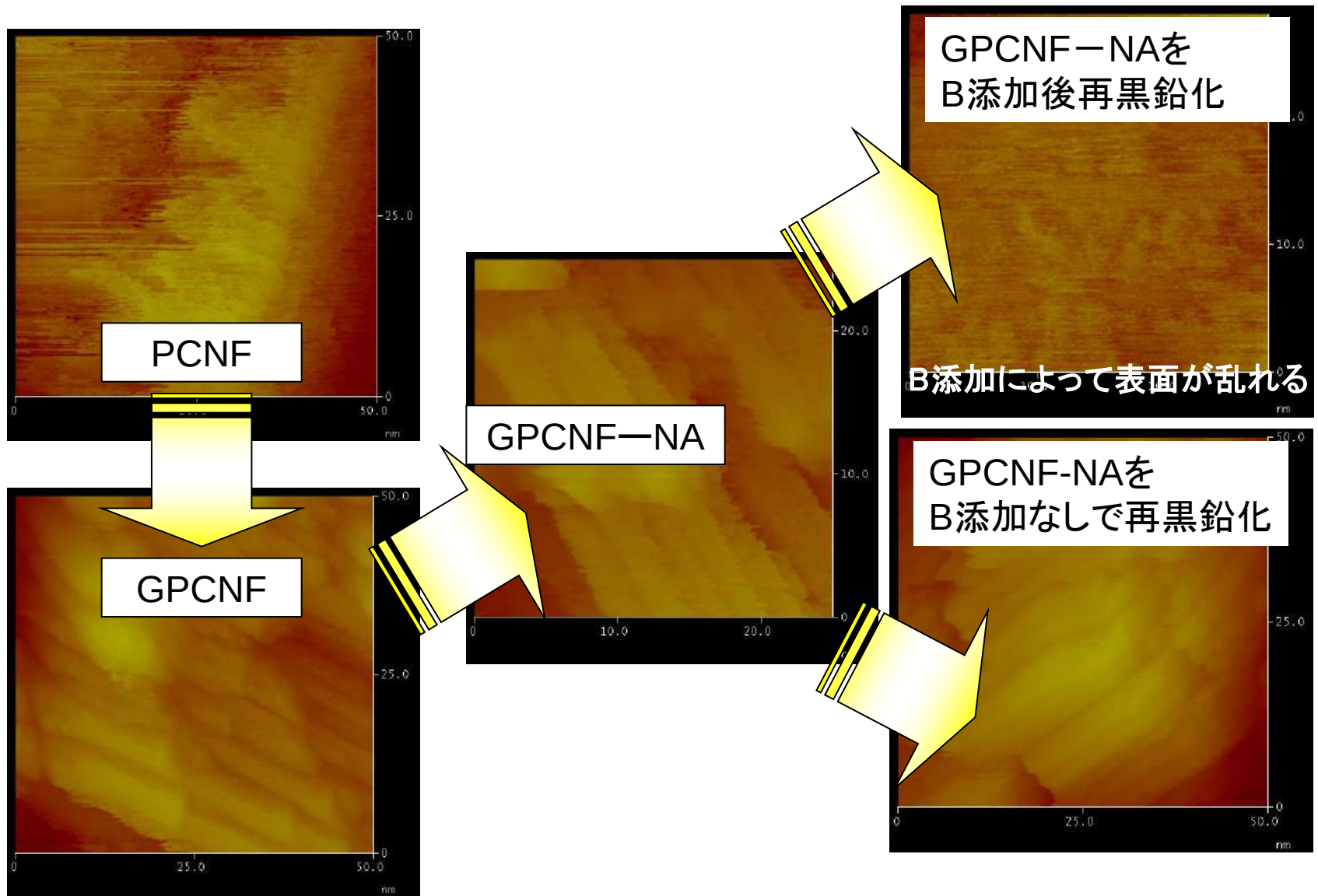


	Preparation conditions	d ₀₀₂ (nm)	L _{c(002)} (nm)
PCNF	Fe catalyst, 620, CO/H ₂ : 4/1	0.3365	72
G-PCNF	2800°C heat treatment of PCNF	0.3364	83
G-PCNF-N	30% HNO ₃ treatment of GPCNF for 50°C, 8hs	0.3362	152
GG-PCNF-N	2800°C heat treatment of GPCNFN	0.3362	106
BA-G-PCNF	Boric acid added heat treatment of PCNF	0.3359	115
BA-GG-PCNF-N	30% HNO ₃ treatment of GPCNF for 50°C, 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% HNO ₃ treatment of GPCNF for 50°C, 8hs Boron carbide added heat treatment	0.3354	167

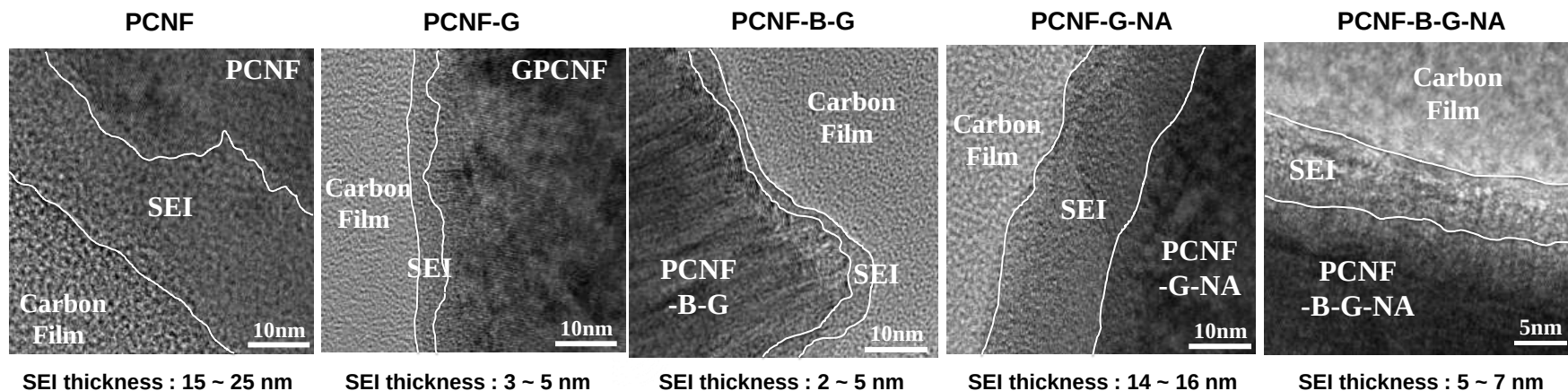
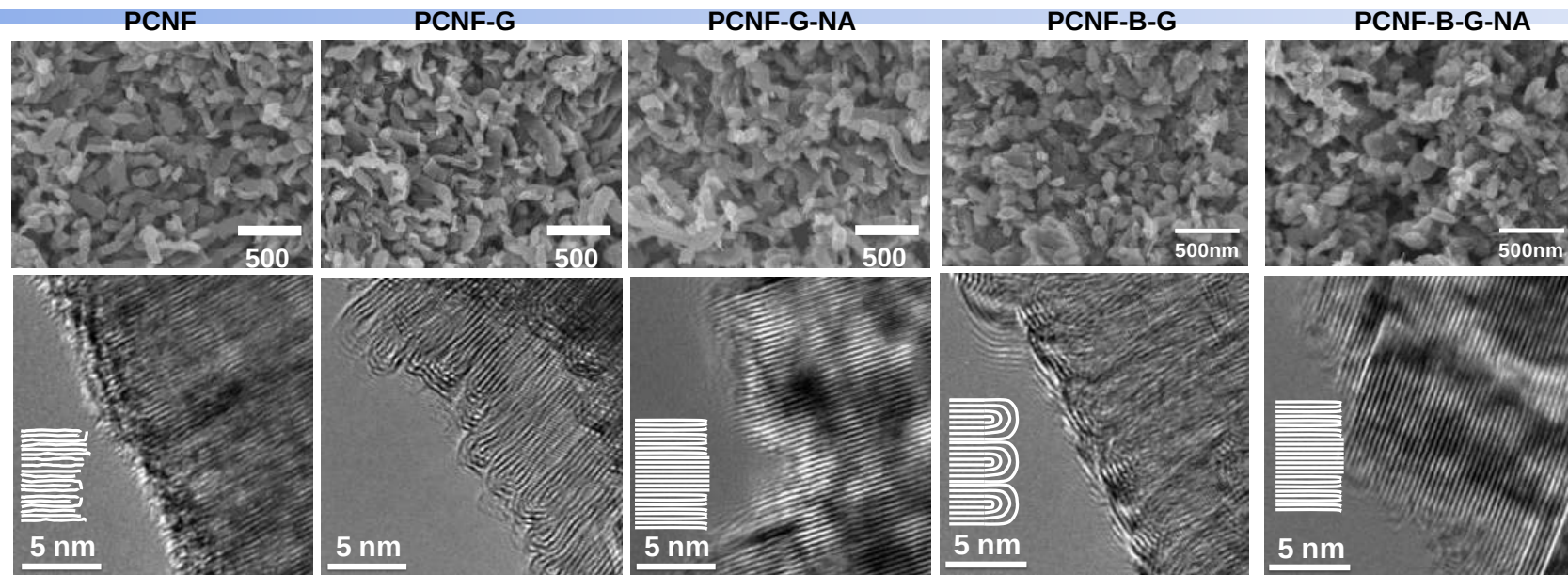
TEM of GPCNF (B addition)



STM of GPCNF (B addition)



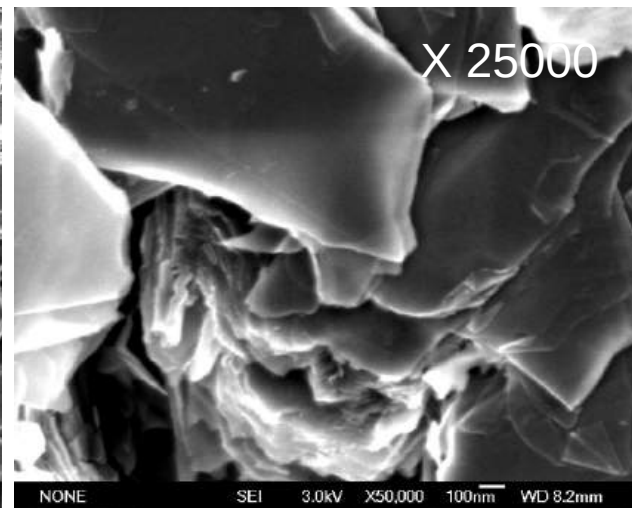
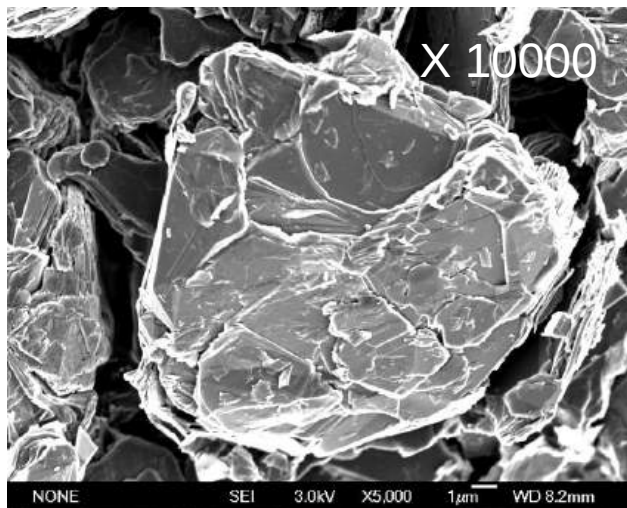
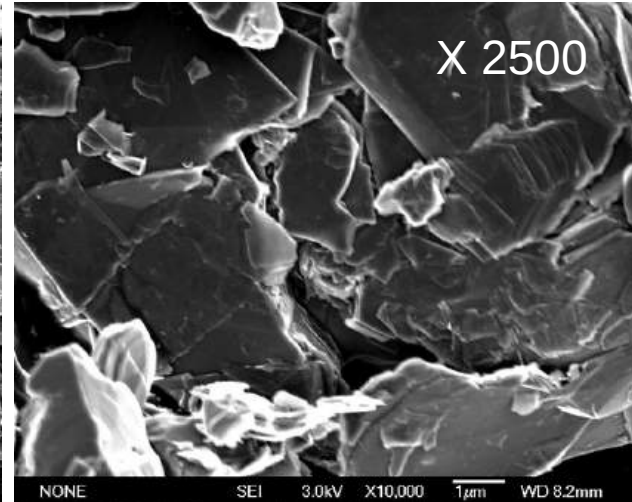
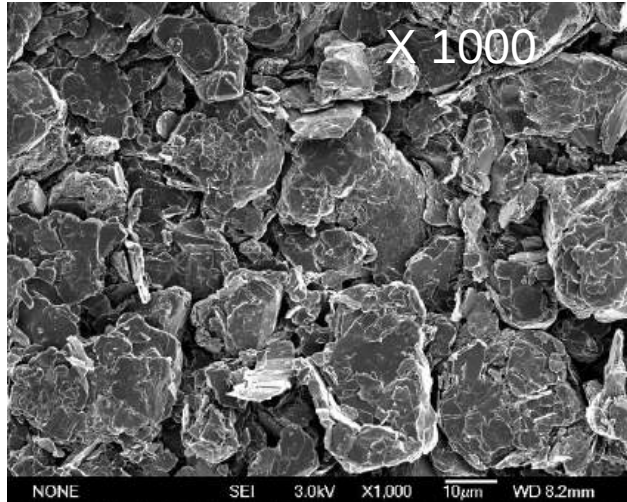
Microscopic observation of PCNFs





Typical Synthetic Graphite

(MAG; Hitachi Chemical Co.)

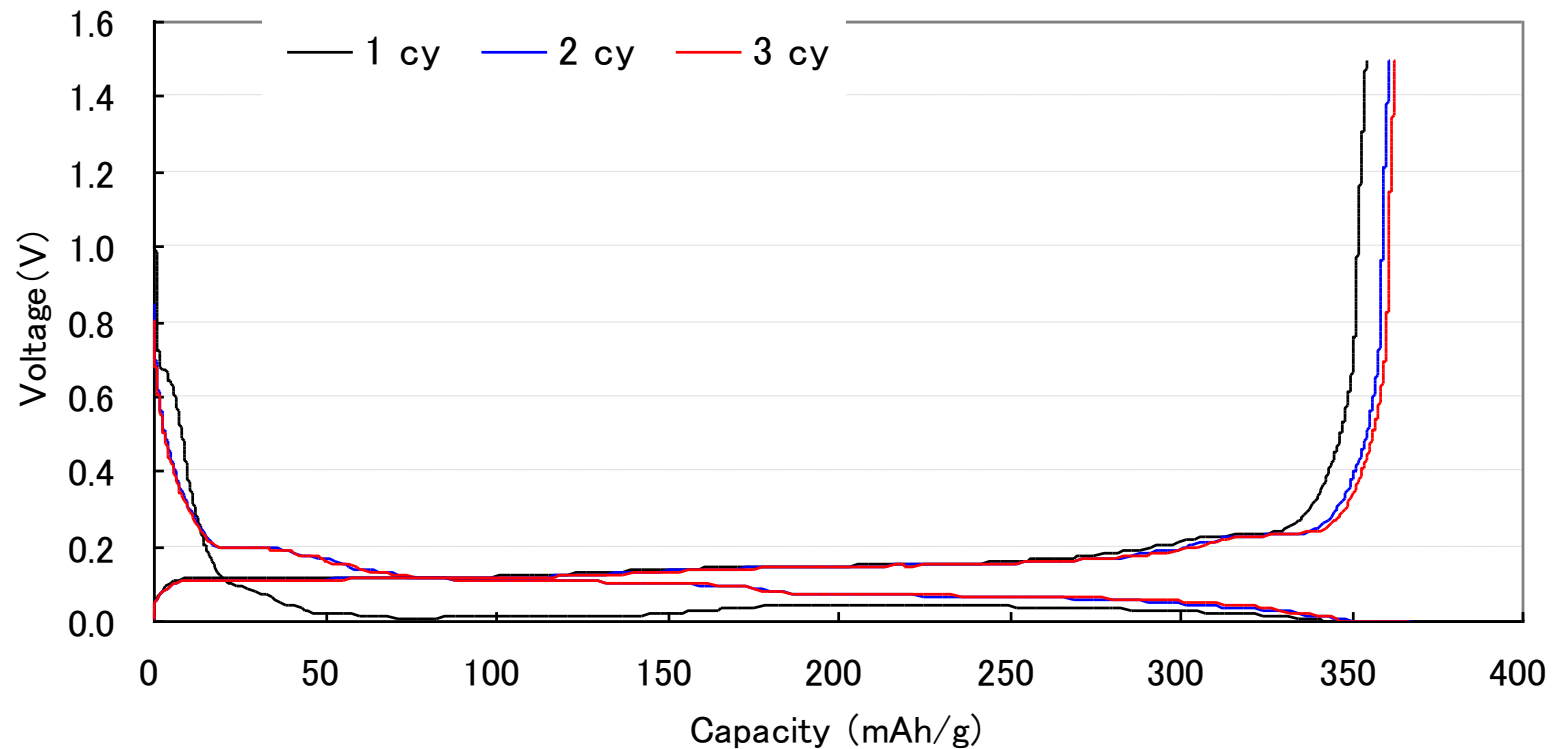




Typical Synthetic Graphite

(MAG; Hitachi Chemical Co.)

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





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

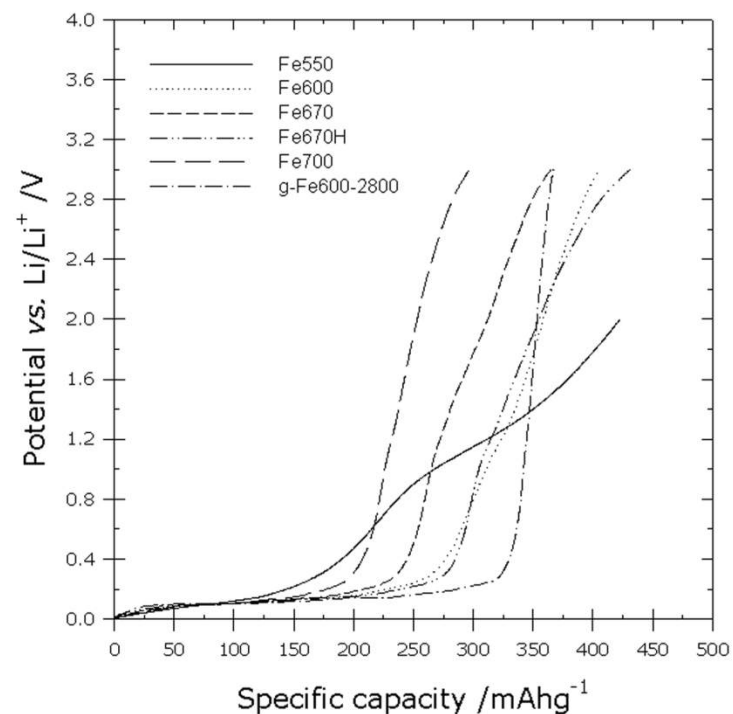
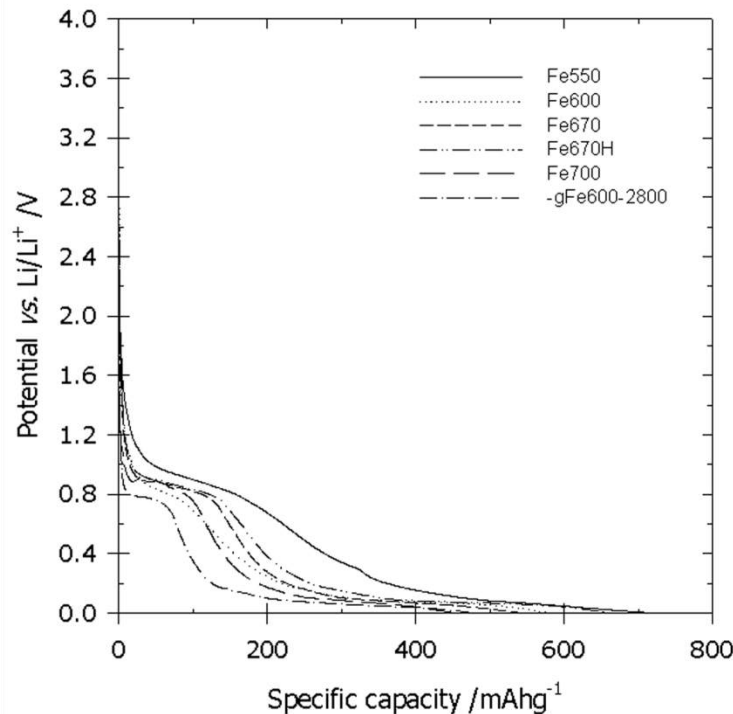
High Power

CNF + Graphite + ? : for high power
Demands for high speed charge and discharge : Hybrid Vehicle, UPS, PC

Applying CNF Composites for Problems Solving



Electrode Materials for Li-ion Batteries (Basic Property)



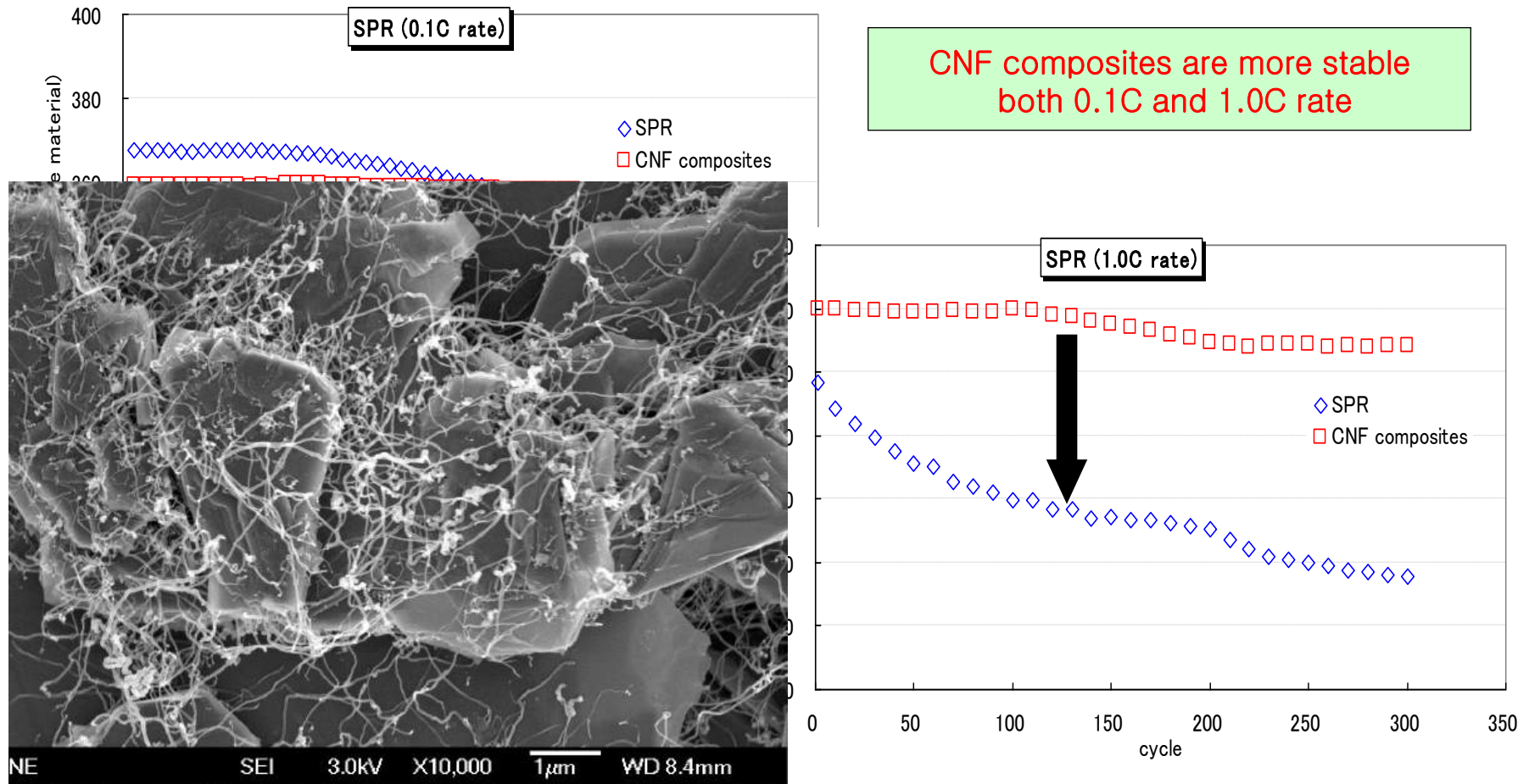
100% of PC Solvent for Electrolyte can be used to P-CNF anodic carbon

- 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)



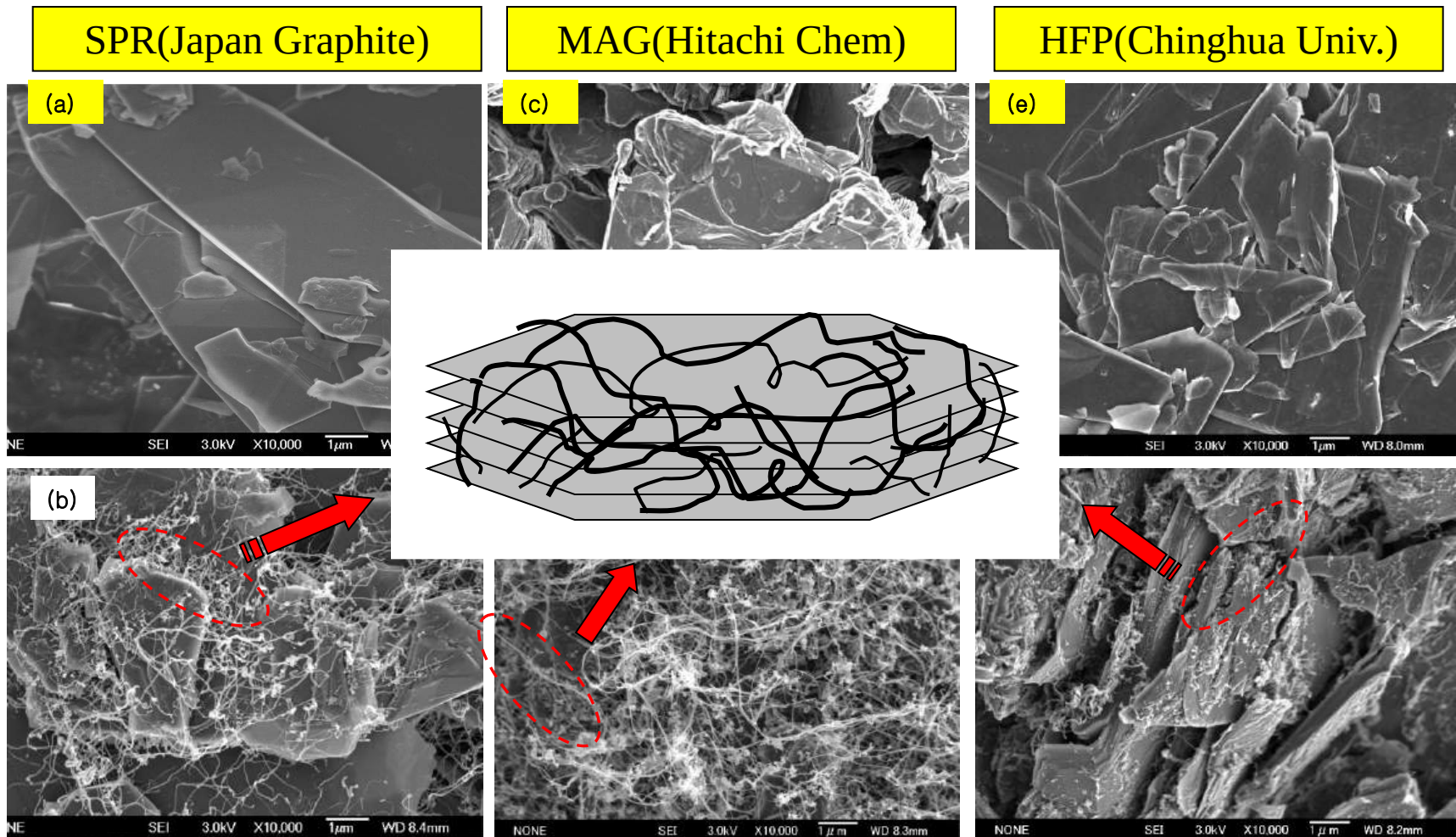
Rate Characteristics of SPR & SPR-CNF Composites

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



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)

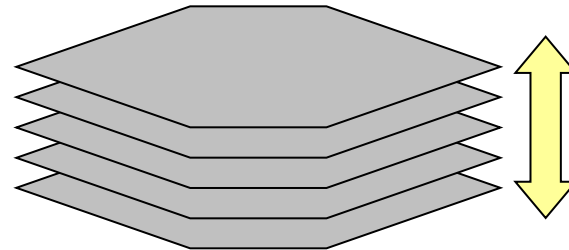
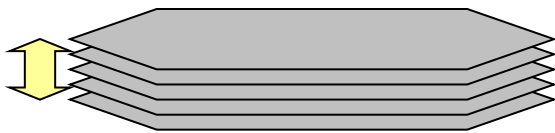


Schematic models of charge states

Low rate

High rate

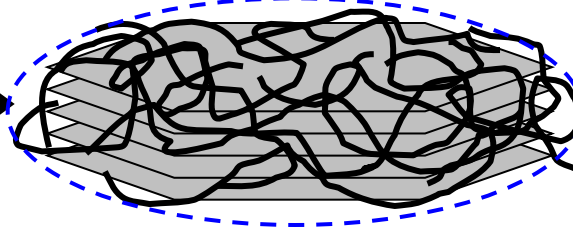
(a)



Bad
Performance
at high rate

Volume expanded slowly

(b)



Good
Performance
at high rate

Expanded Rapidly

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



- Glassy Carbon;

Larger Capacity per Weight

→ Larger Capacity per Volume

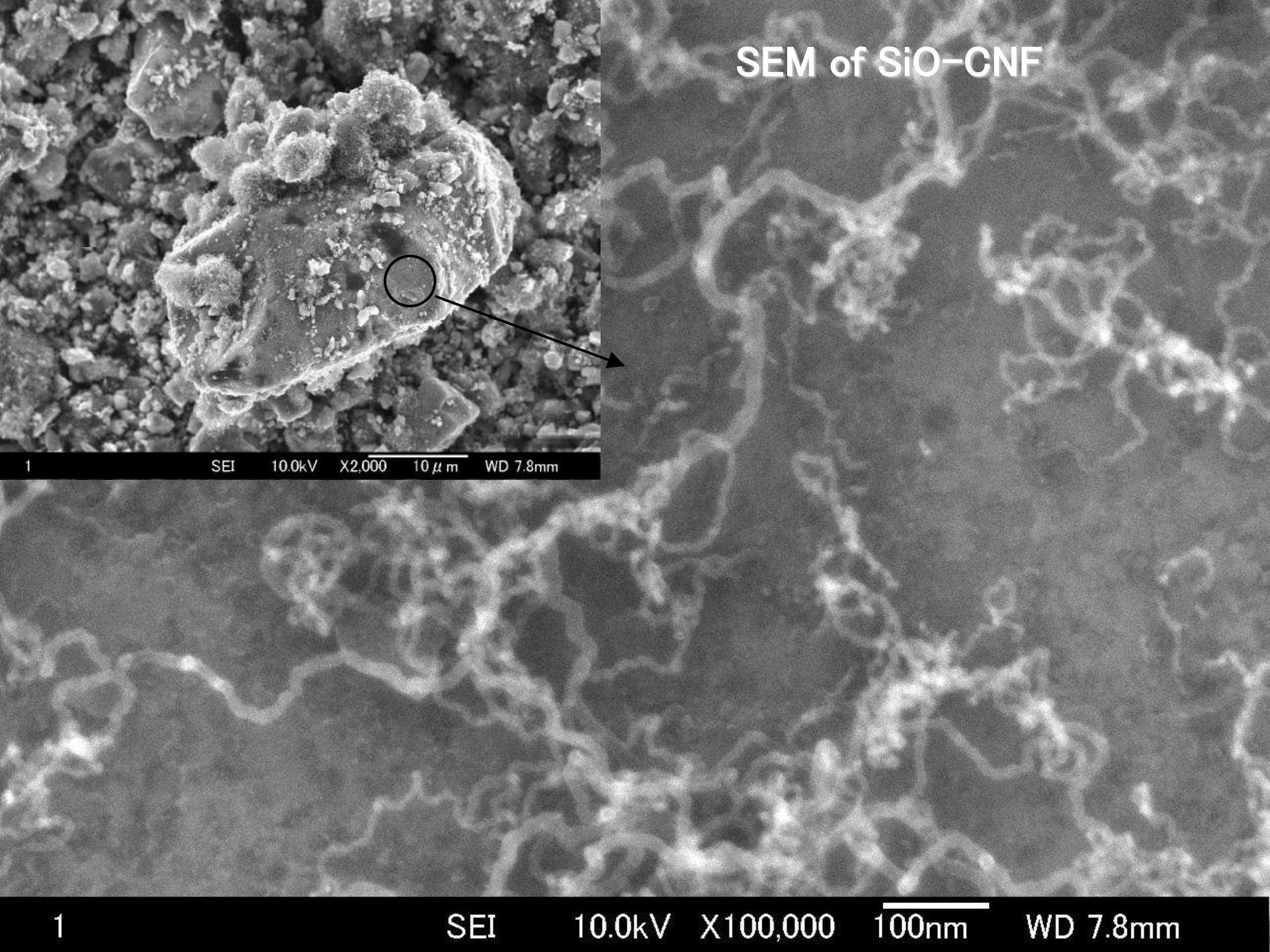
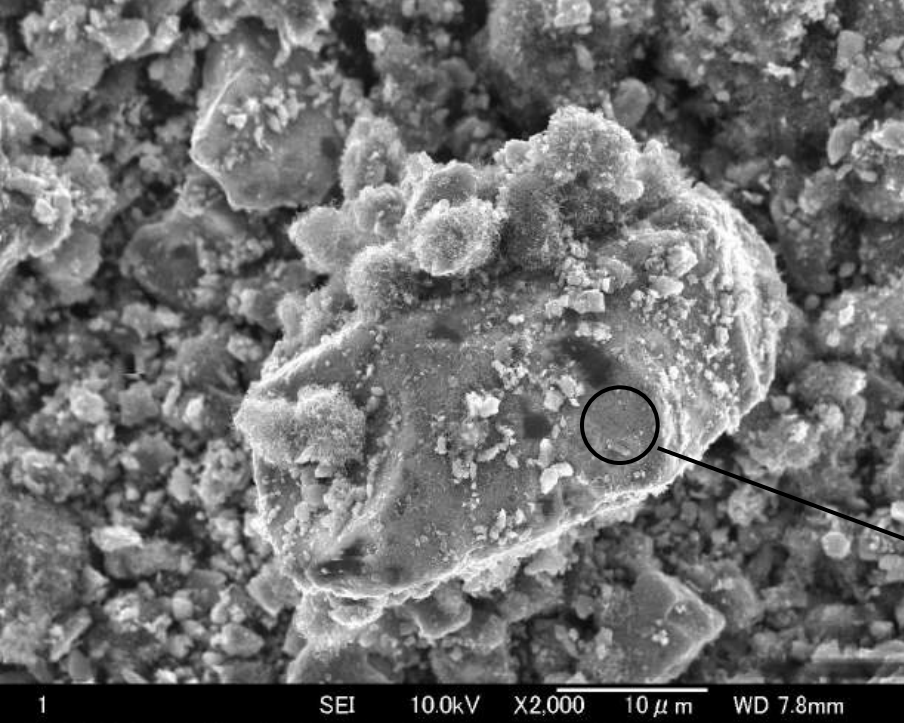
- Non-carbon Materials;

Si Materials }
Sn Materials }

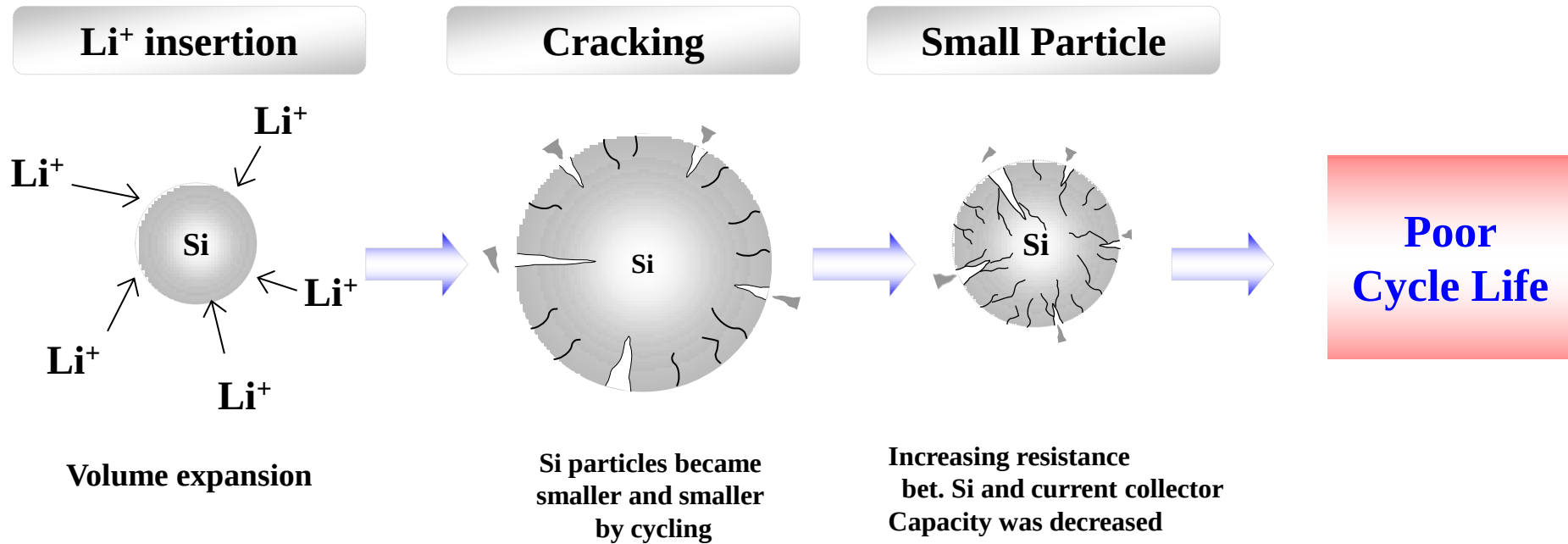
Large Expansion

→ Poor Cycle Stability

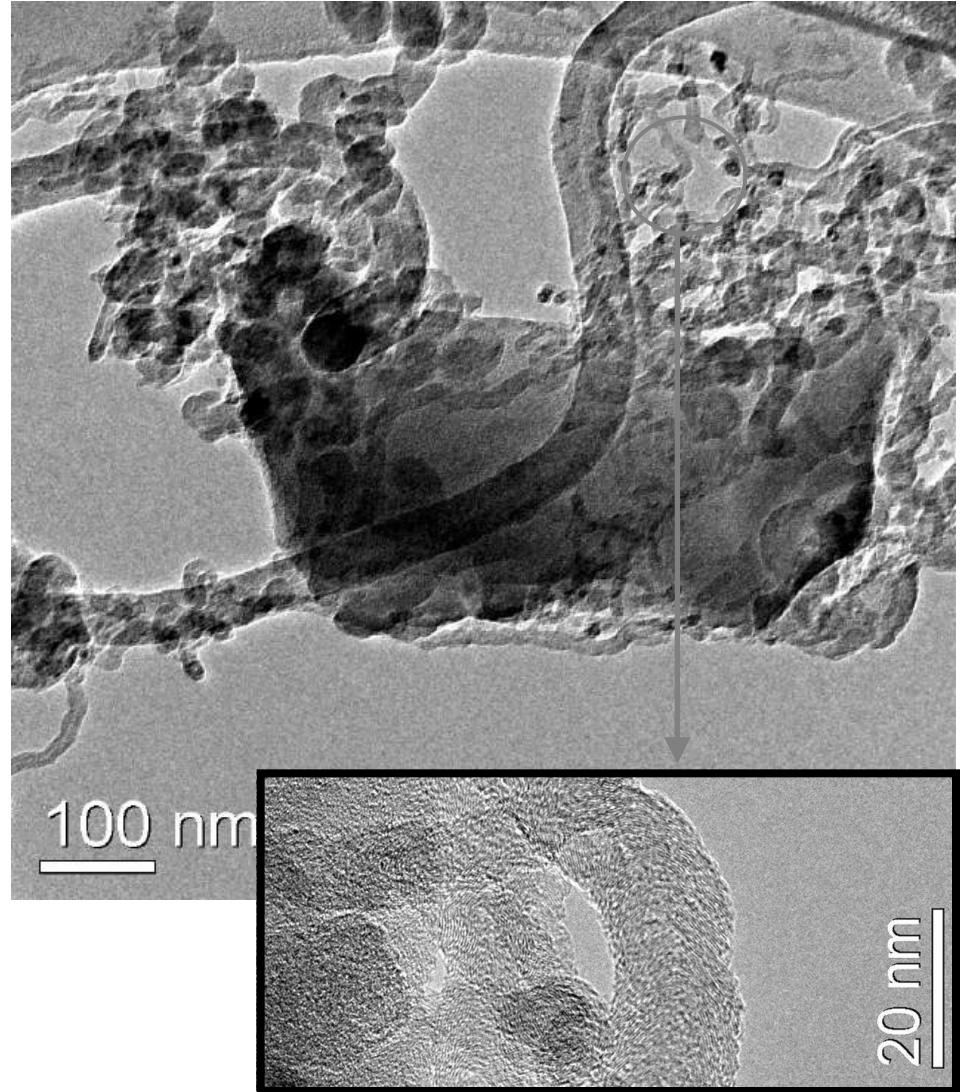
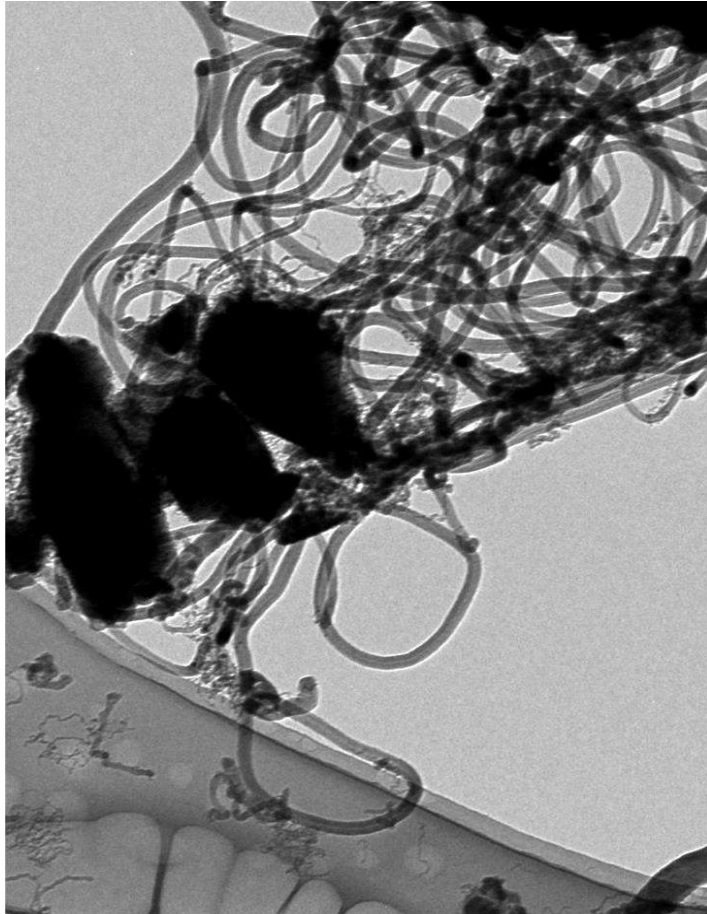
SEM of SiO-CNF



Structural Problem in CH-DCH processes



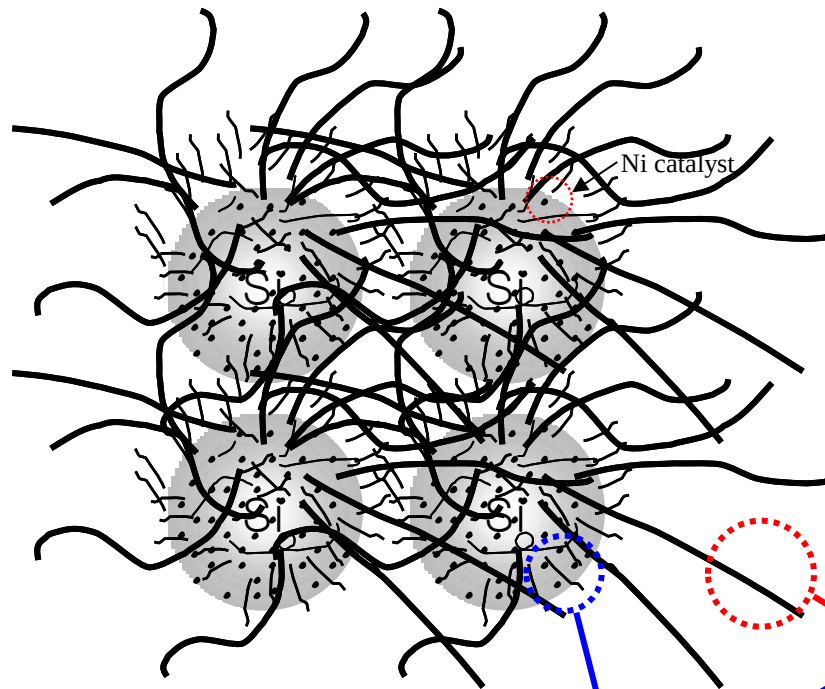
TEM images of Si-CNF composites



Schematic Model of CNF synthesized Si

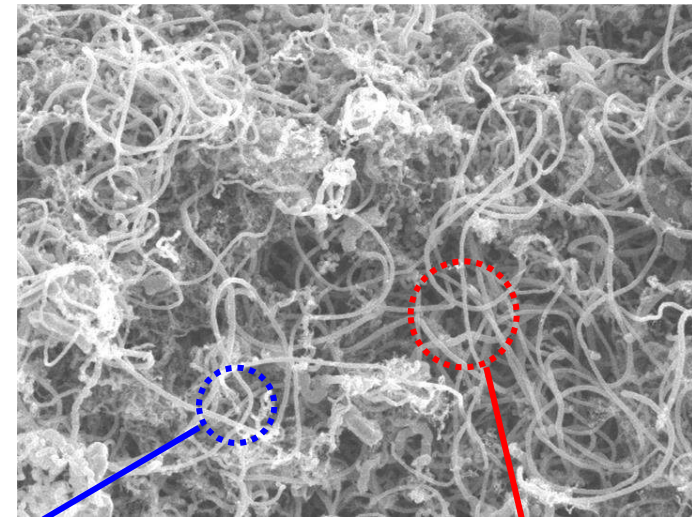


Conjectured mechanism of composed CNF to improve electrochemical properties



1. Thin CNFs

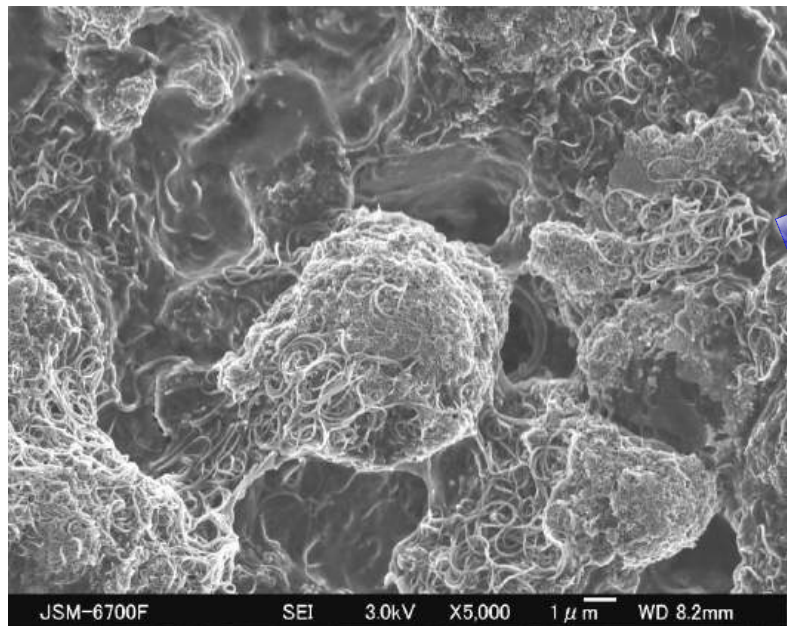
Thickness : 10~50nm
Seems Like Ivy
Afford the **electric conductive path**
of Si powder.



2. Thick CNFs

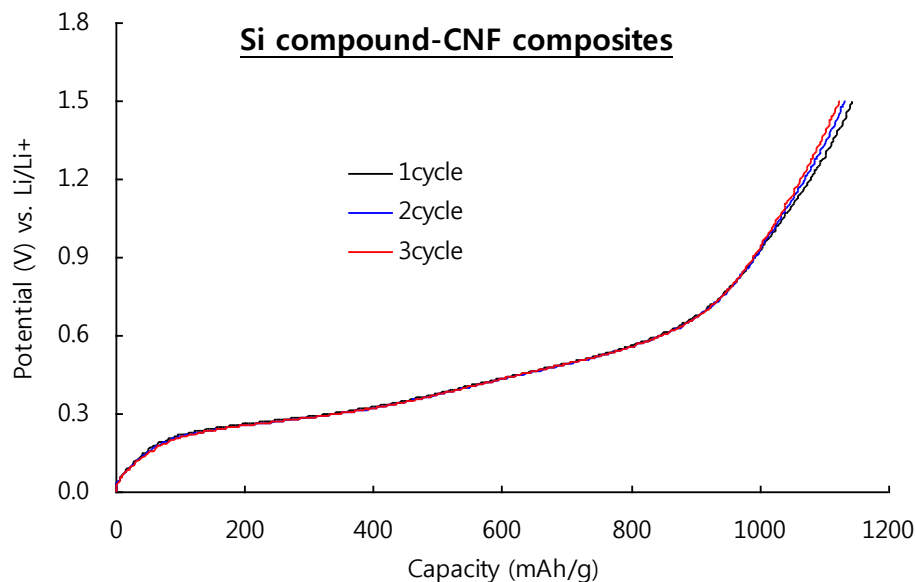
Thickness : 100~300nm
Channeling effect between the particles
⇒ **Compose conductive network**

Schematic Model of CNF synthesized Si



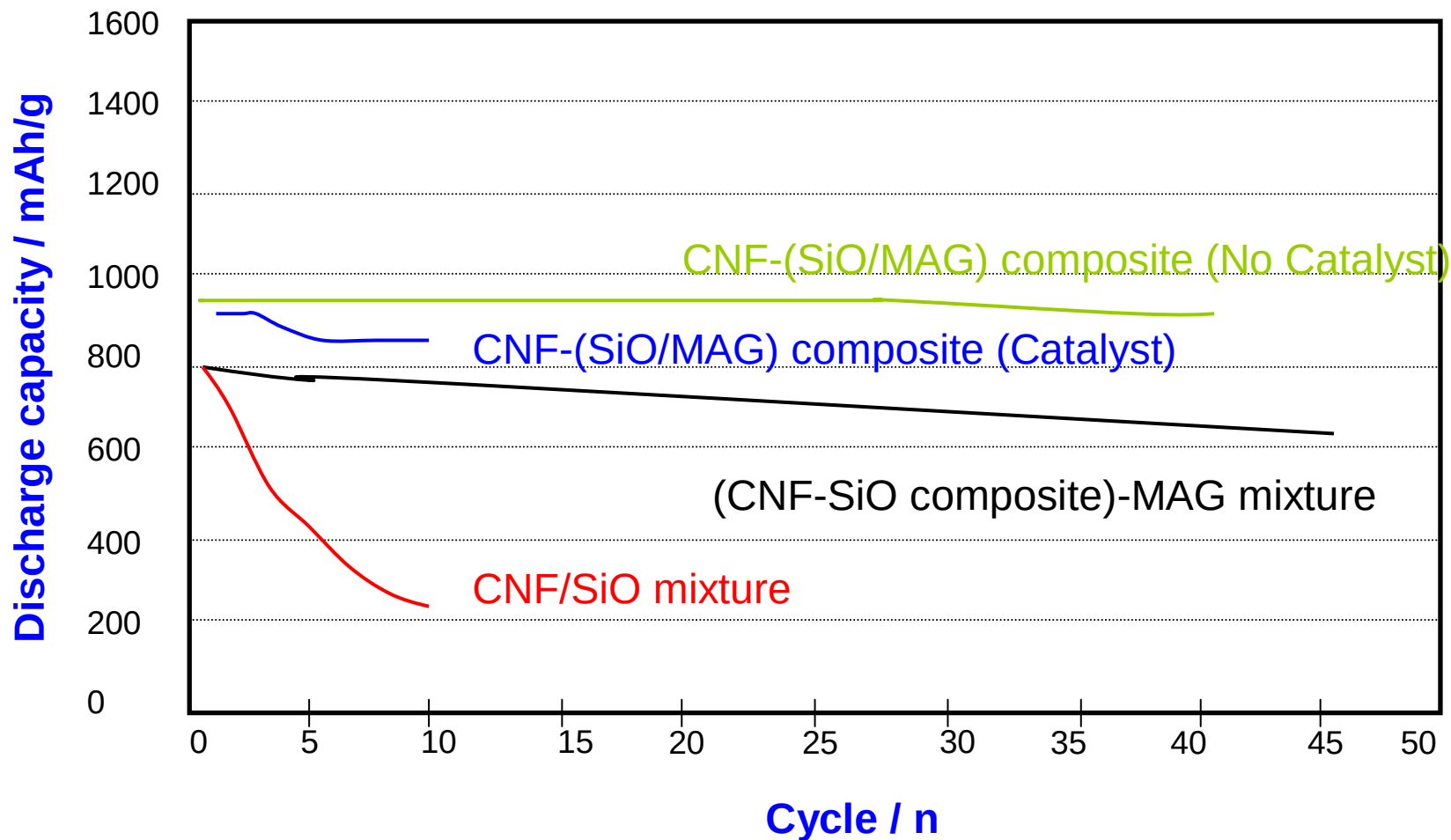
3. Steric effect

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



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

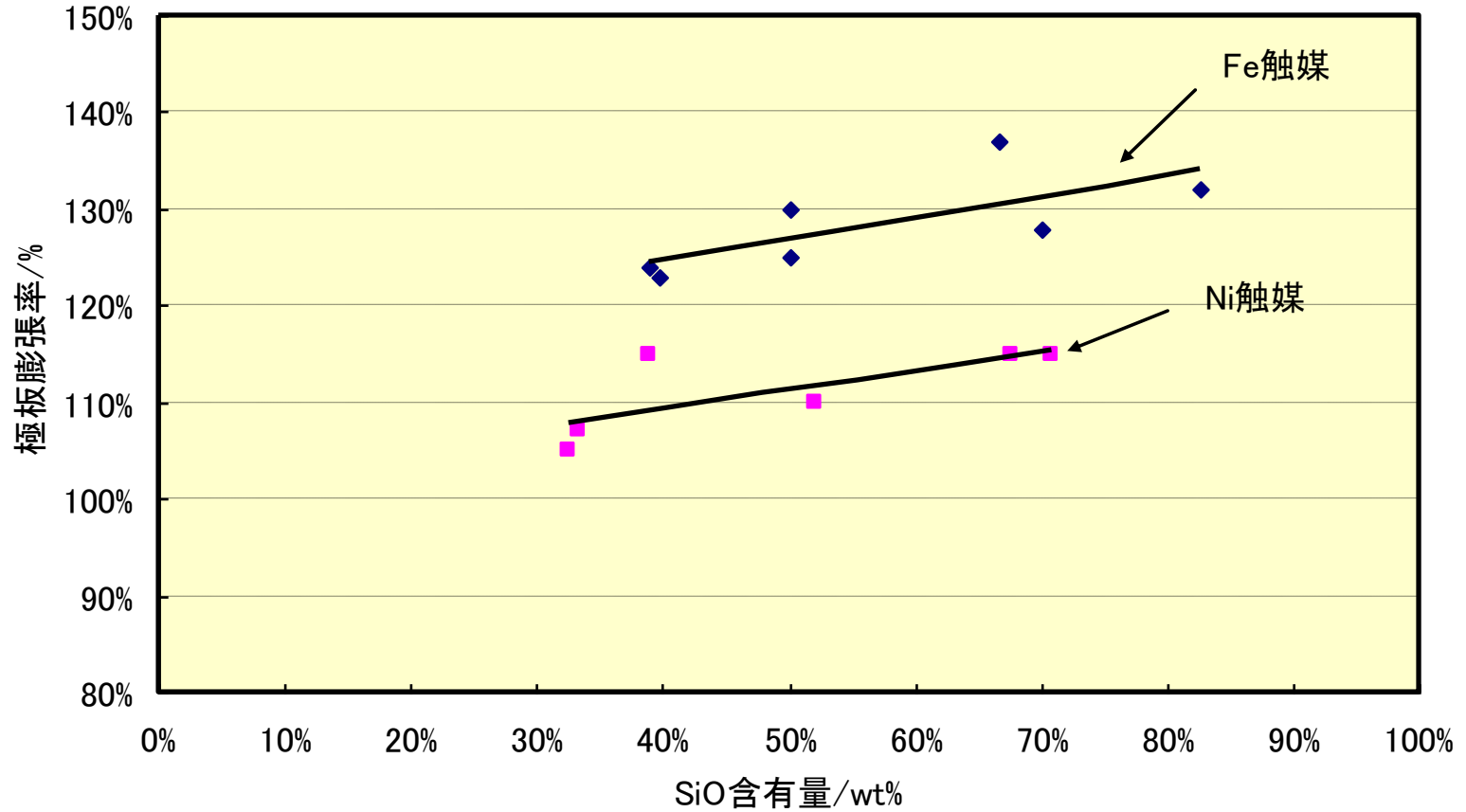
Cycle ability



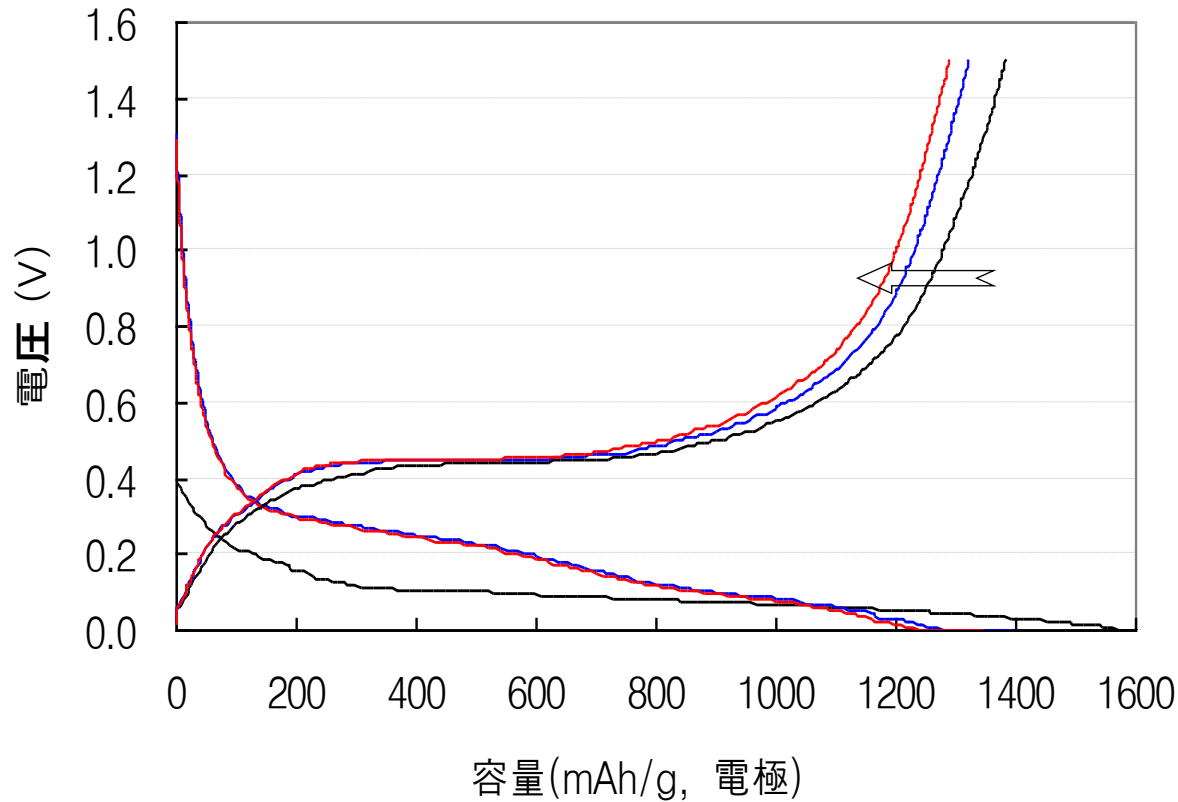
Expansion Ratios



SiOの含有量と極板膨張の関係



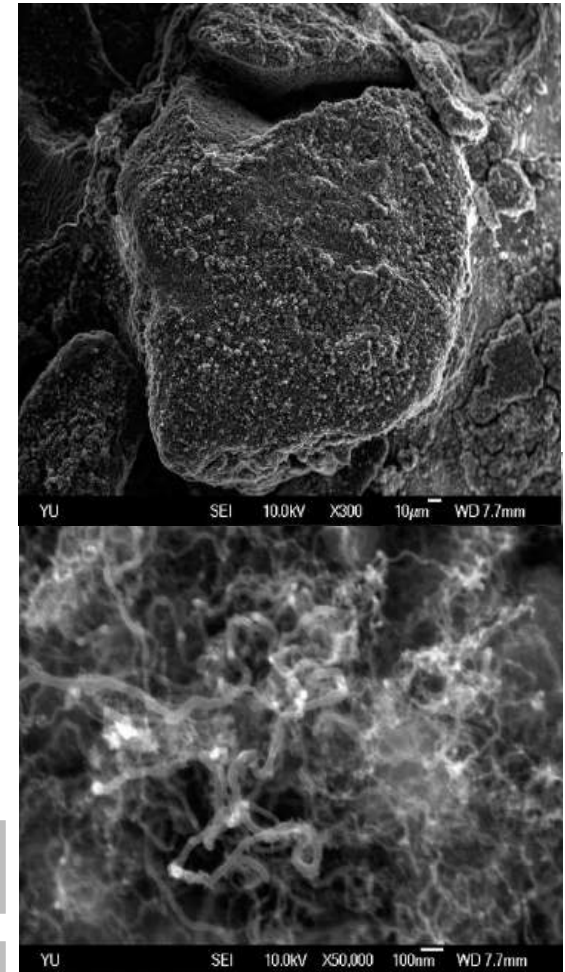
Si-CNF



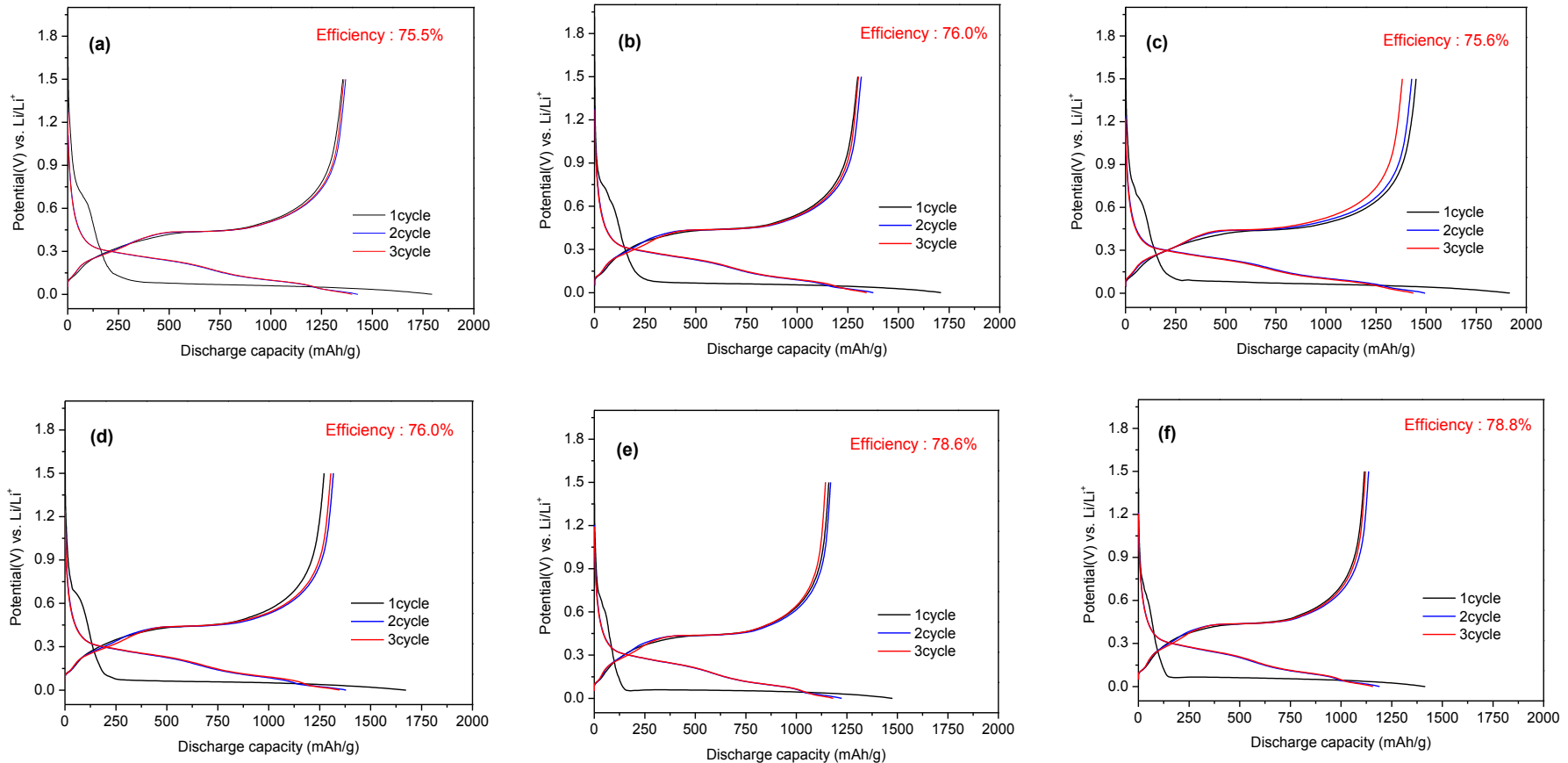
サイクル特性はまだ完全ではない。

改善

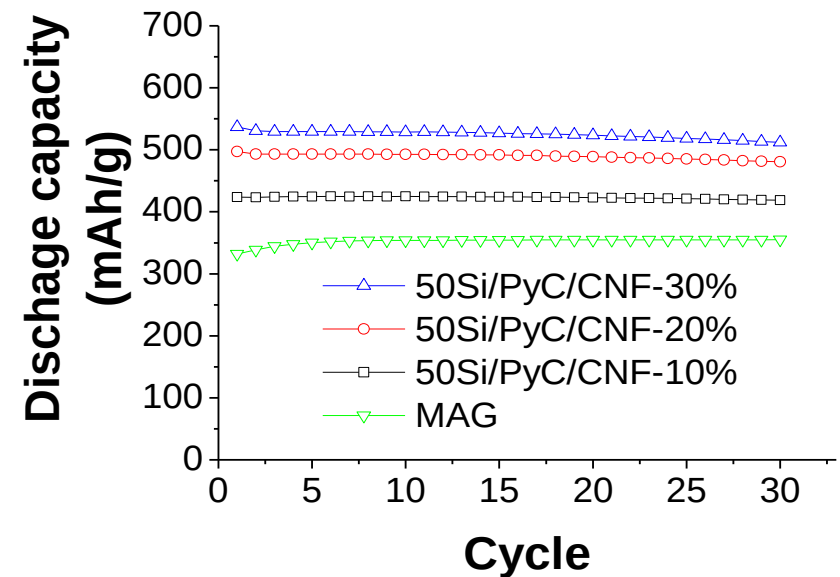
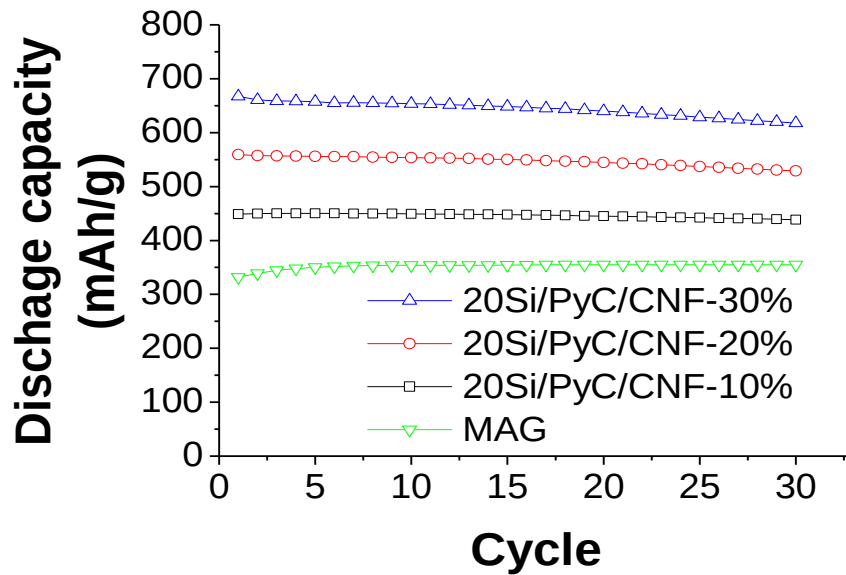
Siの適切なAmorphous化が必須
表面密着性の改善が必要



0.4 μm Siの P/C形成 段階別 3cycleまでの特性評価



(a, c, e) : 0.4 μm Si(As received), (b, d, f) : P/C形成された 0.4 μm Si
a, b : Si-CNF 複合体, c, d : 触媒除去, e, f : P/C 再形成





CNF for Capacitor

Edge effect

Polarization

Pseudo Capacitance

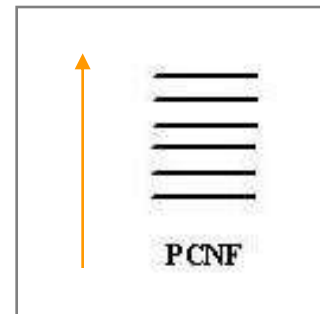
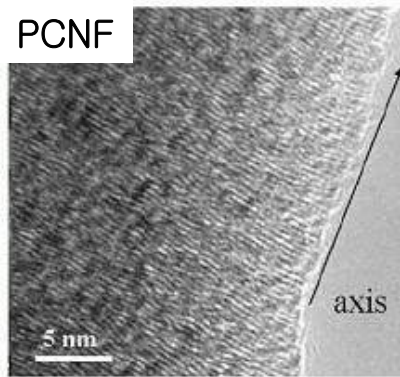
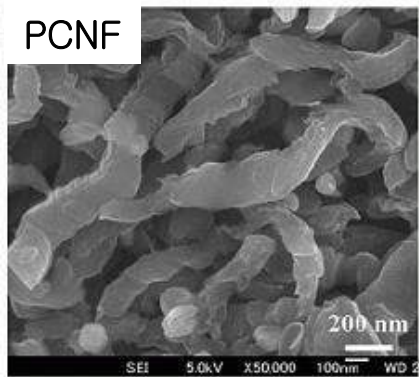


Basal }
Edge } of Hexagonal Planes

Typical Surface of Carbon Nano Fibers

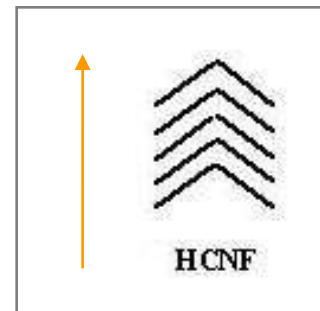
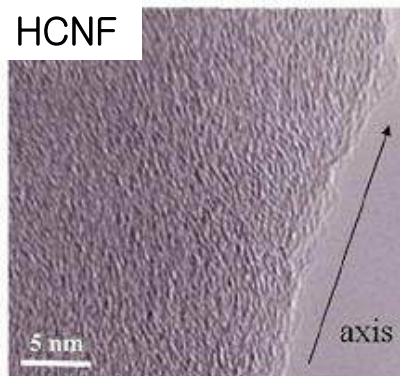
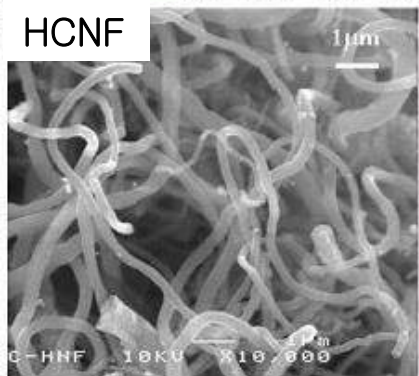
Strong Dependence of Capacitance
over Graphite Surface Structure

Various CNFs



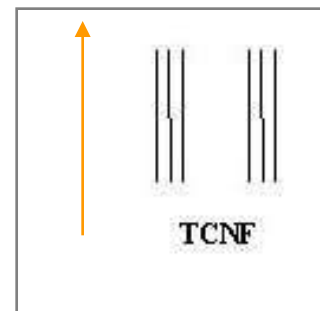
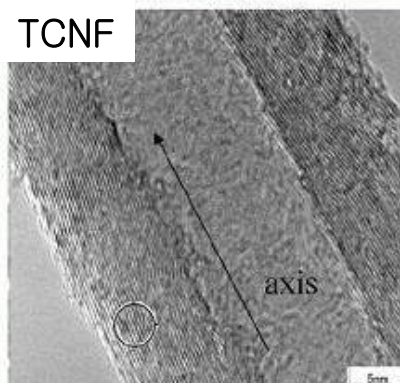
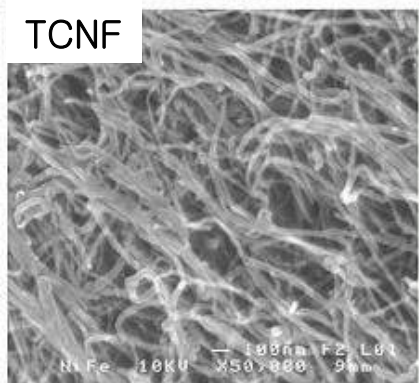
Surface edges

Perpendicularity to the fiber axis



Surface edges

Decline to the fiber axis

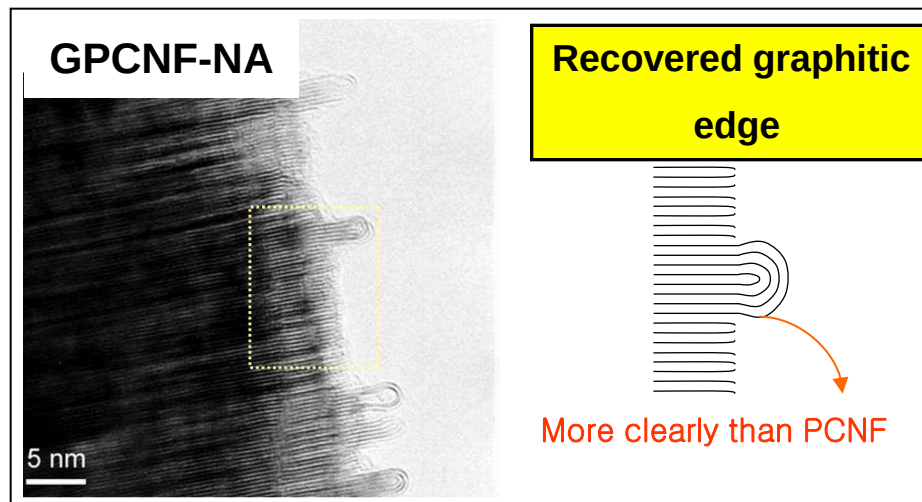
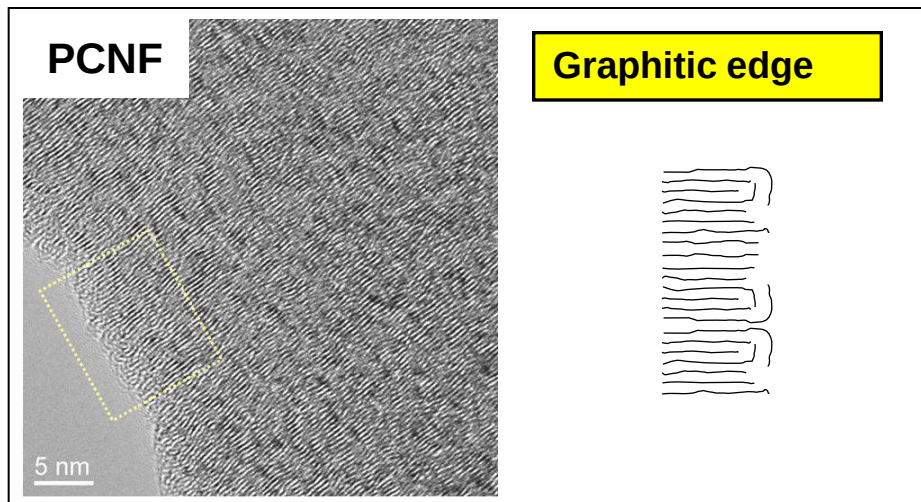


Surface basal planes

Parallel to the fiber axis

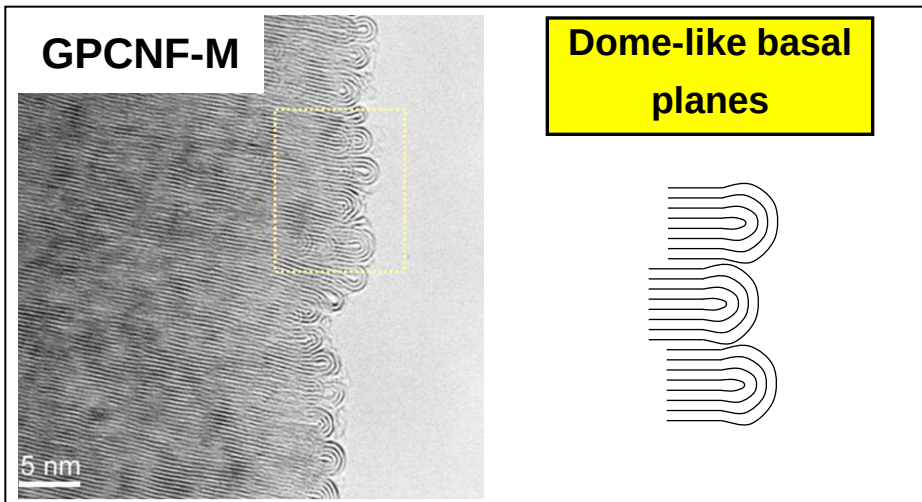
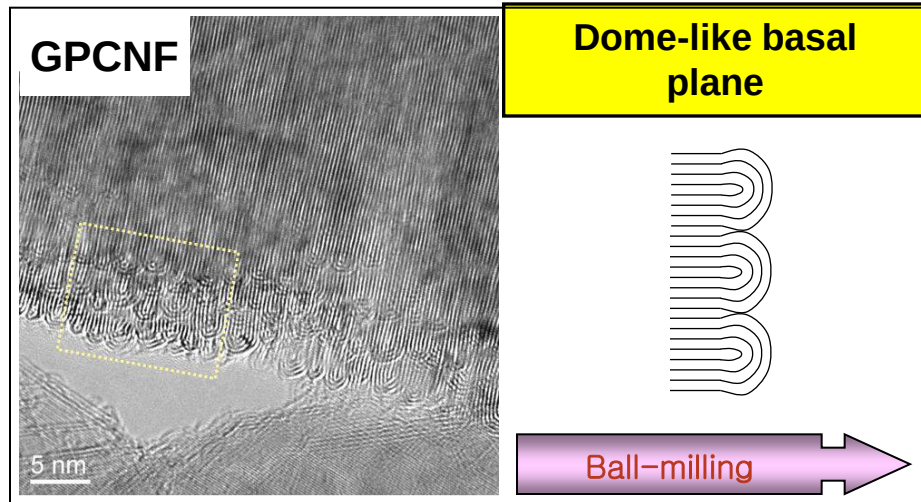


Surface-modified PCNFs



Graphitization at 2800 °C

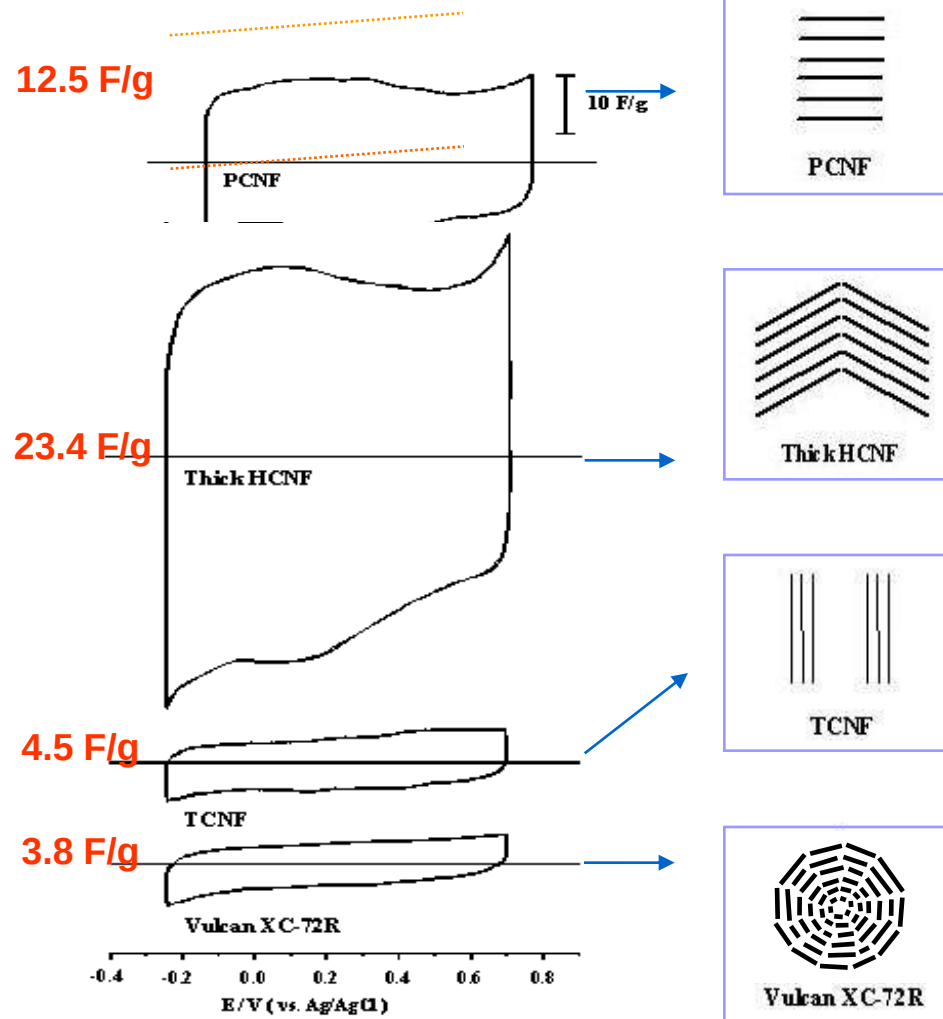
10 wt% HNO₃





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

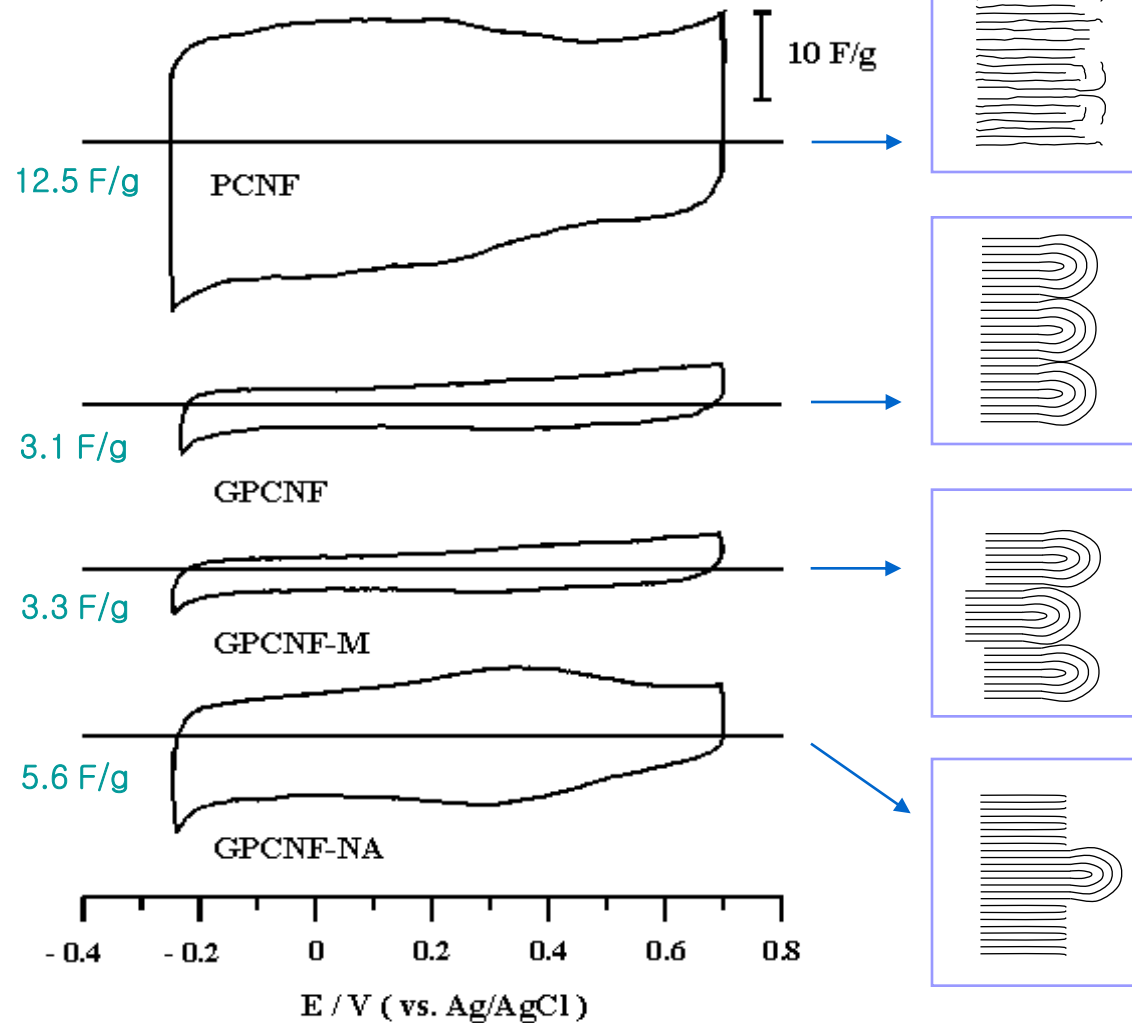
→ Reversible redox peak at about 0.1 V

→ Pseudocapacitance by effect of edge surface



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 plane (GPCNF, GPCNF-M)

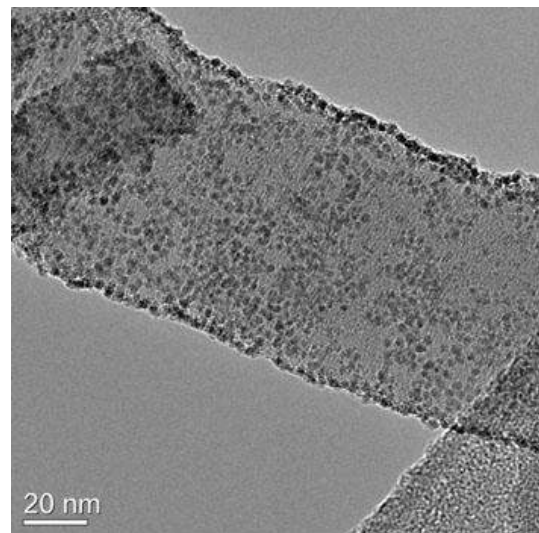
→ Capacitive charging current

Graphitic edge surface (GPCNF-NA)

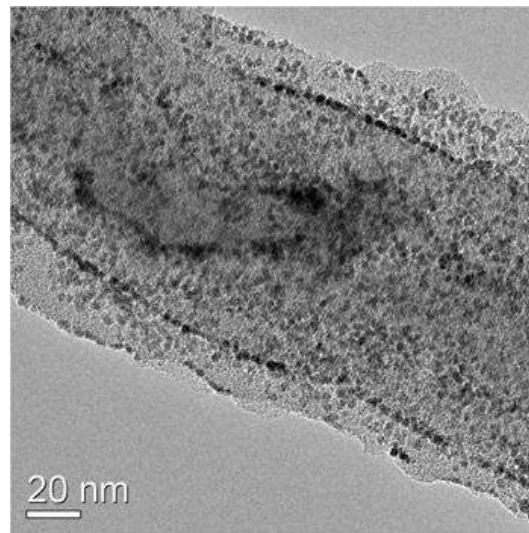
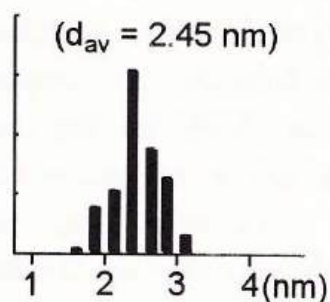
→ Reversible redox peak at about 0.3 V

→ Pseudocapacitance by effect of oxygenated surface species

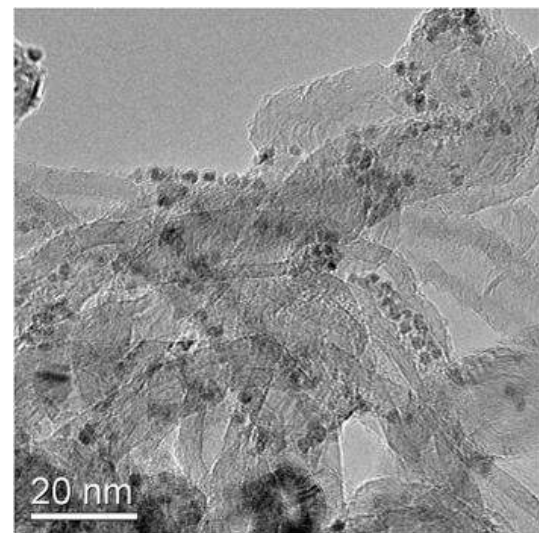
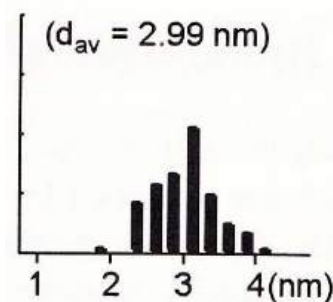
TEM and ICP-MS results of Ru/CNFs



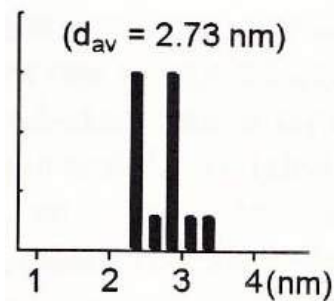
Ru/PCNF



Ru/HCNF



Ru/TCNF



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



- **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:

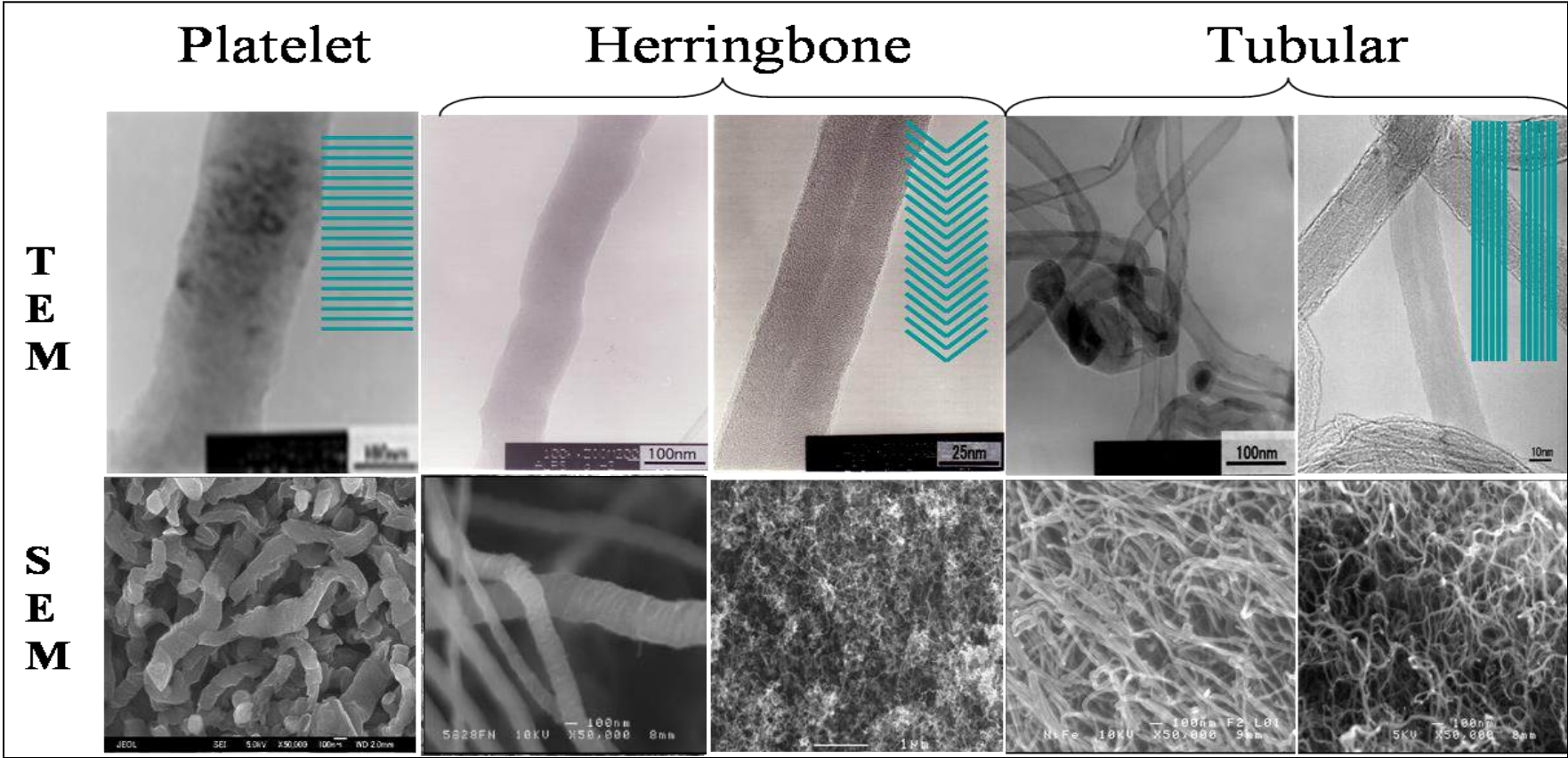
Searching further increasing methods for catalytic activity

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



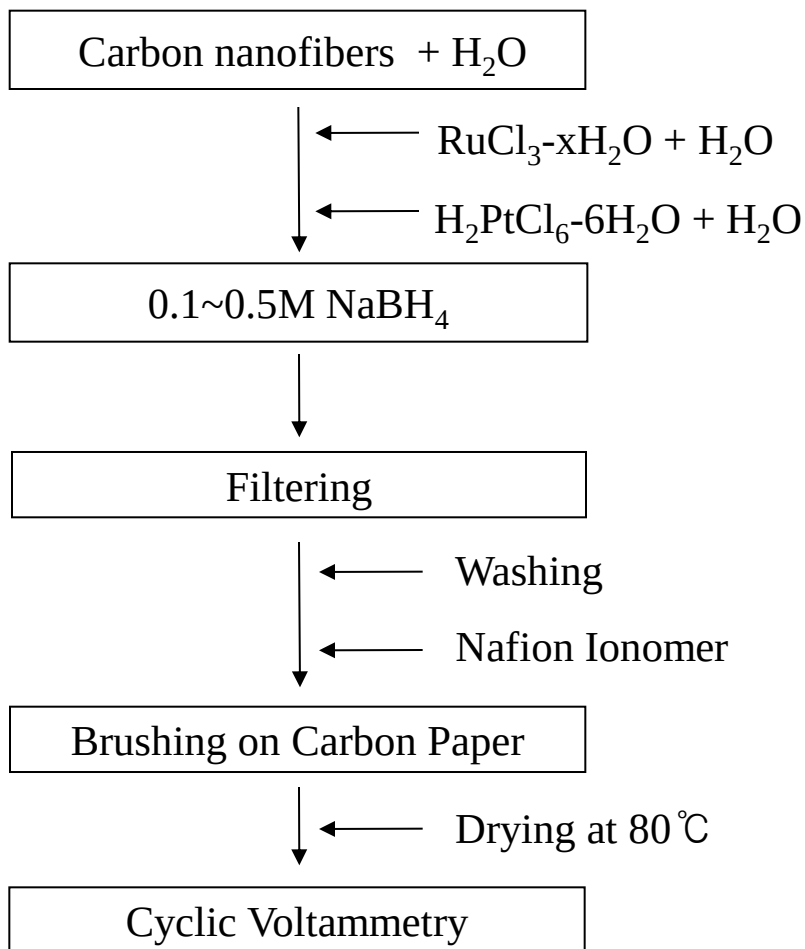
Dia. (nm)	150	150~200	10~70	20~40
Code	P-CNF	Thick H-CNF	Thin H-CNF	T-CNF

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

Preparation of Catalysts



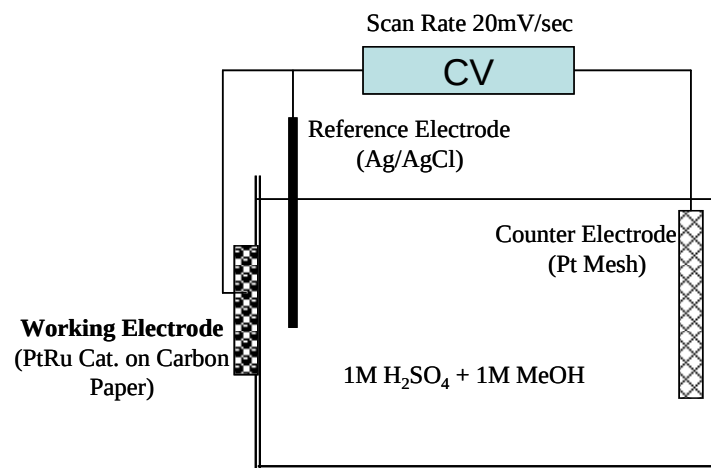
Equipments



Single Cell Test Kit



Half Cell Test

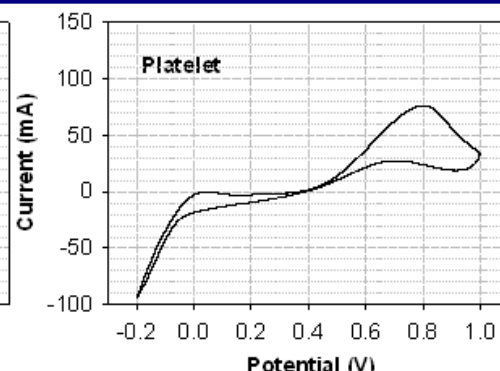
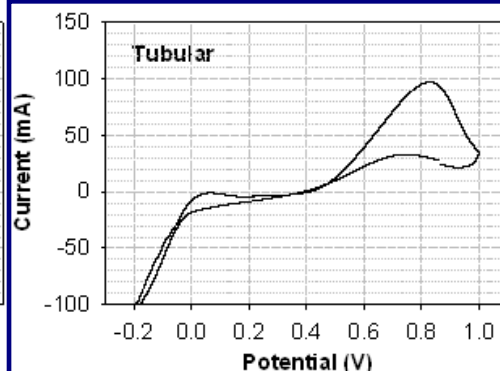
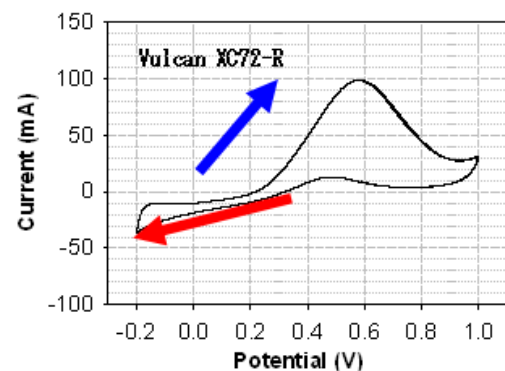


Electrode	Carbon Paper (ϕ1cm)				Gold (ϕ1cm)			
Catalyst Amount (mg)	PtRu 60wt% 5mg Slurry	Pt 2	Ru 1	C 2	PtRu 40wt% 0.3mg Slurry	Pt 0.08	Ru 0.04	C 0.18

Methanol Oxidation Property

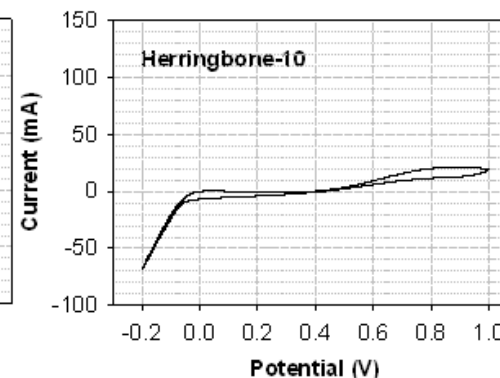
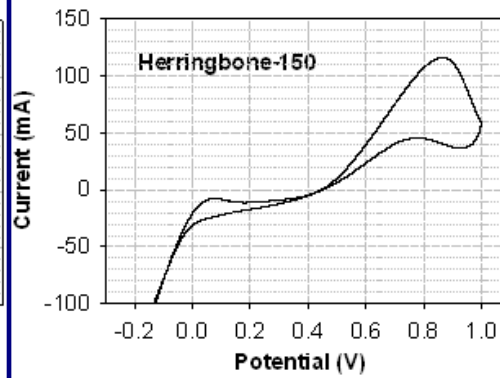
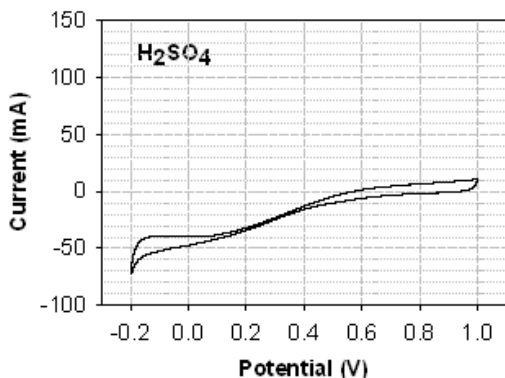


Evaluation by Half Cell Test : 1mol MeOH + 1mol H₂SO₄, 25°C



Tubular, 30nm dia.

Platelet, 200nm dia.



Thick-Herringbone, 250nm dia.

Thin-Herringbone, 10nm dia.



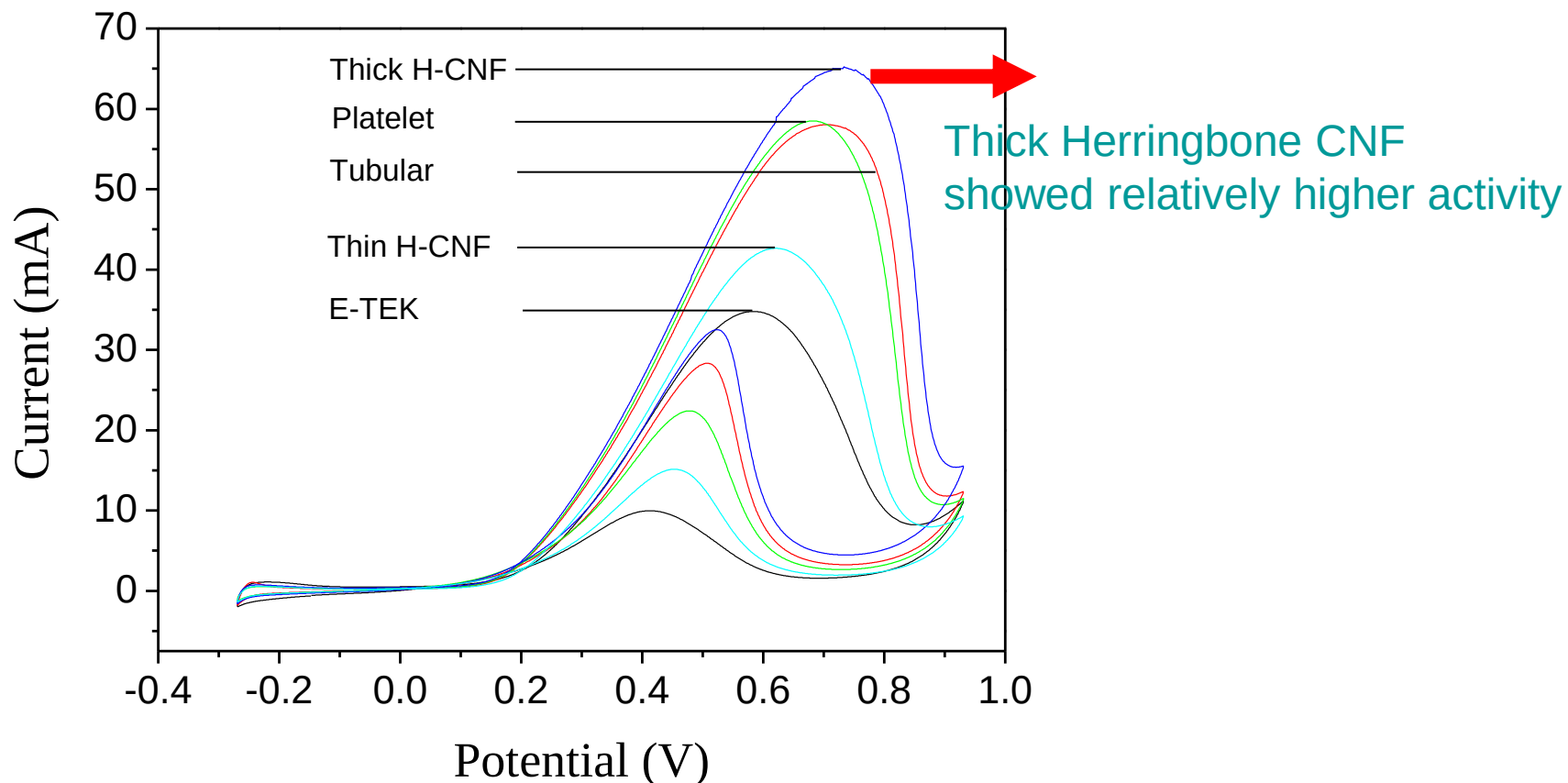
Thick Herringbone CNF showed relatively high activity

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

Methanol Oxidation Property

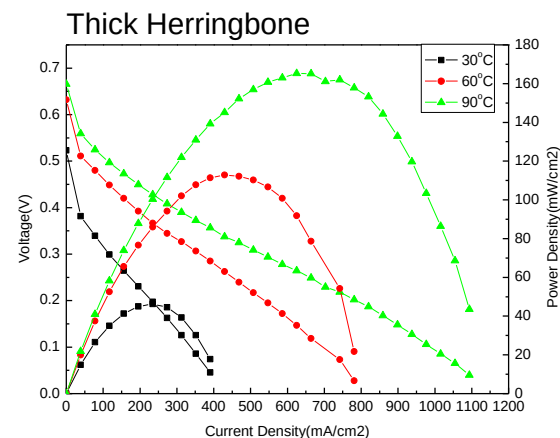
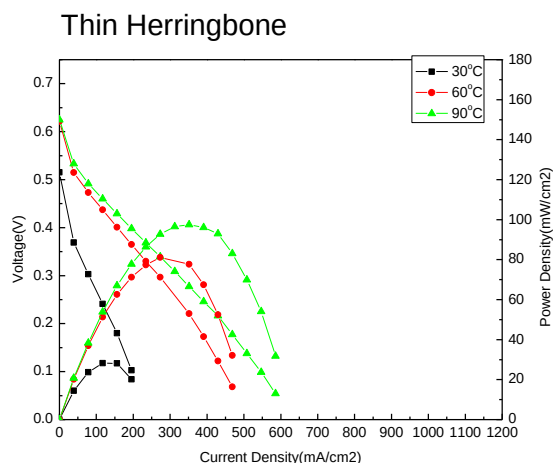
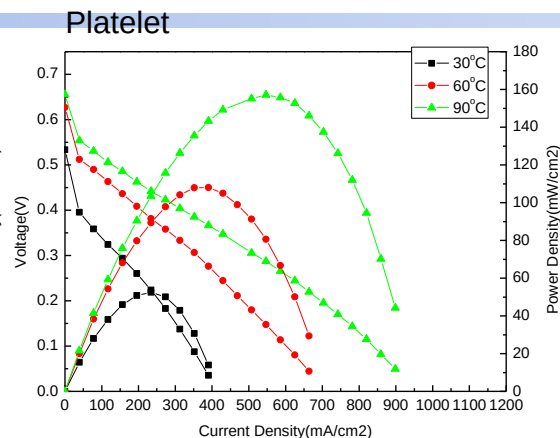
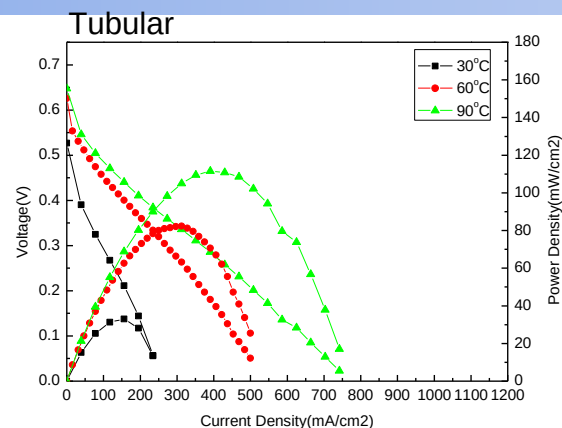


Evaluation by Half Cell Test : 1mol MeOH + 1mol H₂SO₄, 25°C



Noble Metal Content	Slurry Amount (mg/cm ²)	Pt	Ru	C
		(mg/cm ²)		
PtRu 40wt%	0.3	0.08	0.04	0.18

Single Cell Test of Various CNFs



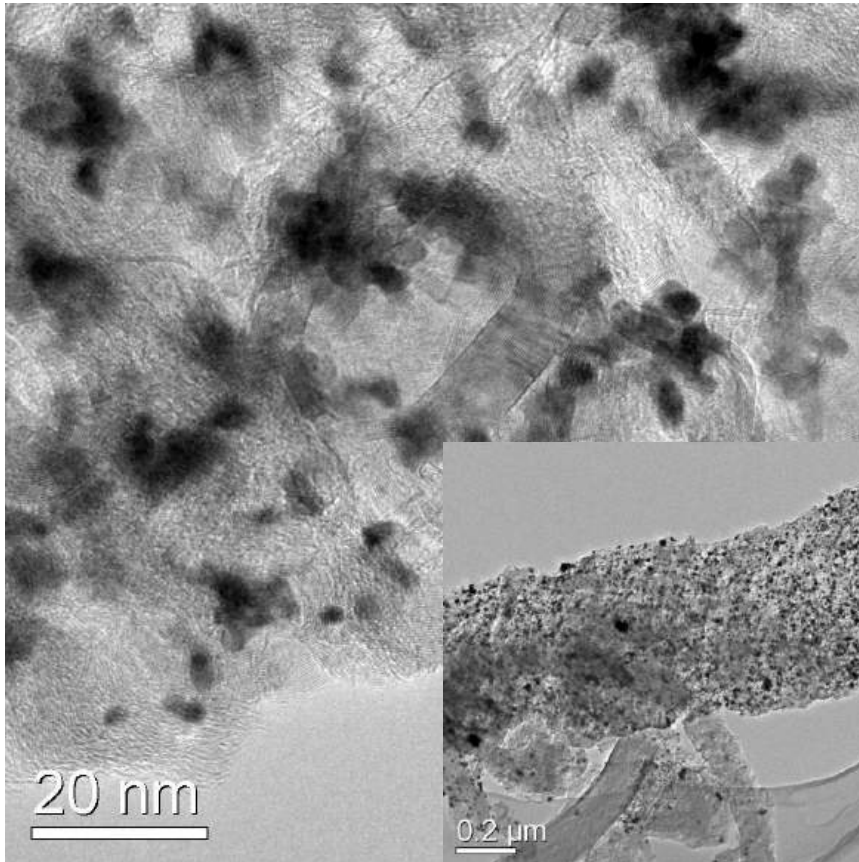
Noble Metal Content	Slurry Amount (mg/cm ²)	Pt	Ru	C
		(mg/cm ²)		
PtRu 40wt%	7.5	2	1	4.5

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

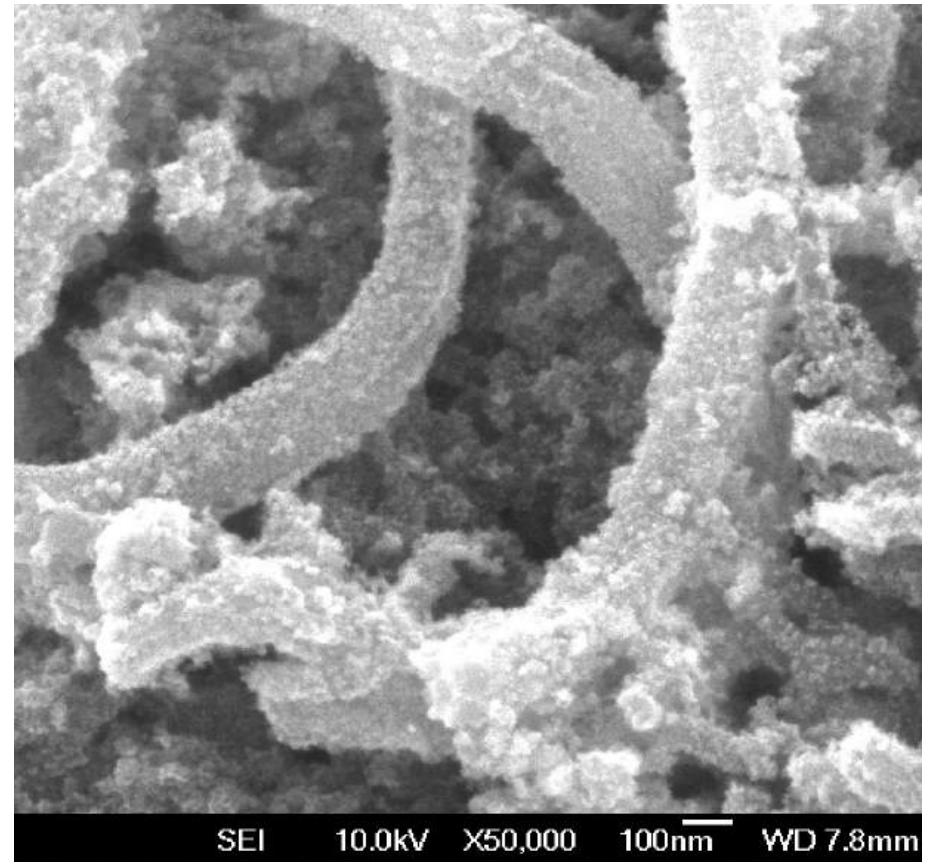


PtRu Catalyst on Mesoporous CNF

TEM



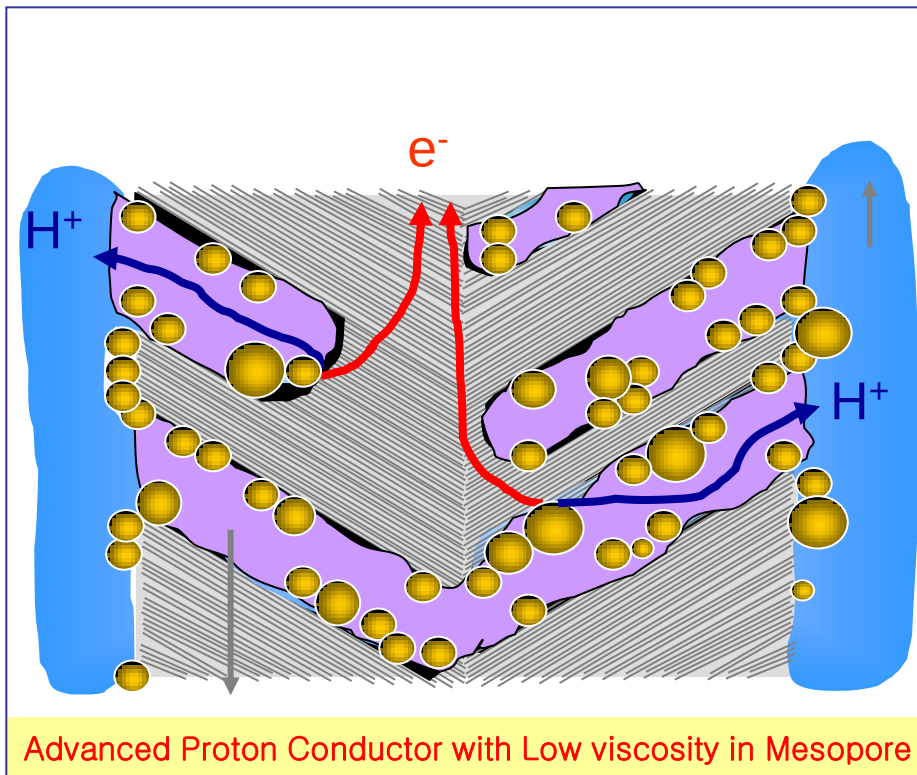
SEM



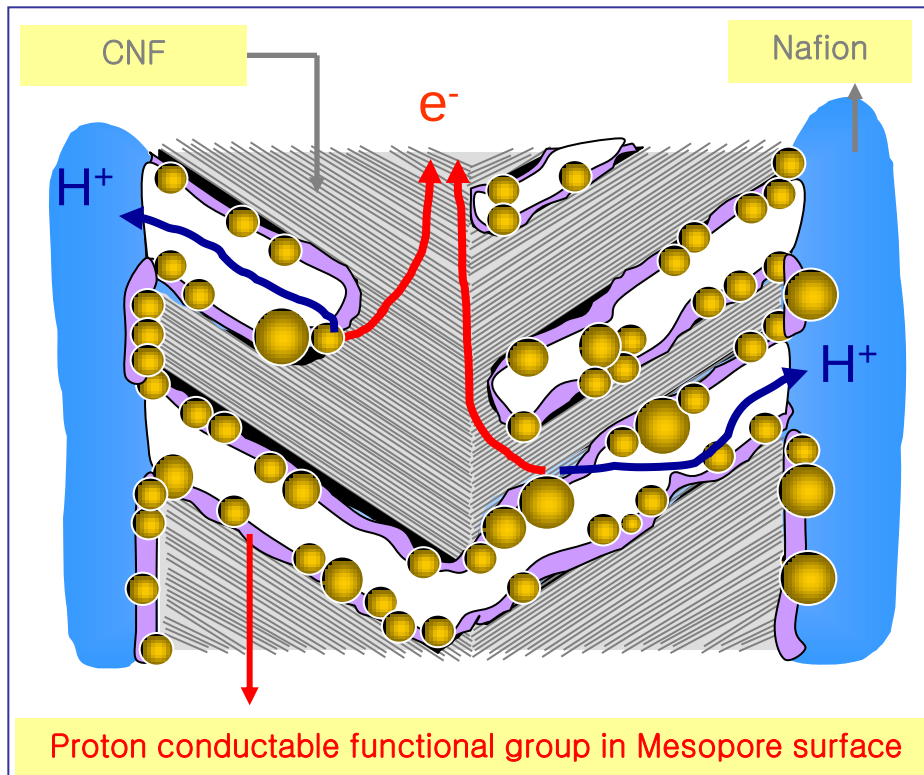
貴金属含有量	Slurry量 (mg/cm ²)	Pt	Ru	C
		(mg/cm ²)		
PtRu 40wt%	5	1.33	0.67	3

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



Advanced Proton Conductor with Low viscosity in Mesopore



Proton conductable functional group in Mesopore surface

- PtRu Particles
- CNF
- Proton Conductable binder and/or surface functional group in Mesopore
- Nafion

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

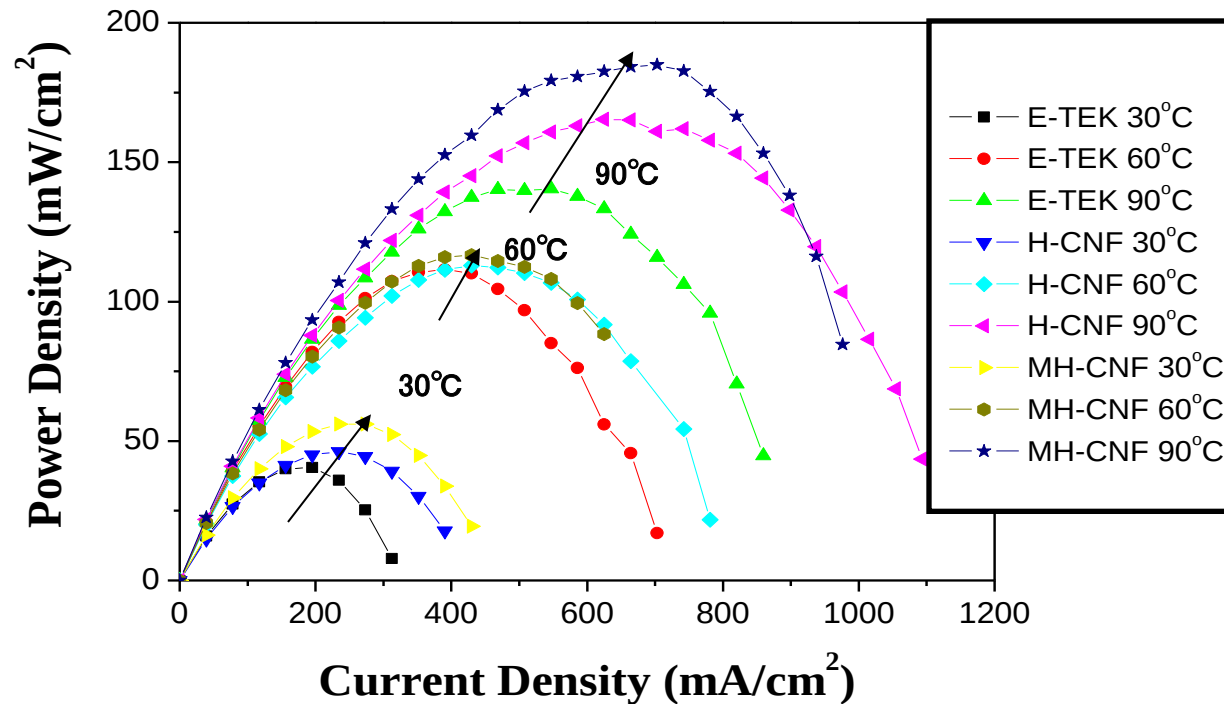


Single Cell Performance

60wt% Pt-Ru/C E-TEK

40wt% Pt-Ru/C Herringbone-CNF

40wt% Pt-Ru/C Mesoporous H-CNF



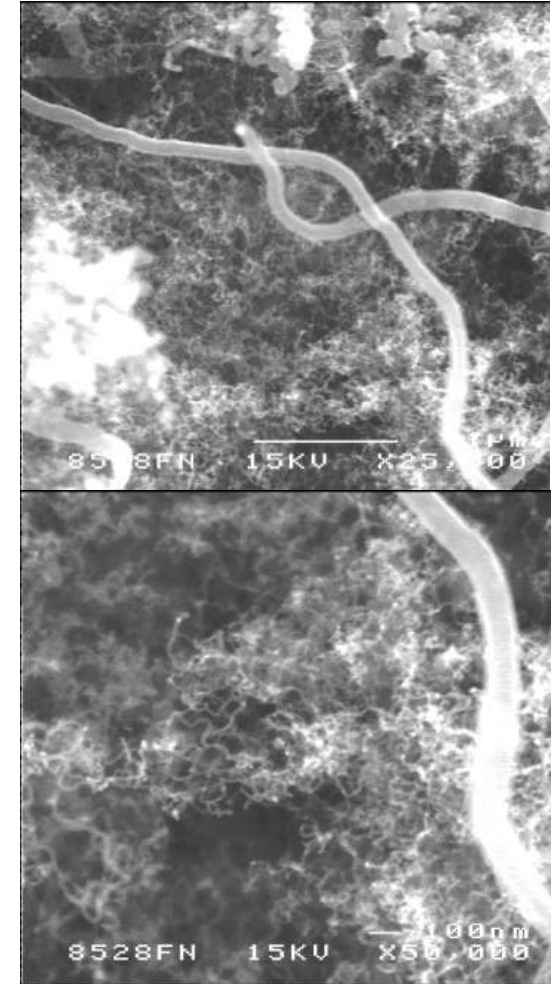
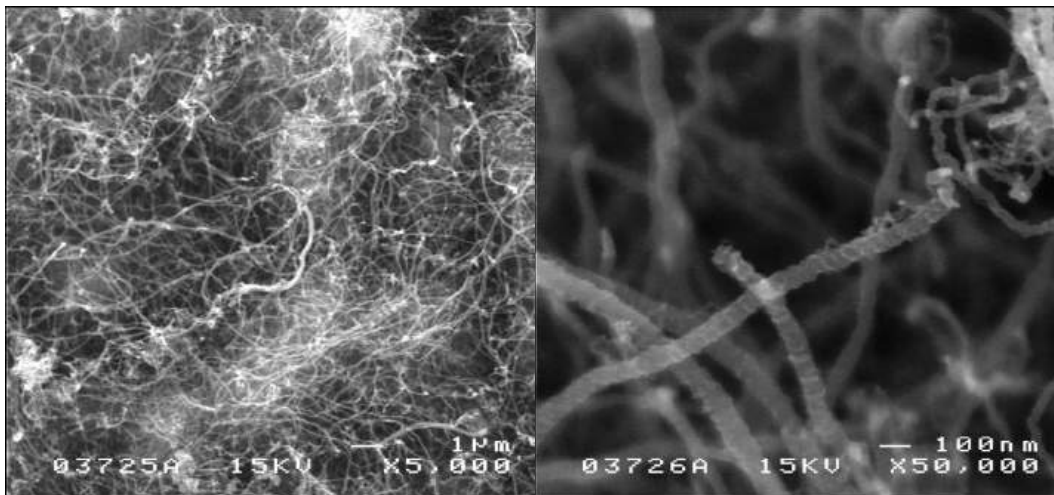
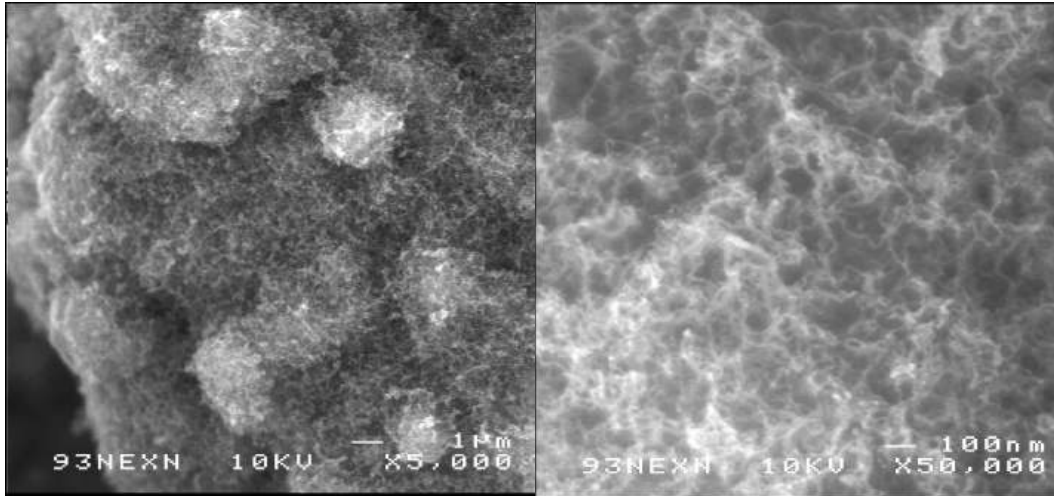
Catalyst	Noble Metal Content (wt%)	Maximum Power Density (mW/cm^2)		
		30°C	60°C	90°C
E-TEK	60	41	102	140
H-CNF	40	46	113	165
Mesoporous H-CNF	40	56	117	185

Discrepancy of half cell and full cell performances



Preparation of Thin H-CNF

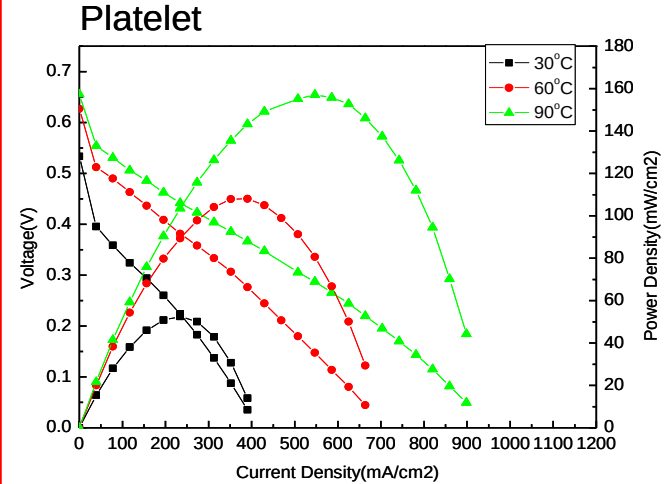
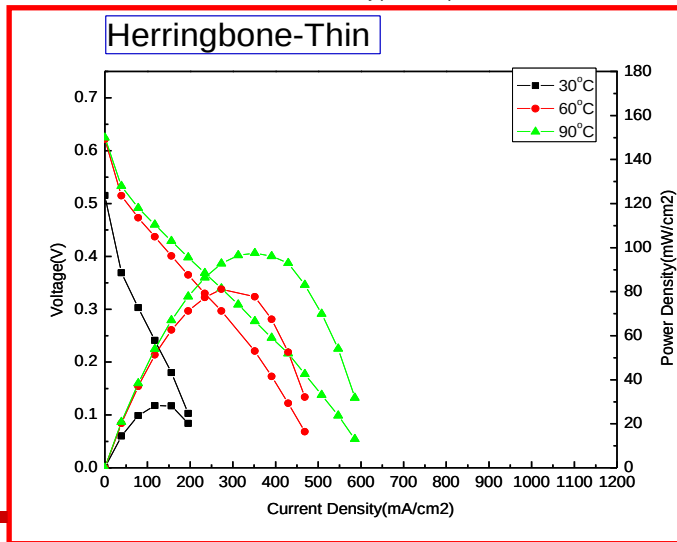
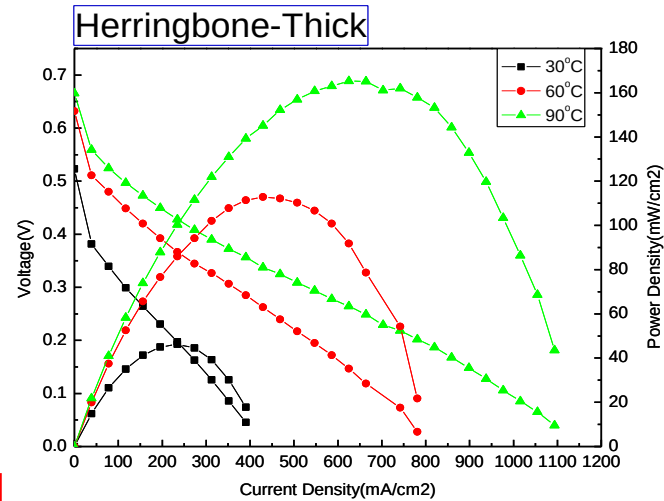
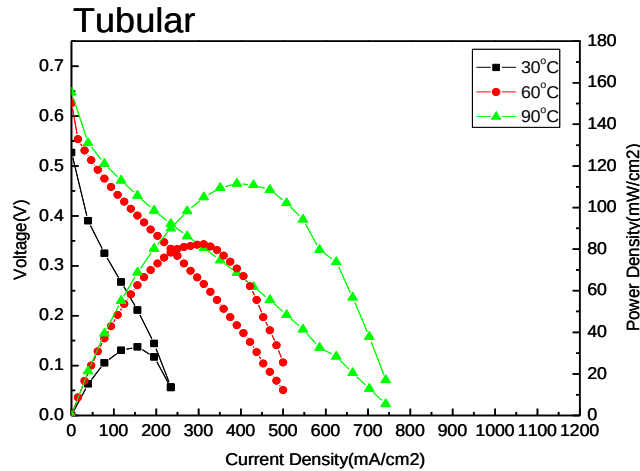
Under 30 nm Diameter of H-CNF, Difficulty of Dispersion
FeNi Catalyst, Thin H-CNF





Thin H-CNF as Support Material

Various Structures of CNFs, Single Cell Performances



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

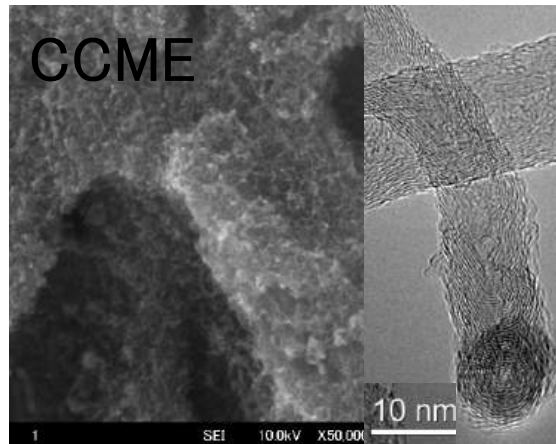
Catalyst	Noble Metal Content	Slurry Amount (mg/cm ²)	Pt	Ru	C
			(mg/cm ²)		
CNF	PtRu 40wt%	5.0	2	1	4.5

Preparation of Various Diameters of H-CNF

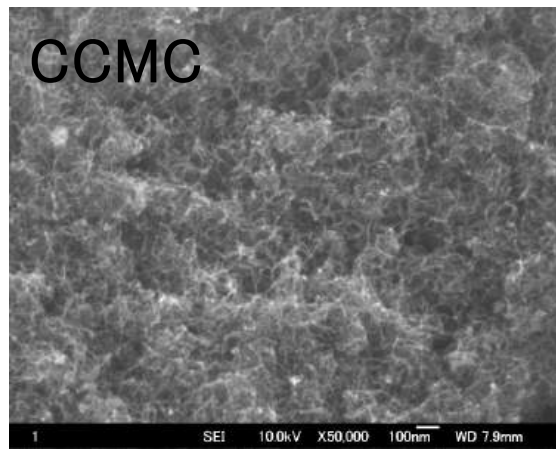


Difficulty of Dispersion in Thin H-CNF、Good Dispersion of Medium and Thick H-CNF
Optimization of Catalyst Preparation

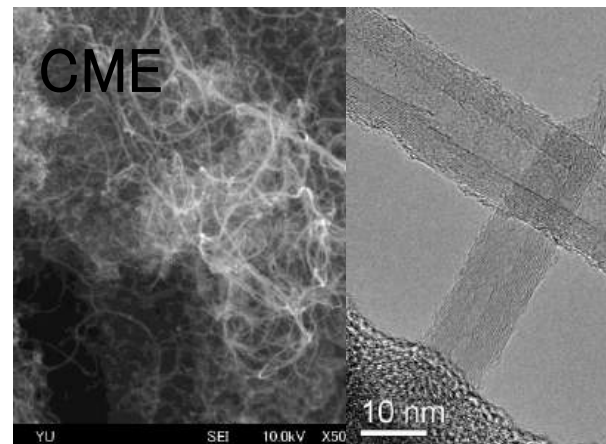
(Thin H-CNF、 ϕ 5~30nm)



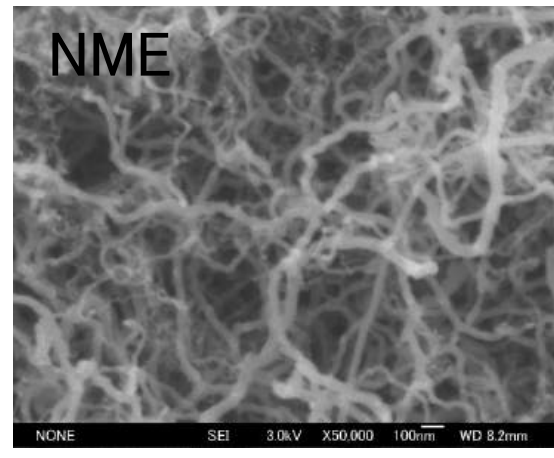
CCMC



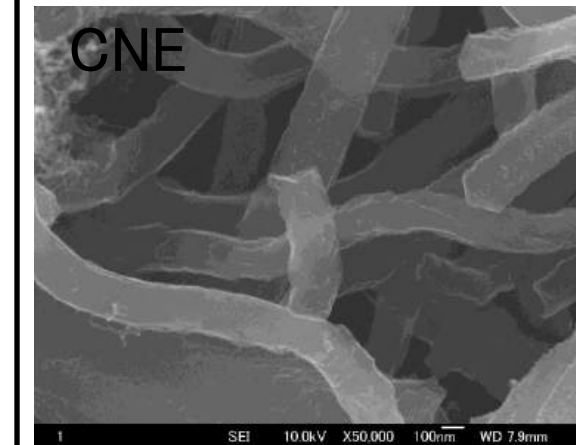
(Medium H-CNF、 ϕ 30~70nm)



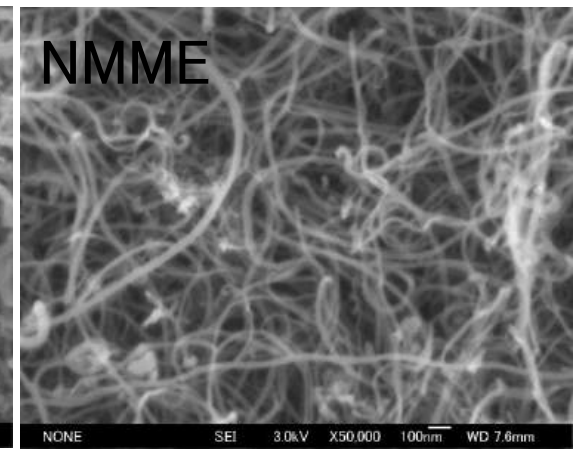
NME



(Thick H-CNF、 ϕ 70~300nm)



NMME



Difficult Dispersion

Good Dispersion

Catalytic Activity of Highly dispersed Thin H-CNF

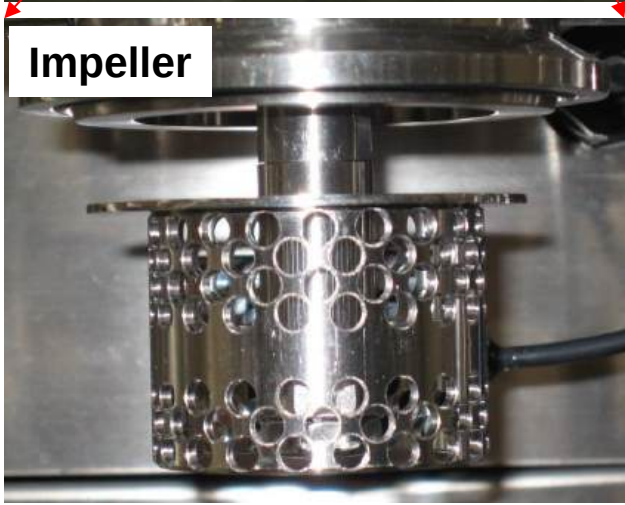


Nano-dispersed Equipment、16500rpm、1min、30 times

- Ⓐ 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°C Preparation



Nano-dispersion Equipment



Impeller

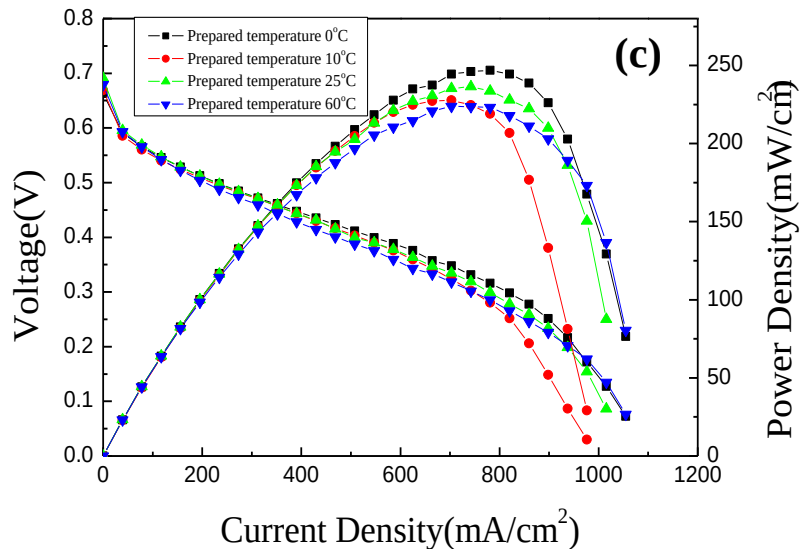
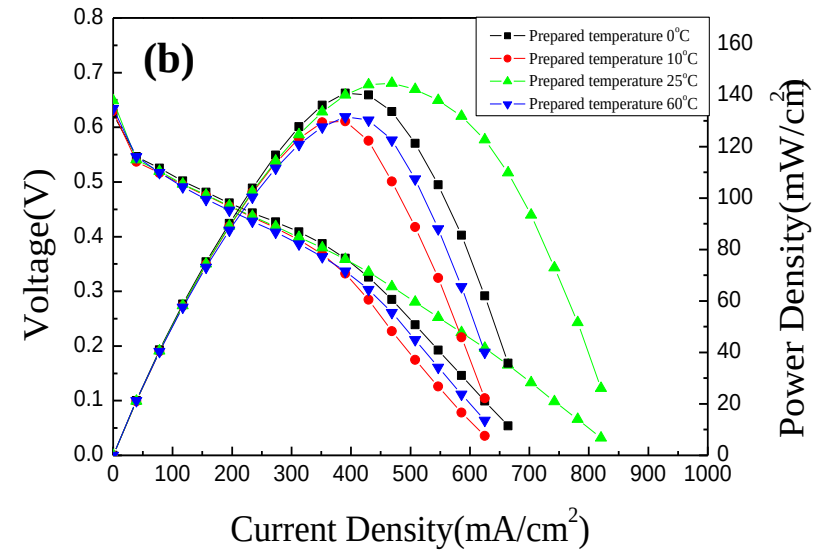
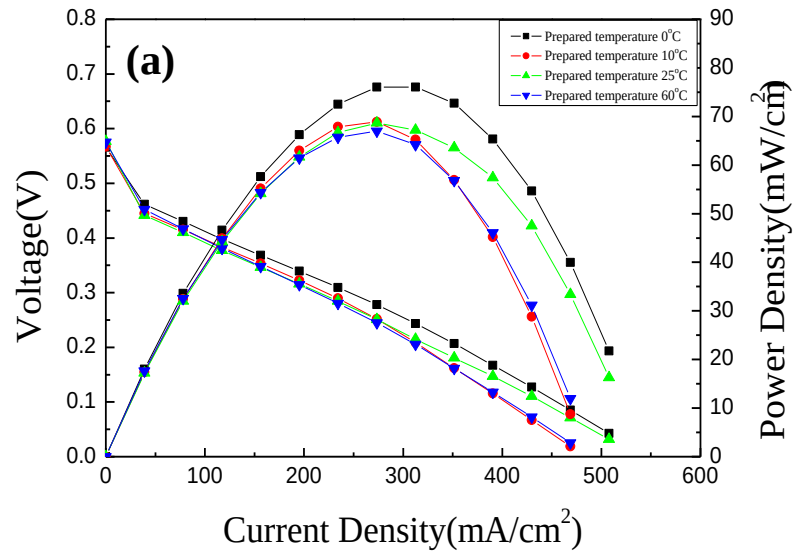
	Single Cell Max. Power density (mW/cm ²)		
	30°C	60 °C	90 °C
Not treated	28	81	97
NM55	52	108	182
NMM415	34	95	168
FMM415	40	92	158
NFM415	56	118	184
CM55	49	108	176
Johnson M. 60wt%, Pt 2mg/cm ²	55	121	162

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

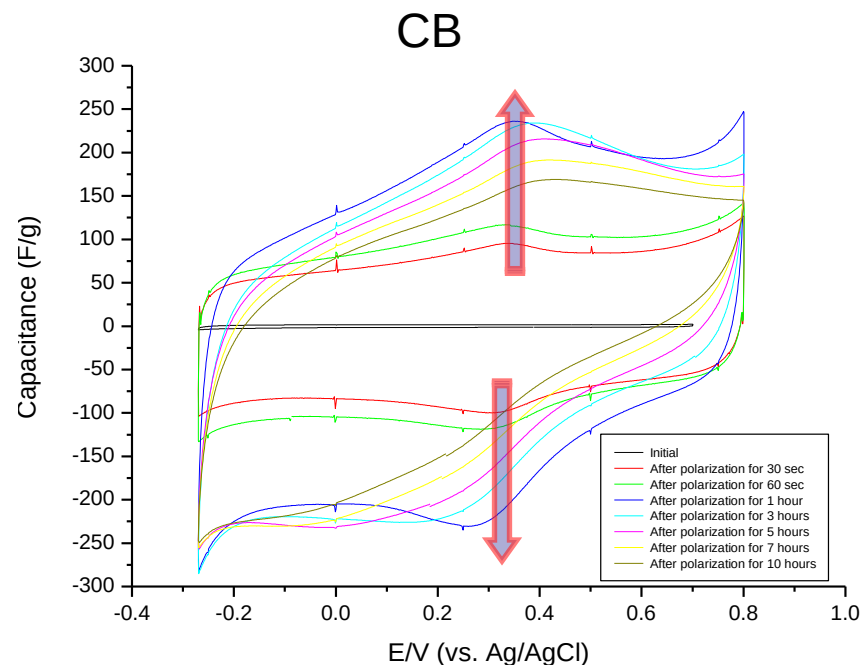
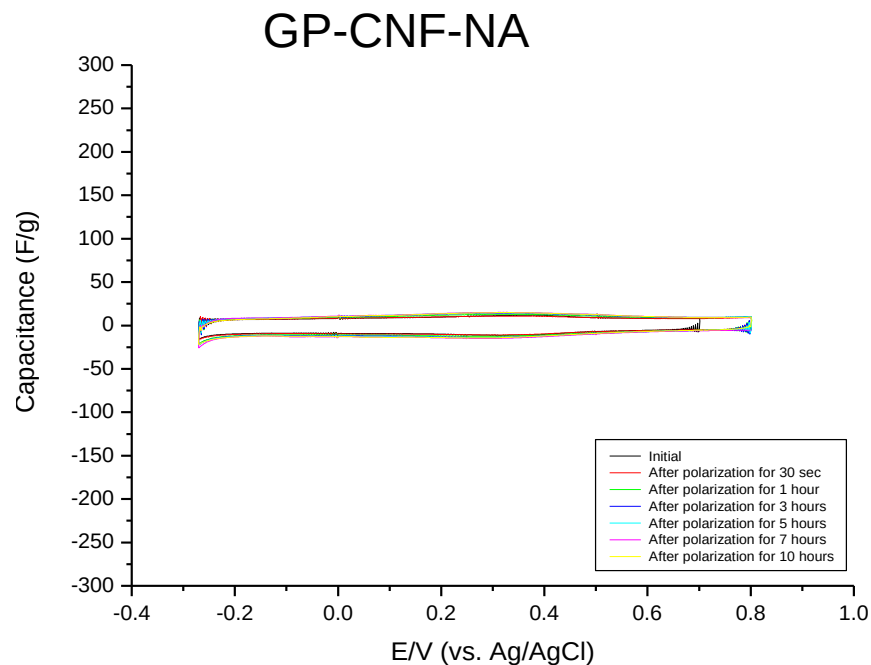
based on the unit electrode area



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/cm ²)		
	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

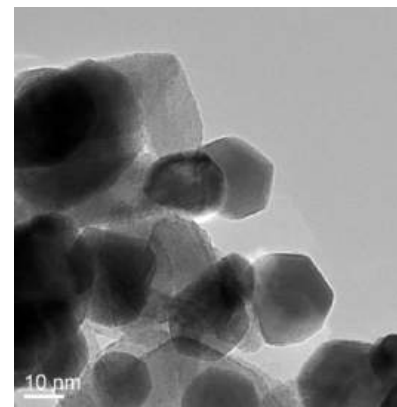
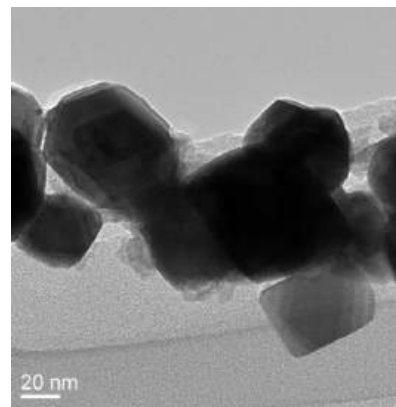
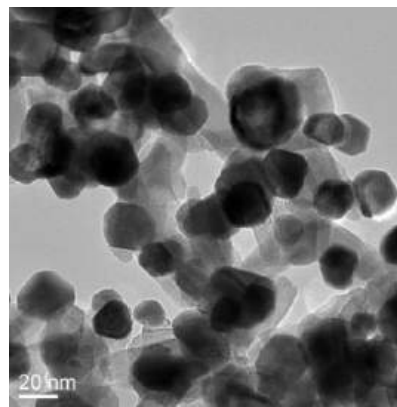
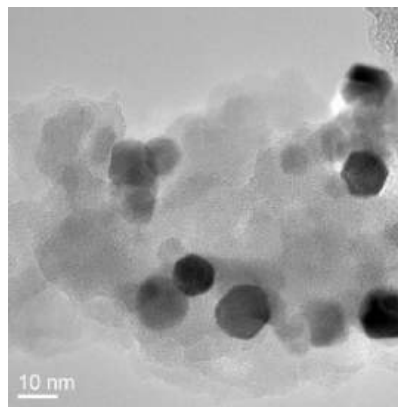
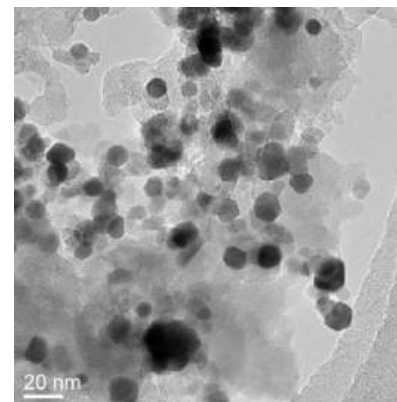
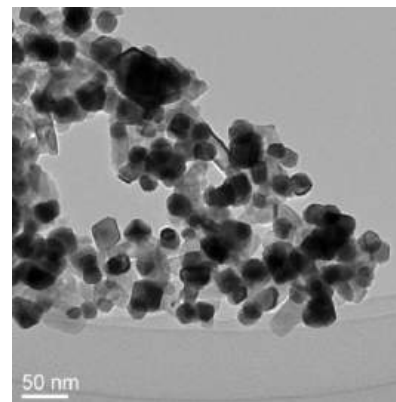
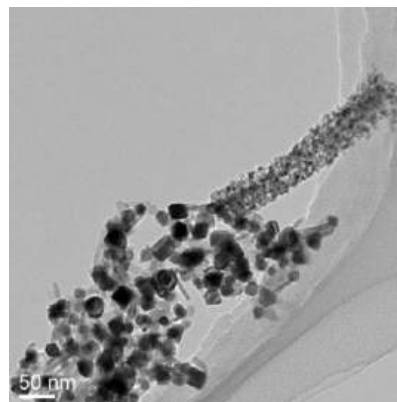
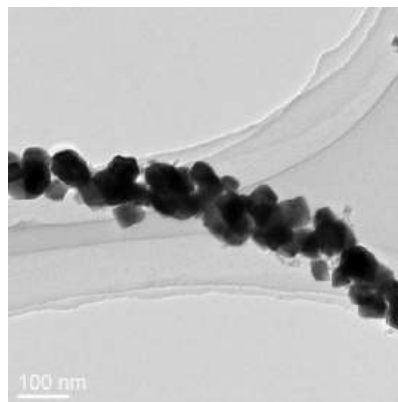
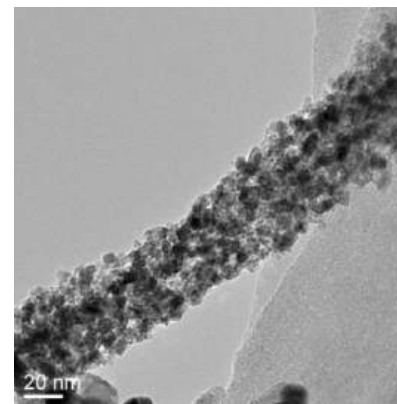
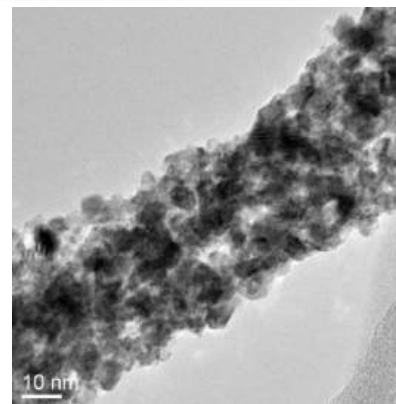
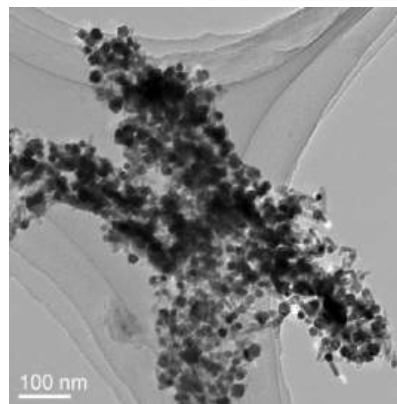
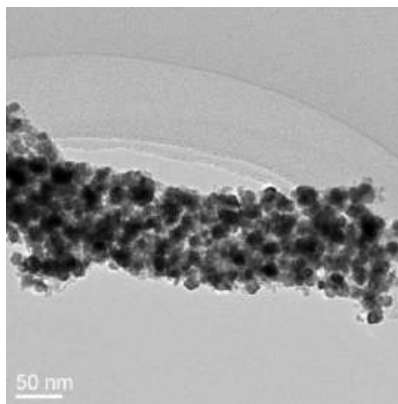


- ◆ カーボンブラックは電気化学的な酸化還元反応が起こり、キャパシタンスが増加する。
- ◆ GP-CNF-NAは電気化学的な酸化還元反応が起こらないためプロファイルがほとんど変わらない。

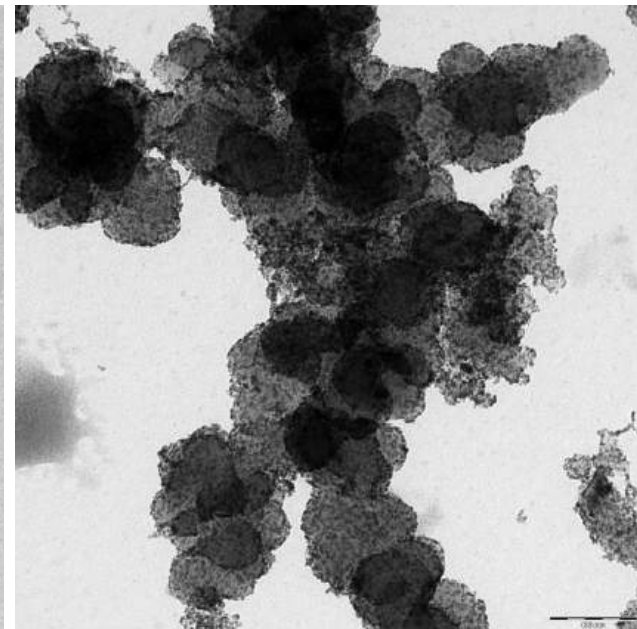
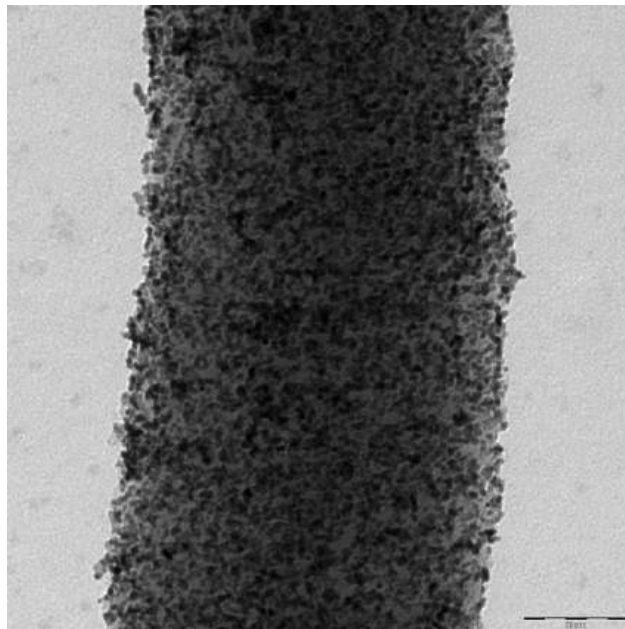
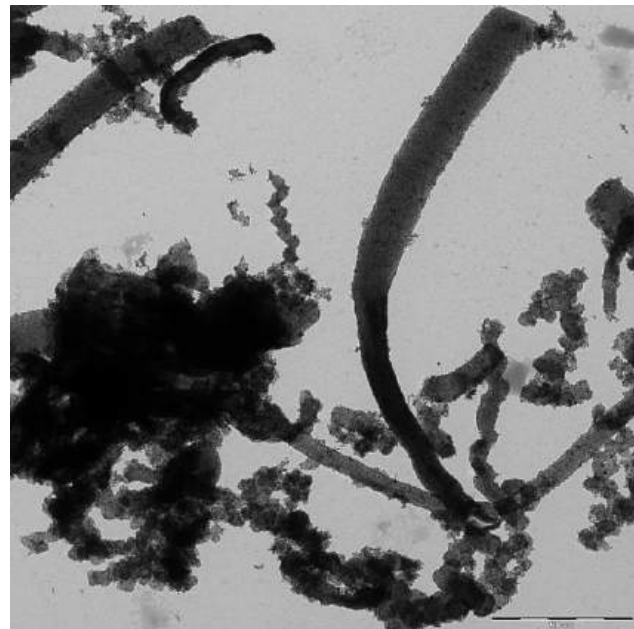
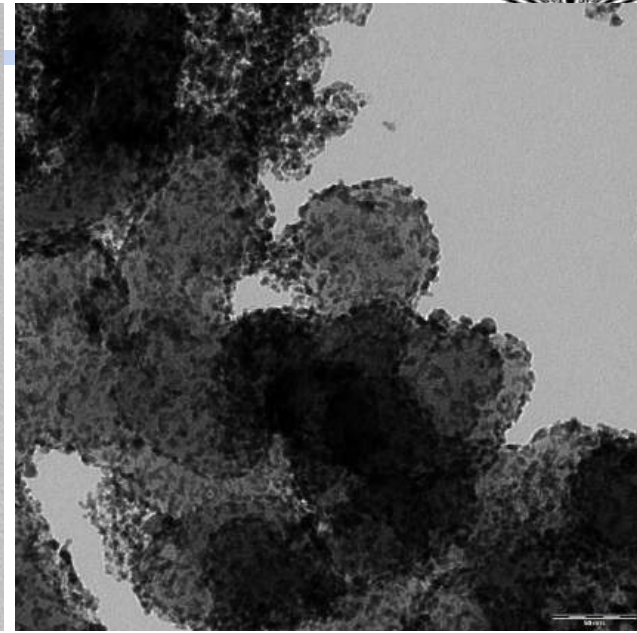
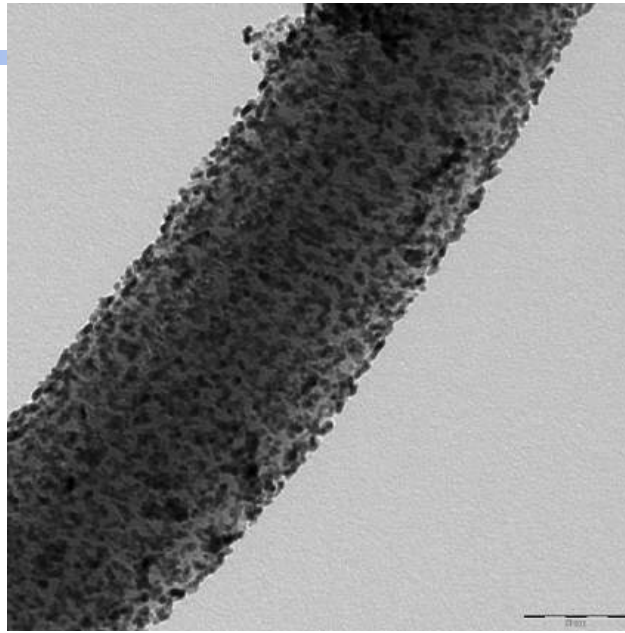
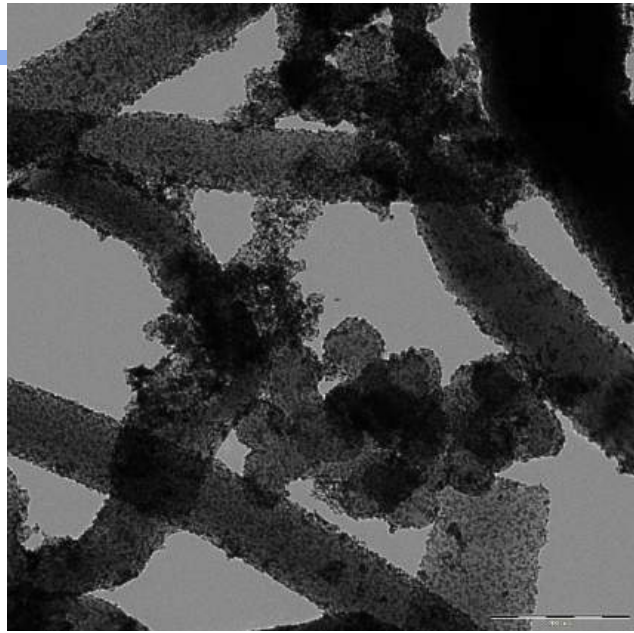


PtRu Nano-chains

10 wt% PtRu nanochain

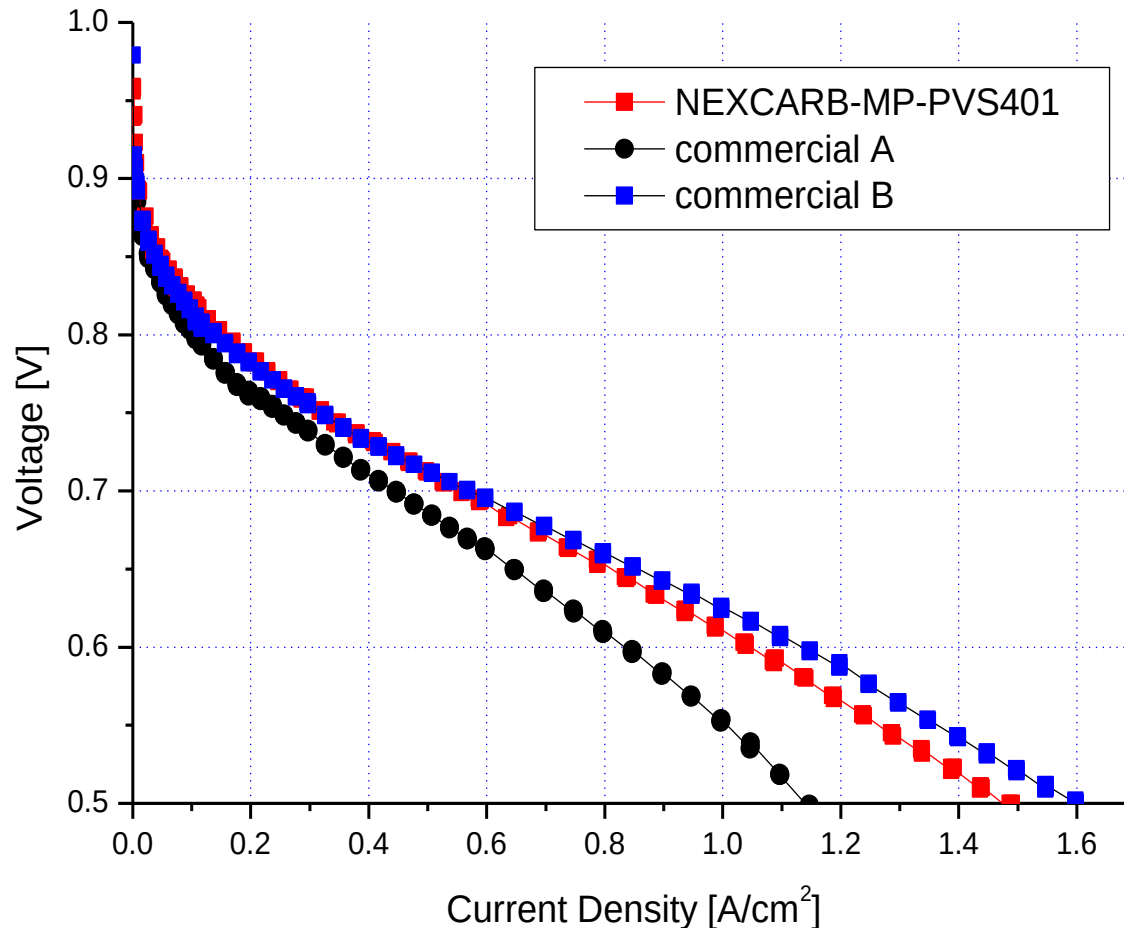


TEM images of 40%Pt/PCNF+CB





Evaluation of 40%Pt/PCNF+CB



Operating Condition

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

Very similar
performance with Gore
Japan MEA

Data from Suntel Co. Ltd.

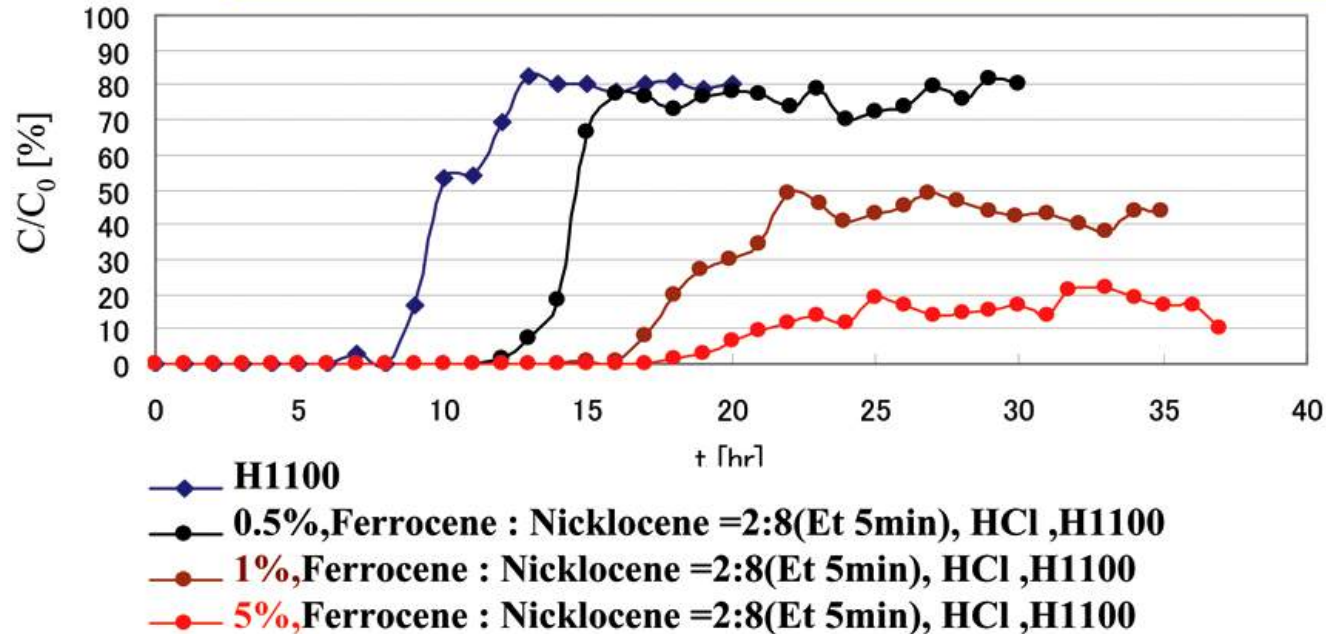


CNF for Air Purification



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℃)



	Breakthrought time[hr]	Steady state activity [%]	Surface Area [m²/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

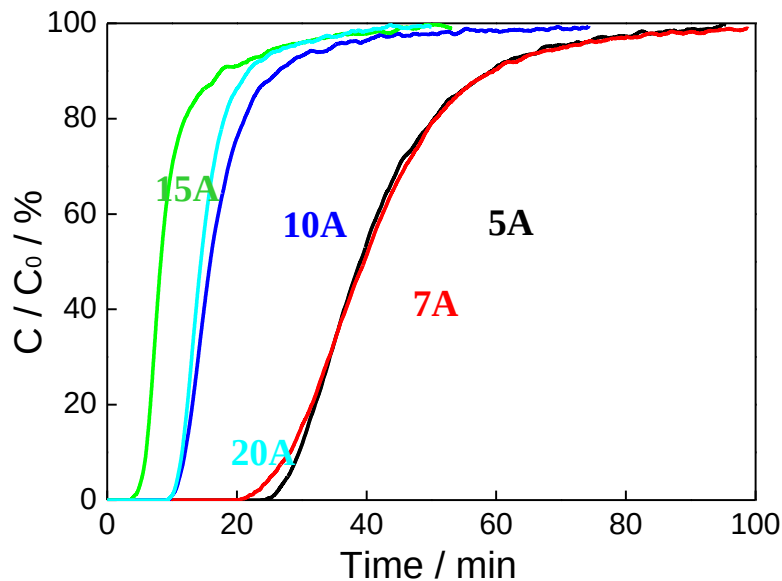
Pitch based ACF	BET (m ² / g)	Elemental analysis (wt %)				N / C
		C	H	N	O	
OG5A	563	92.4	0.6	0.7	6.0	0.007
OG7A	901	93.0	0.6	0.8	5.4	0.007
OG10A	1085	95.3	0.6	0.5	3.4	0.004
OG15A	1606	95.2	0.6	0.3	3.4	0.003
OG20A	1924	94.1	0.6	0.4	4.8	0.003

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

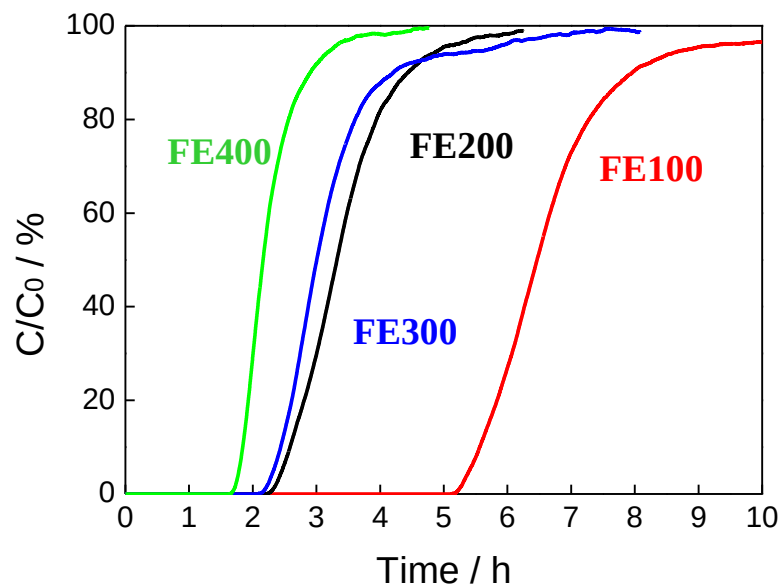
HCHO adsorption characteristics of ACFs



HCHO : 22 ppm
Sample weight : 0.1g
Gas flow rate : 100ml / m



HCHO : 22 ppm
Sample weight : 0.1g
Gas flow rate : 100ml / m



Break through time

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

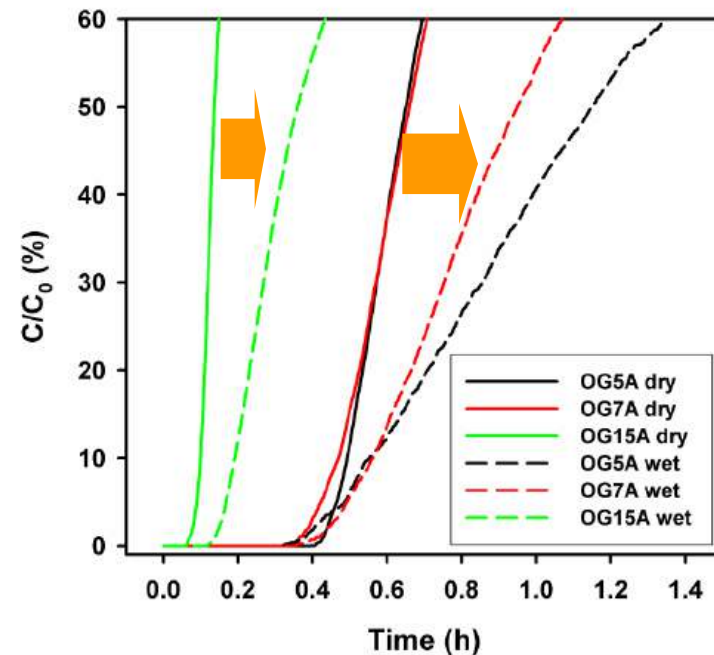
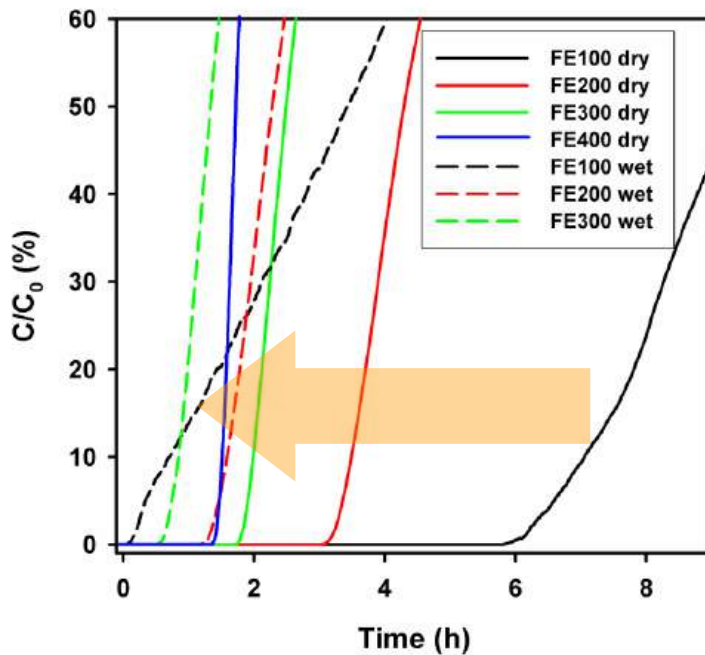
◆PAN-base ACF : FE400 < FE300 < FE200 < FE100



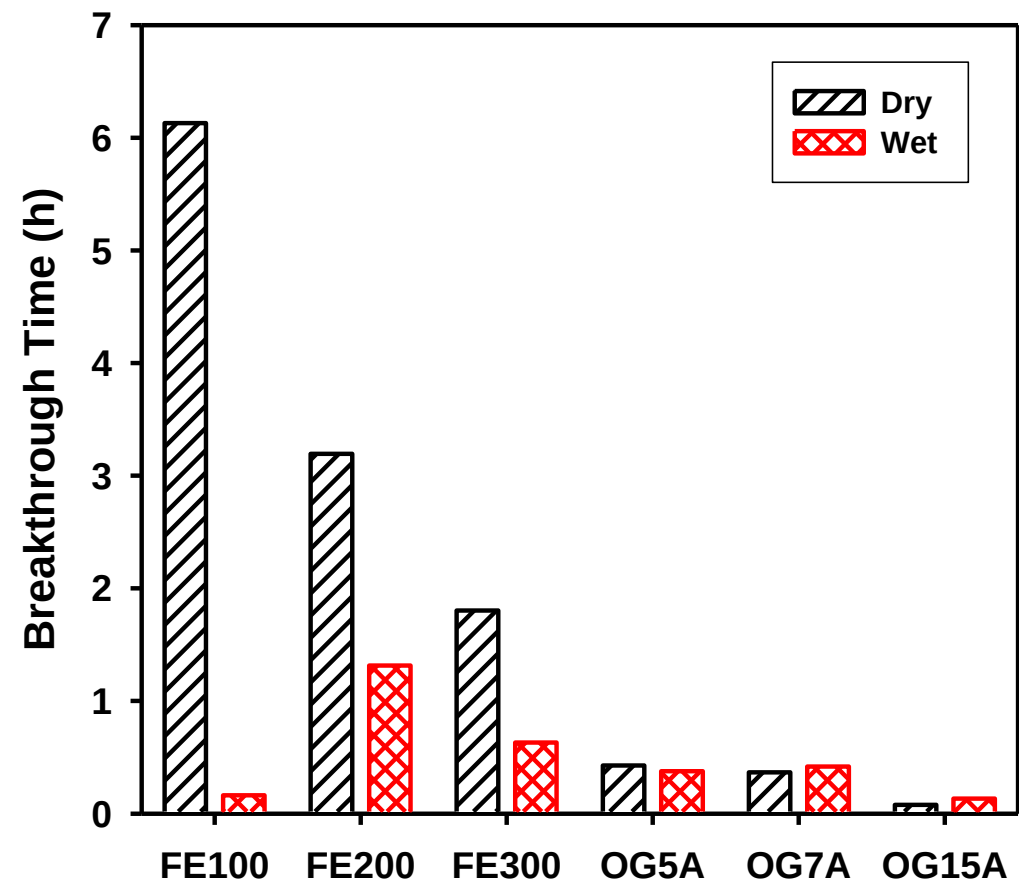
Breakthrough curves of formaldehyde adsorption

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



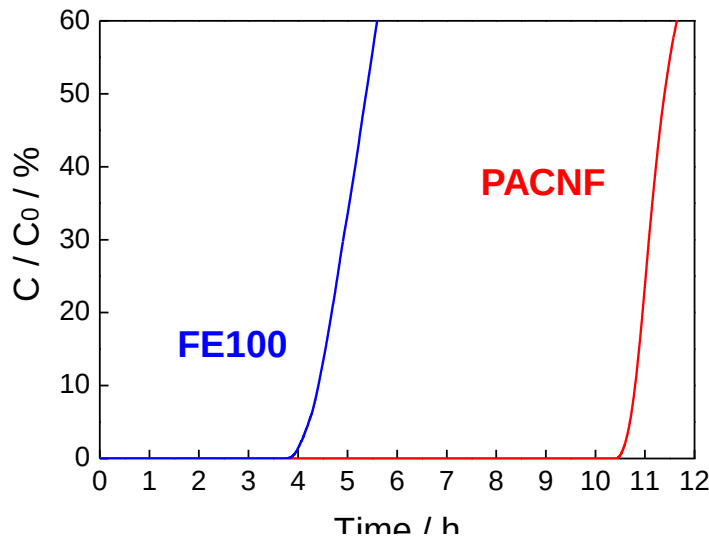
Comparison of formaldehyde adsorption in different ACFs between dry and wet condition





HCHO adsorption characteristics of PACNF in humidified atmosphere

RH	BET	Elemental analysis (wt%)					N / O	Microporous ratio (%)
	(m ² / g)	C	H	N	Odif	ash		
90%	375	68.06	1.19	18.02	11.41	1.32	1.80	94.7%



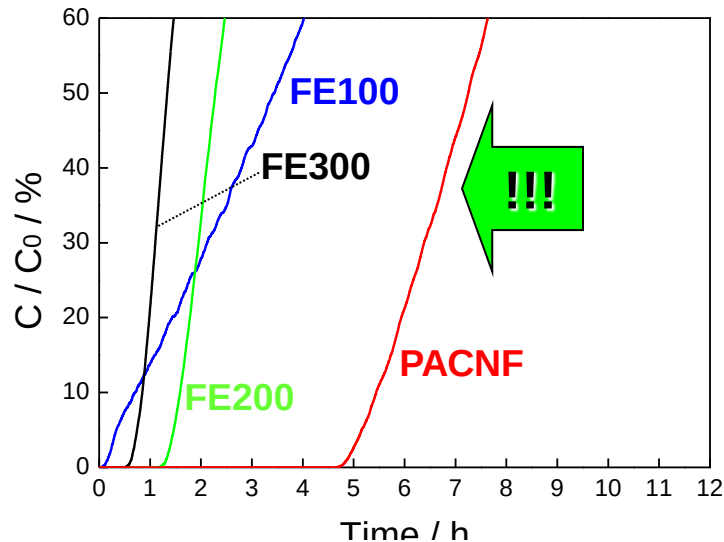
Experimental

HCHO : 11 ppm

Sample weight : 0.05g

Gas flow rate : 100ml / ml

Humidity of condition : 0%



Experimental

HCHO : 11 ppm

Sample weight : 0.05g

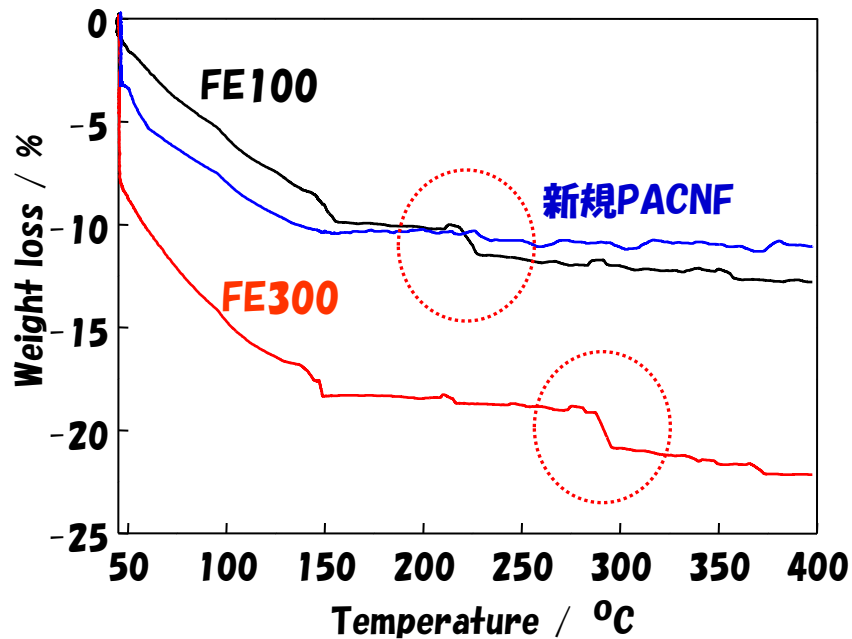
Gas flow rate : 100ml / ml

Humidity of condition : 50%

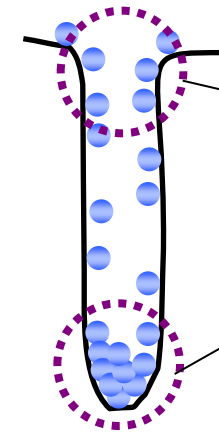
Under the circumstances of humidity (RH=50%), PACNF shows specific prominent adsorption characteristics for formaldehyde.

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



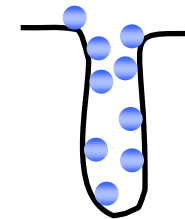
Deep pore



低温での重量変化
細孔上部に吸着してい
る水分子の蒸発

高温での重量変化
深い細孔の底部に凝集
している水分子の蒸発

Shallow pore



低温での重量変化
浅い細孔に吸着してい
る水分子の蒸発



CNF Support for Heterogeneous Catalysts

Oxidation and/or Reduction

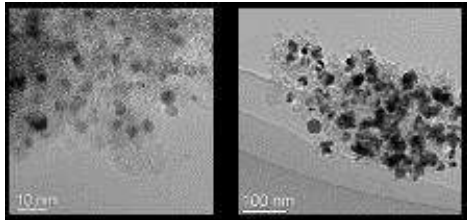
Desulfurization/Denitrogenation

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

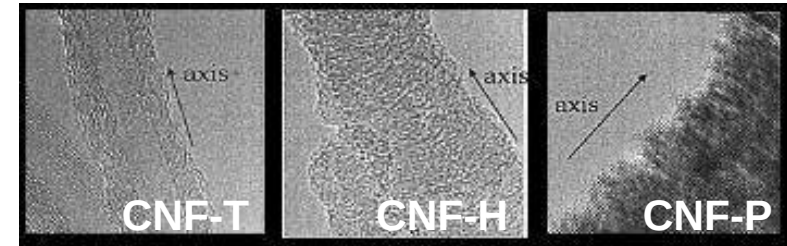


不均質な炭素表面
不均質な担持
活性・効率・再現性に問題

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

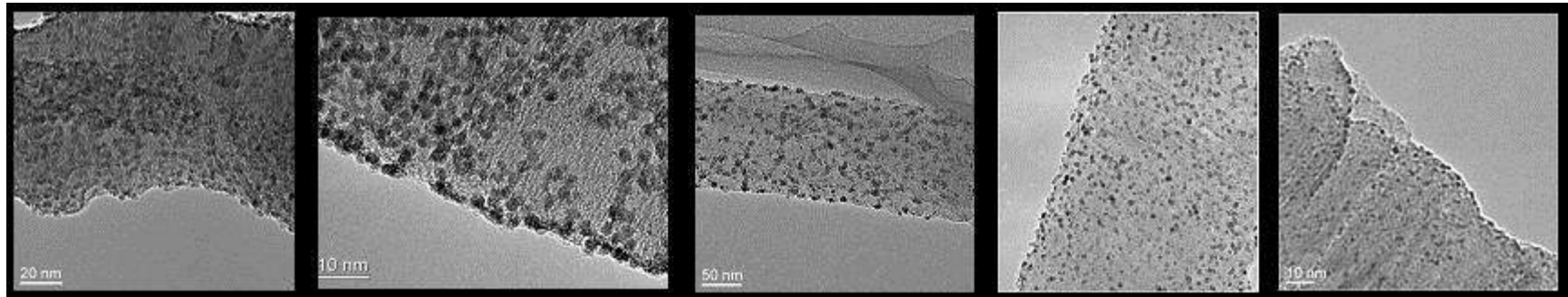


+

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
 $d_{av} = 5.0 \text{ nm}$

Ru/CNF-P
 $d_{av} = 2.5 \text{ nm}$

Rh/CNF-P
 $d_{av} = 7.6 \text{ nm}$

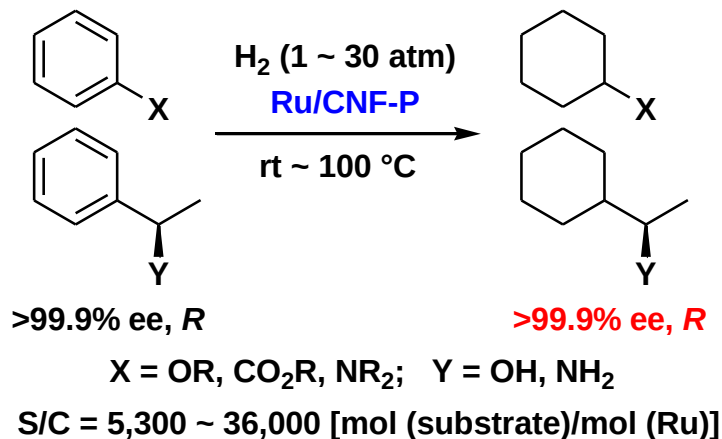
Pd/CNF-P
 $d_{av} = 4.2 \text{ nm}$

Pt/CNF-P
 $d_{av} = 1.4 \text{ nm}$

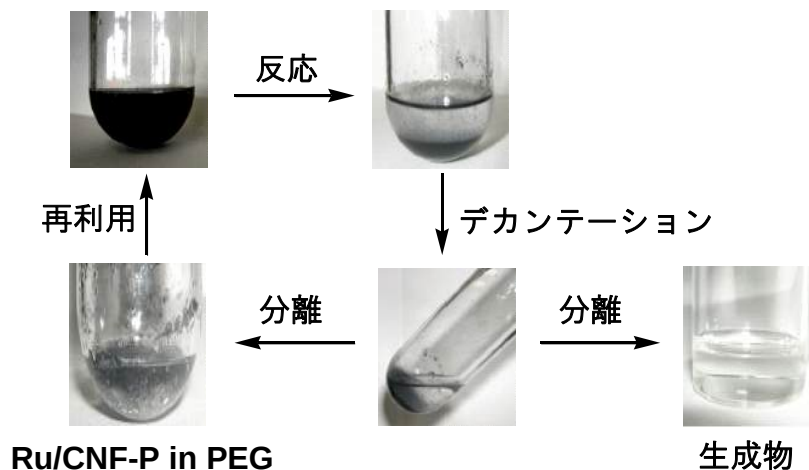
金属ナノ粒子担持炭素ナノ繊維の応用例



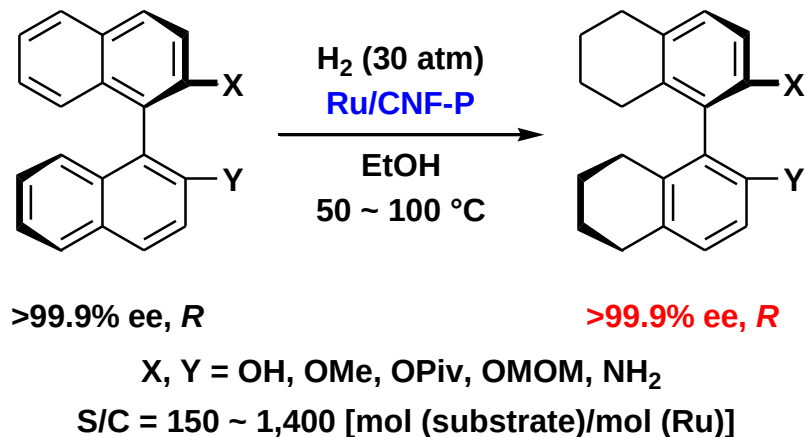
高活性芳香環水素化触媒 高耐久性・高選択性



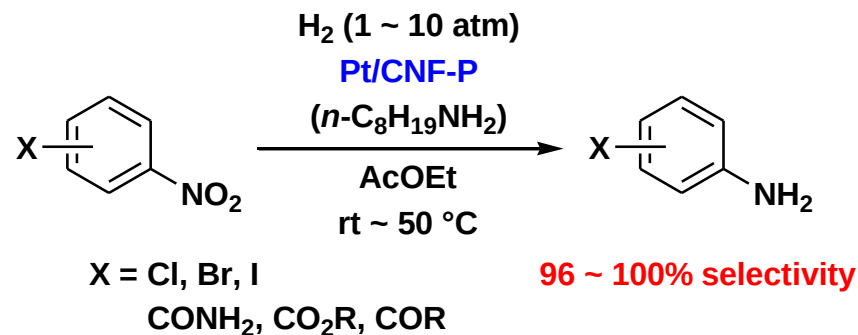
PEGを用いた容易な触媒再利用システム



ビナフチル化合物の部分水素化による 光学活性H₈-ビナフチル誘導体の効率合成



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

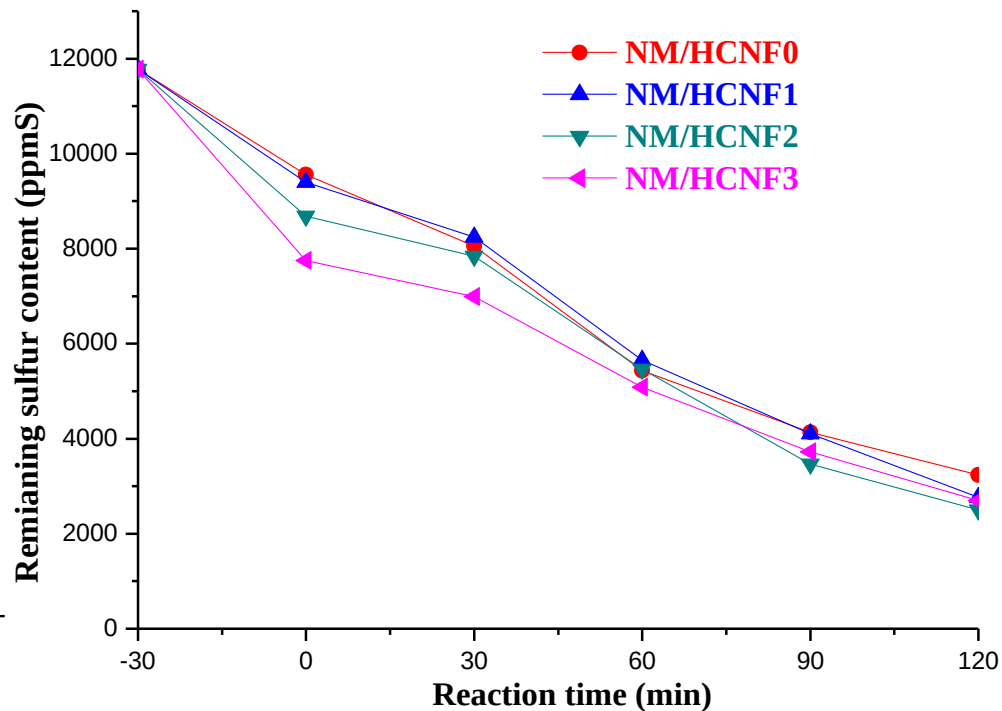
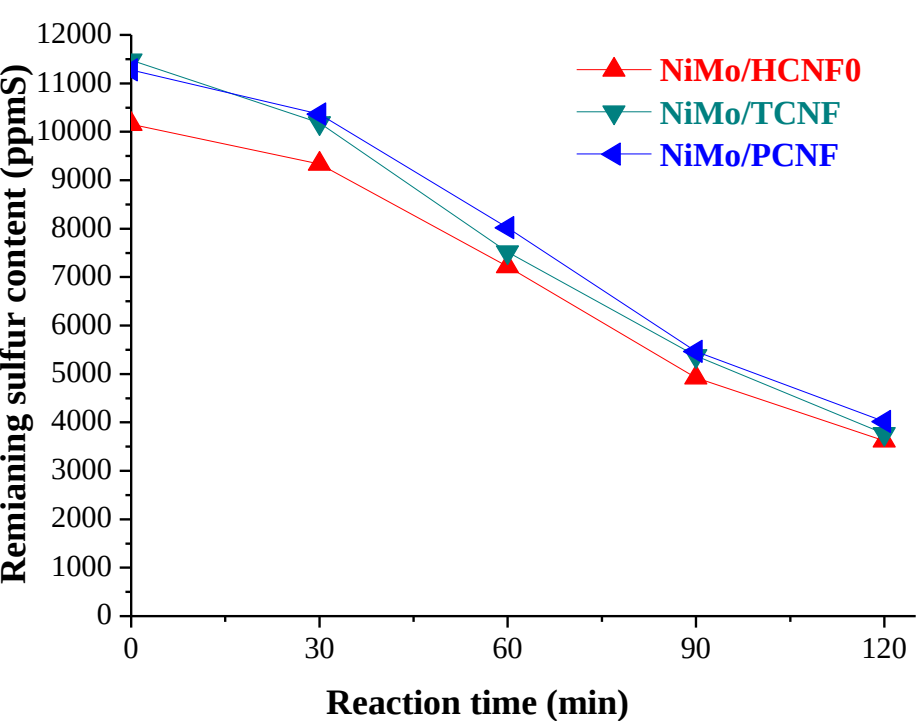




CNF as supports for NiMo catalysts

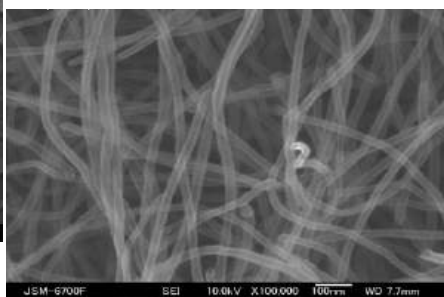
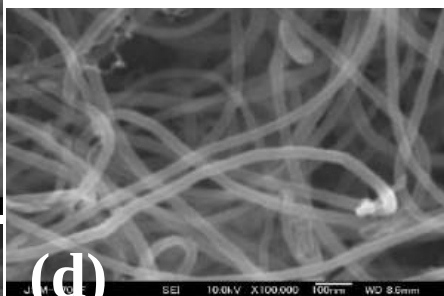
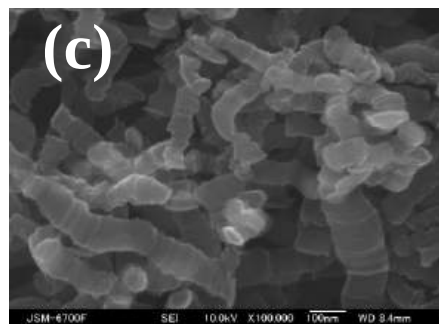
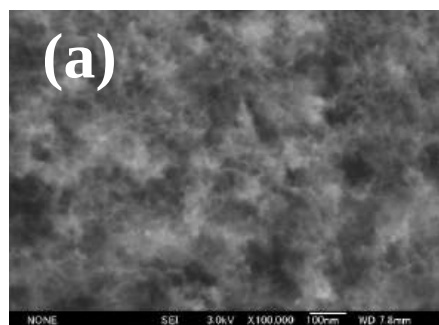
- The potential of several kinds of carbon Nanofiber as supports for NiMo catalysts in hydrodesulfurization of SRGO (Straight Run Gas Oil) and HSRGO (Hydrotreated Straight Run Gas Oil)
- The performance were compared with NiMo/Al₂O₃ commercial catalyst to get the relationship between the some supports 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

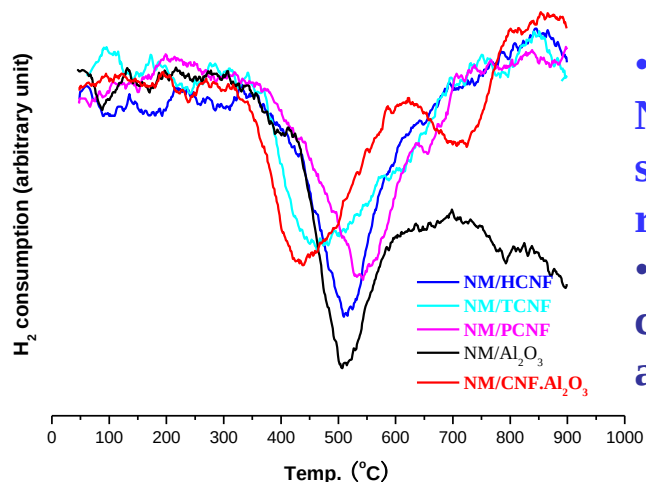
Physical and chemical characteristics of supports and catalyst



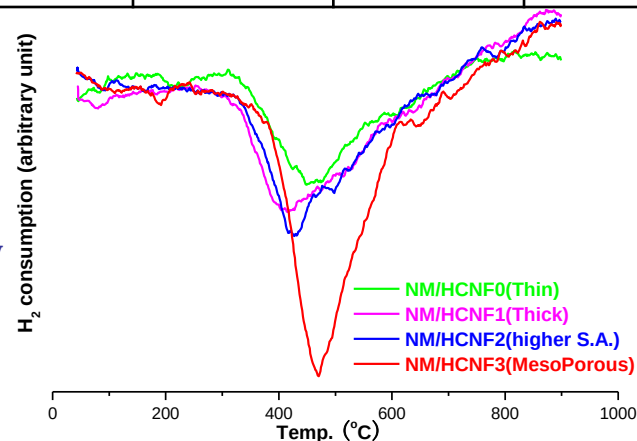
(a)HCNF/ Al_2O_3 (b)HCNF
(c)TCNF (d)PCNF

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

Sample	R_p (nm)	$S(\text{m}^2/\text{g})$	$V_p(\text{cc/g})$
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 consistency with HDS activity





CNF for Luminescence



Objective

- Development of FEBL using CNF instead of CNT

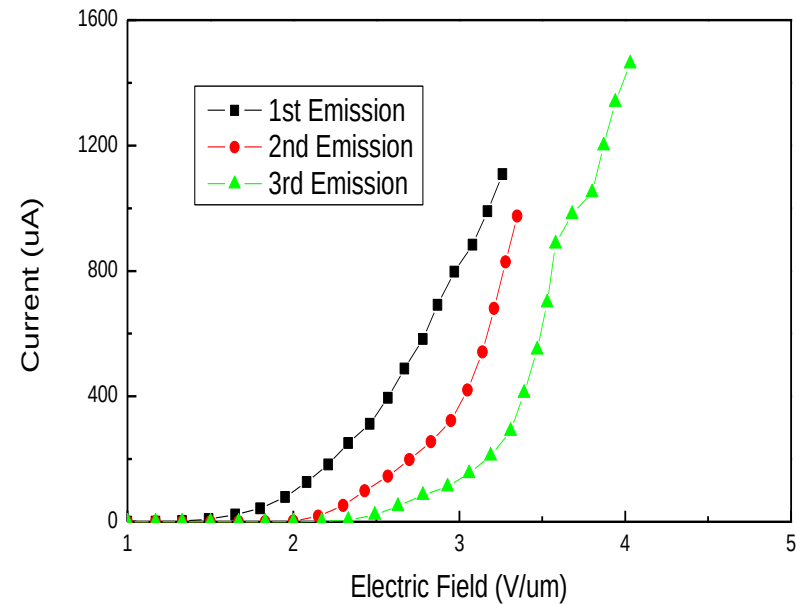
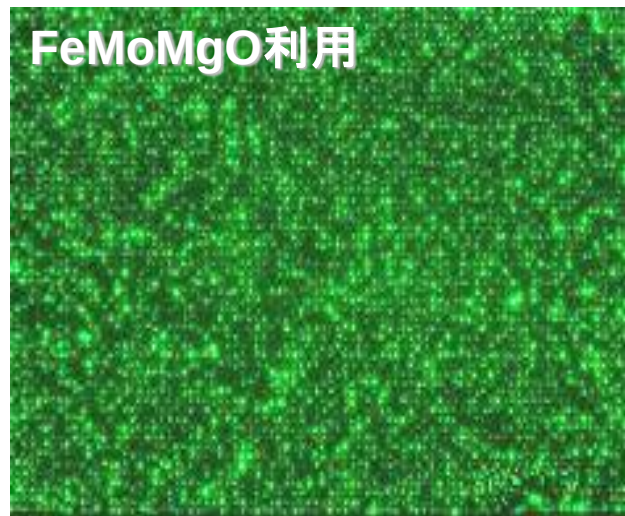
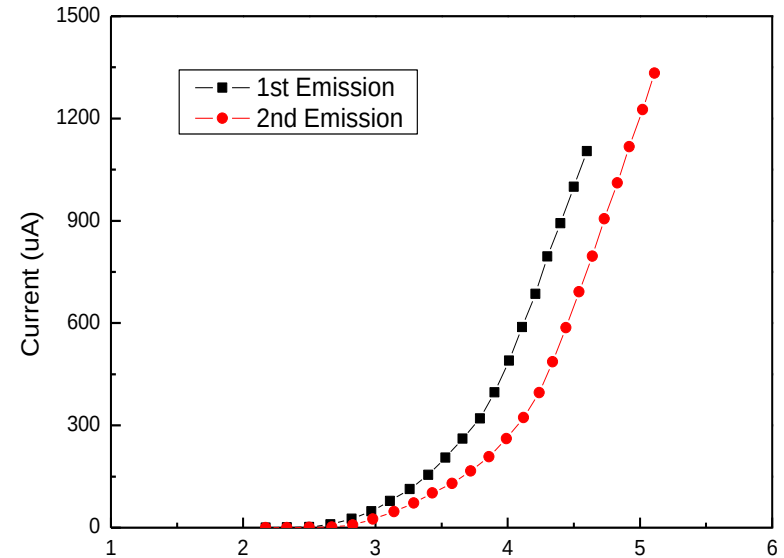
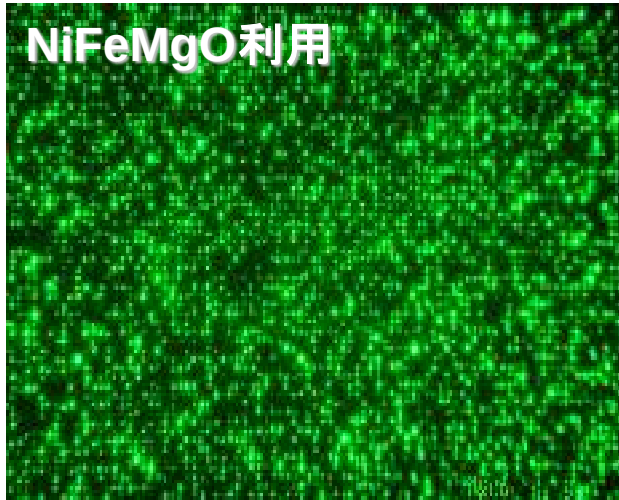
Expectation

- 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/m² (12000 V)

CNF Development



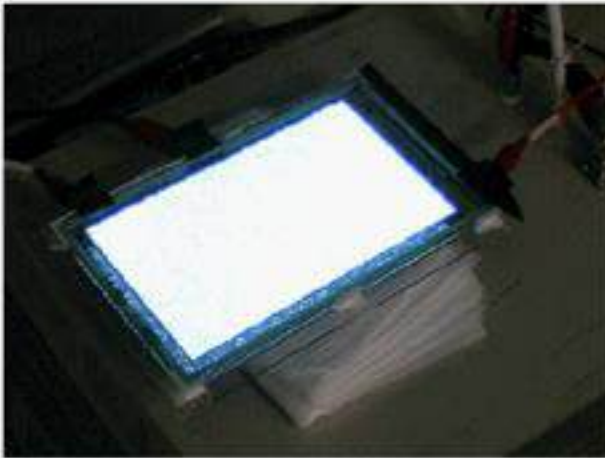
3 E system 7 inch Panel



Cathode 電位、Anode 電位、電流



Diffuser使用





CNF for Composites

Electric conductivity

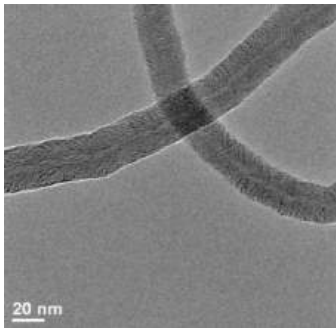
Thermal Conductivity

Tensile Strength and Modulus

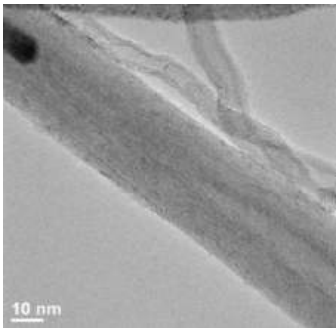
Electric Conductivity for Polymer Composites



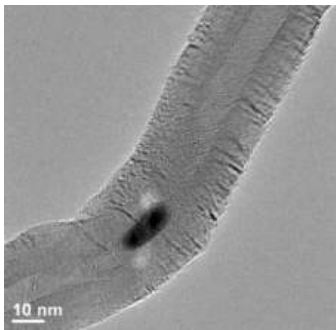
触媒	合成条件	平均収率	繊維径	CNF 構造	電気伝導度
Co:Fe:Cr:Mg=4:2:2:2 (重量比) [触媒前処理: Air, 600℃, 4h]	460℃, 60min, C ₂ H ₄ :H ₂ =160:40	23.1倍	40nm	Herring-bone	Out of range
	600℃, 60min, C ₂ H ₄ :H ₂ =160:40	26.5倍	40nm	Tubular	4.1
	600℃, 60min, C ₃ H ₈ :H ₂ =160:40	25.1倍	40nm	Tubular	5.1/5.6
	700℃, 60min, C ₃ H ₈ :H ₂ =160:40	21.5倍	70nm	Tubular	4



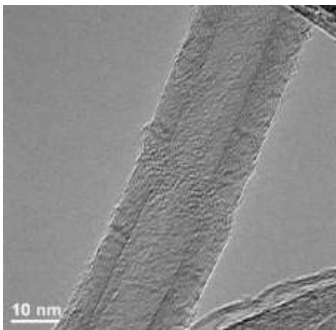
460℃
C₂H₄



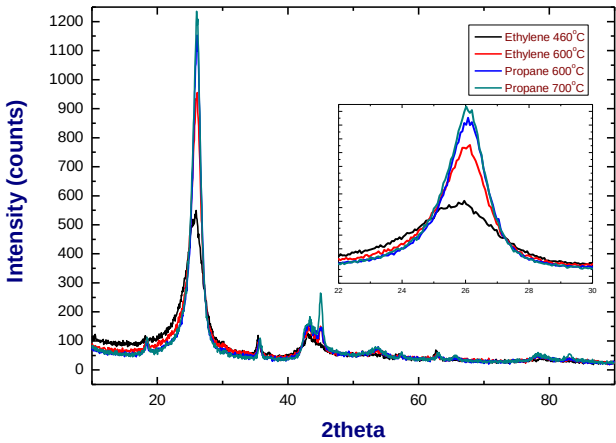
600℃
C₂H₄



600℃
C₃H₈

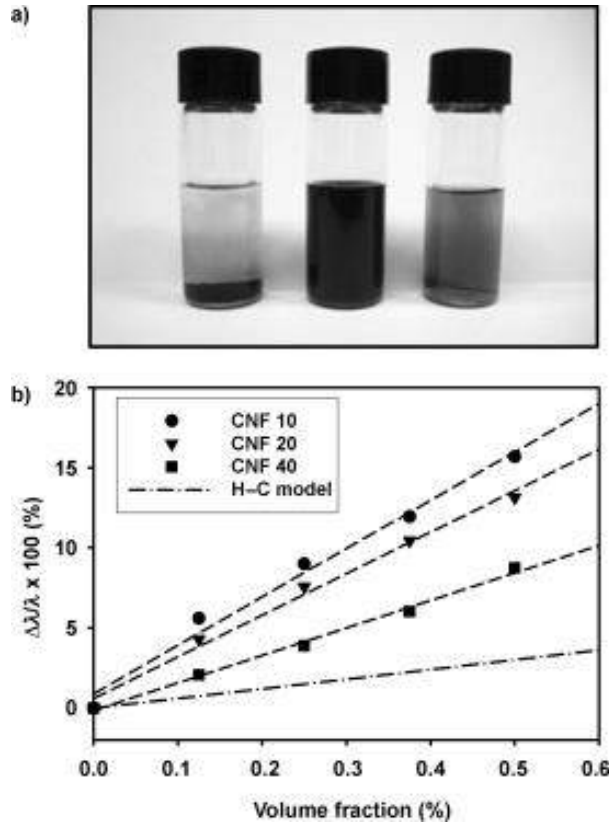


700℃
C₃H₈

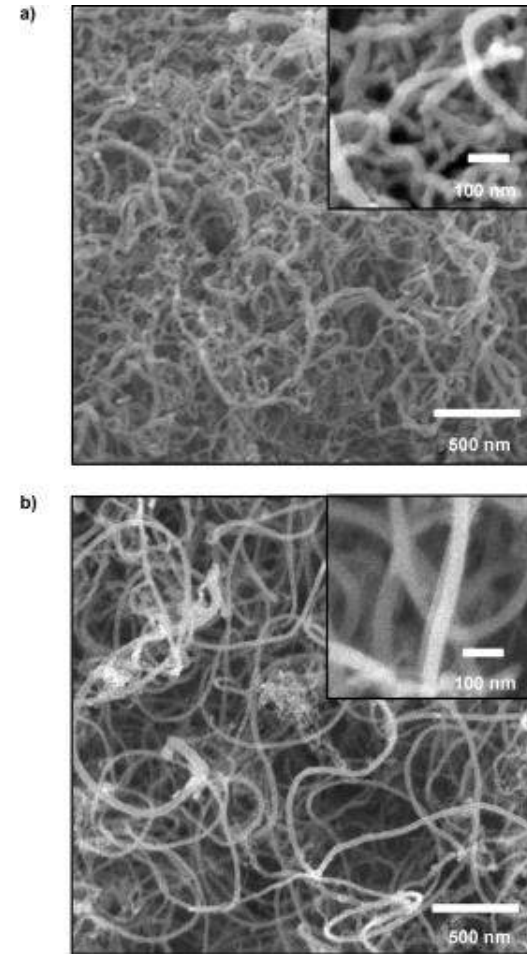


A Novel Nanofiller for Nanofluid Applications

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 繊維径(AS-prepared) – Fe:Ni:Co:Mg=7:0.5:0.5:2 触媒を用いて C₂H₄ 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

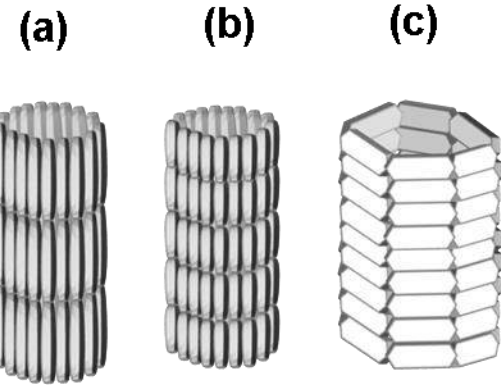
Experimental

Preparation of CNF-MgO composites

Catalysts

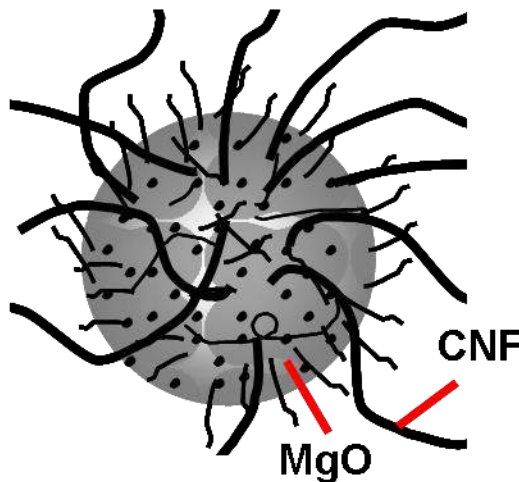
- KNF003(Fe/Mo/MgO)
- CoCrMgO (6/2/2)
- FNMgO(Fe/Ni/MgO)

(a)
(b)
(c)

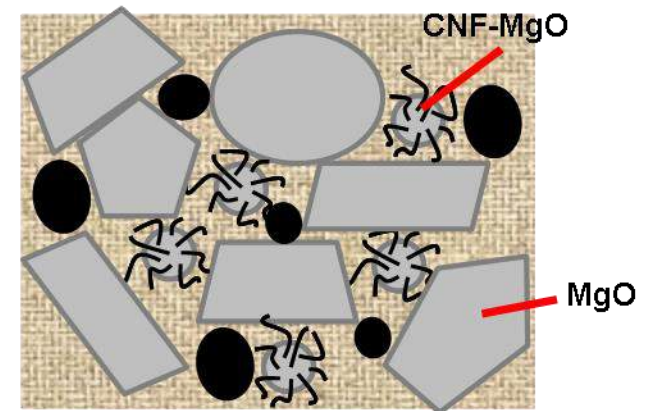
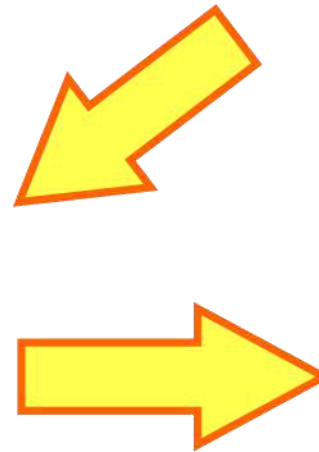


Schematic pictures of CNF structures

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



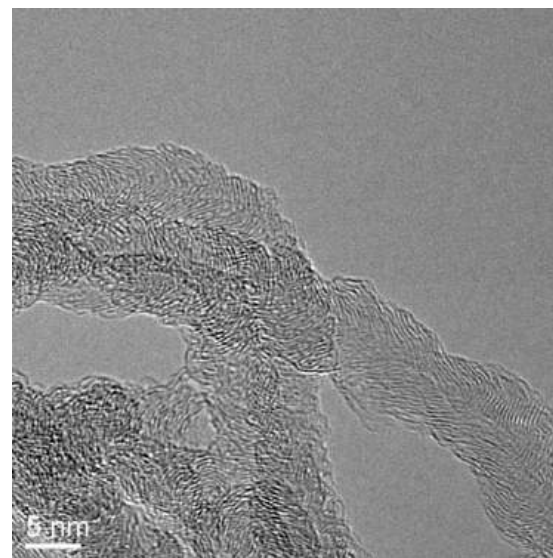
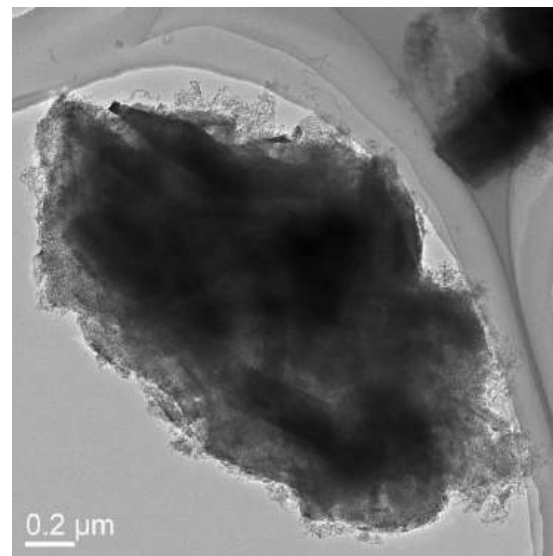
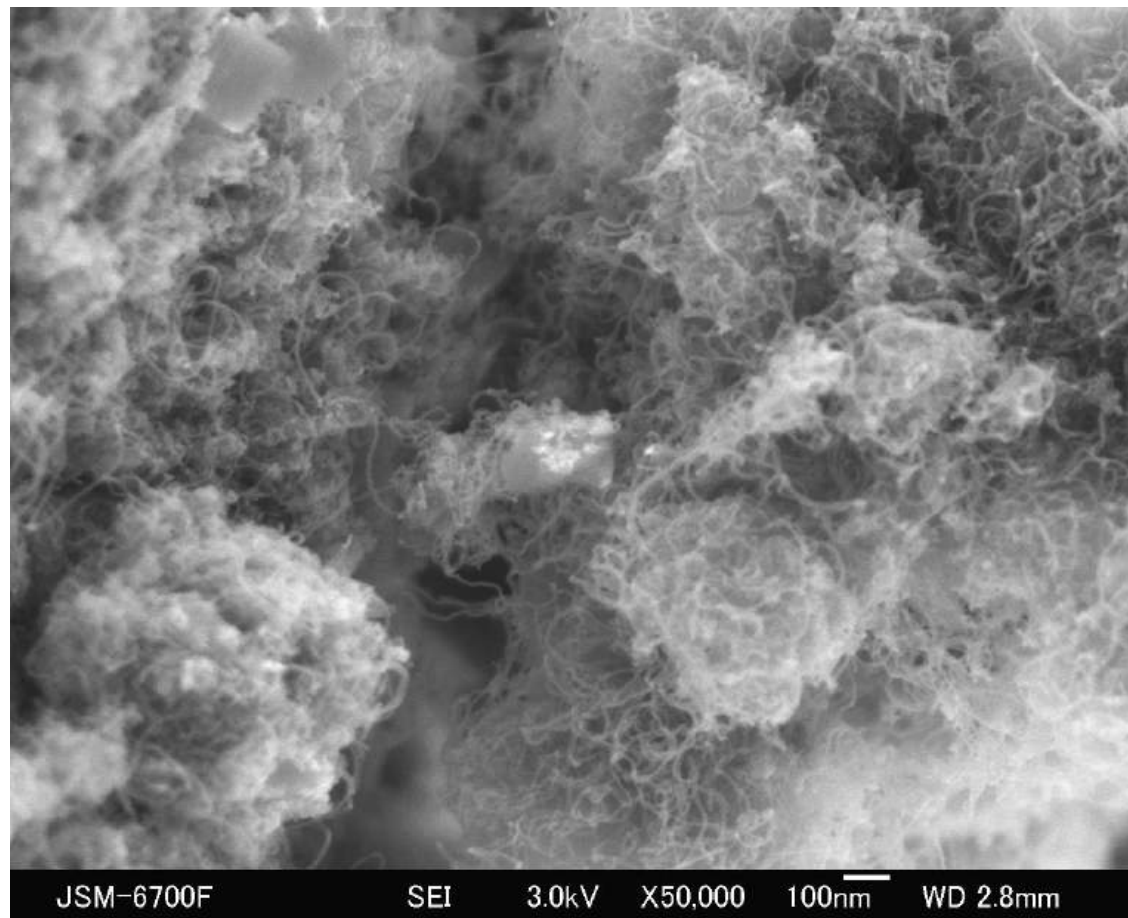
MgO-CNF



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

Not submitted

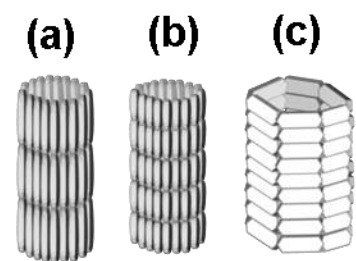
CNF for Ceramic Conductivity



・KNF-MgO-004のSEMとTEM写真:
Herringbone CNF/MgO



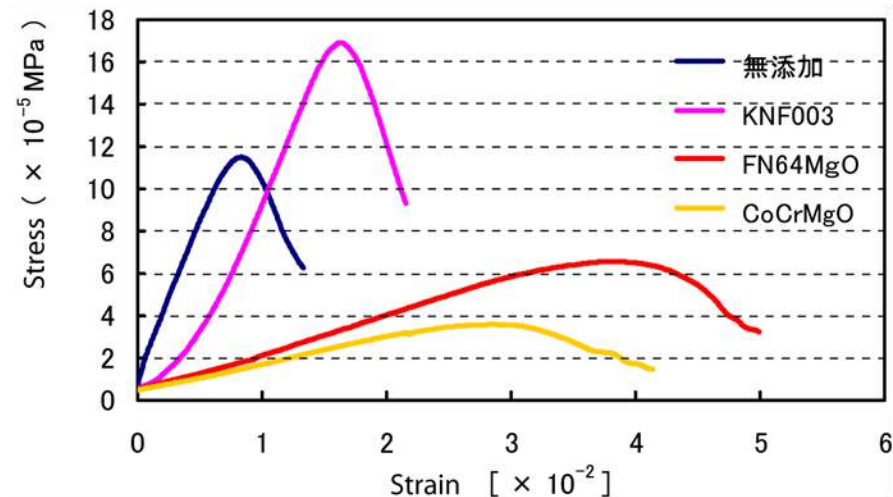
Strength evaluation of CNF-MgO added MgO-C Refractory



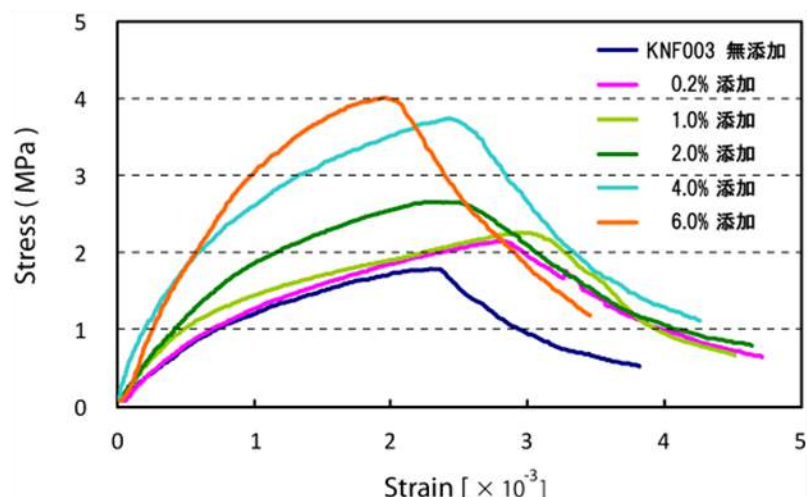
Structural Models of CNFs

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 ₂ H ₄	19.5



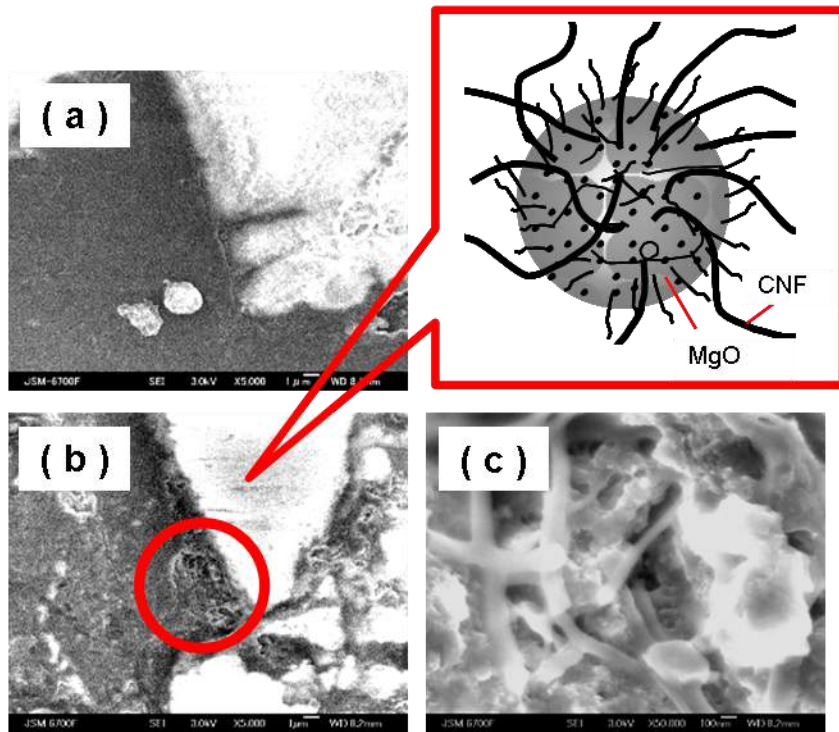
Strain-stress curves of CNF-MgO composite added refractories



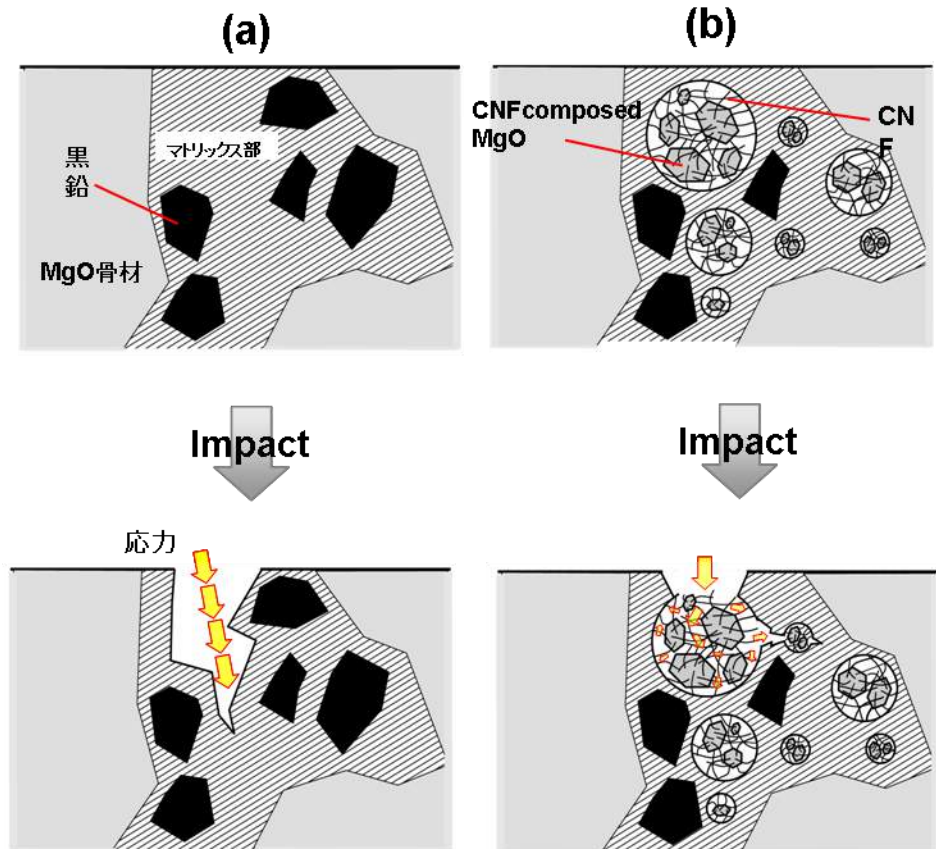
Effect of addition amounts of CNF-MgO composites (Graphite: 15%)

SEM images of KNF003-composed refractory

Crack propagation prevention mechanism



KNF003 composed MgO added MgO-C refractory
(a) None (x5000), (b) KNF003 (x5000), (c) KNF003 (x50000)



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



- 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



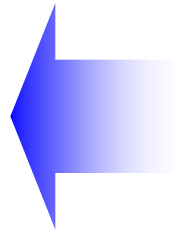
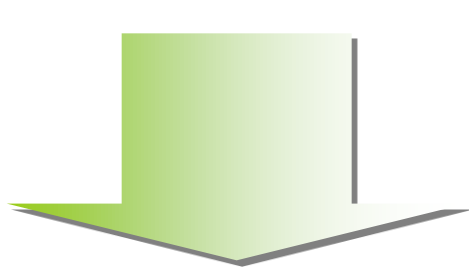
New feasible technology to solve urgent energy and environmental problems which fusion conventional fuel science, carbon technology and nano-carbon technology.

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



- ✓ 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 Master course students
- ✓ 3 Secretary

Staffs for Nano-studies

- Faculties
- 1 Post-doctorate
- 3 Doctor course students



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先端物質化学研究所

Thank you for attentions!