CNF-composite as an effective route for novel functional materials

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Flow of CNF studies in Kyushu University

Standard CNFs

PCNF, HCNF, TCNF
Accordion CNF

Target optimized CNFs

Small CNF,
High SA CNF,
Highly Graphitic CNF
Highly Dispersive CNF
N-doped CNF

CNF functional composites

CNF-Si, SiO, TiSi
CNF-NG、CB
CNF-SiO2, CNF-MgO

Metal & Metal Oxide Nano-chain

Fe3O4, MoO2 nanochain
SiO2, 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 pollutions
Dilute NOx
De-metal, De-particulates¥

Standard Carbon Nanofibers (CNFs)

Platelet CNF

Edge surface

Graphene layer alignment :

Perpendicular to fiber axis

Herringbone CNF

Edge surface

Graphene layer alignment :

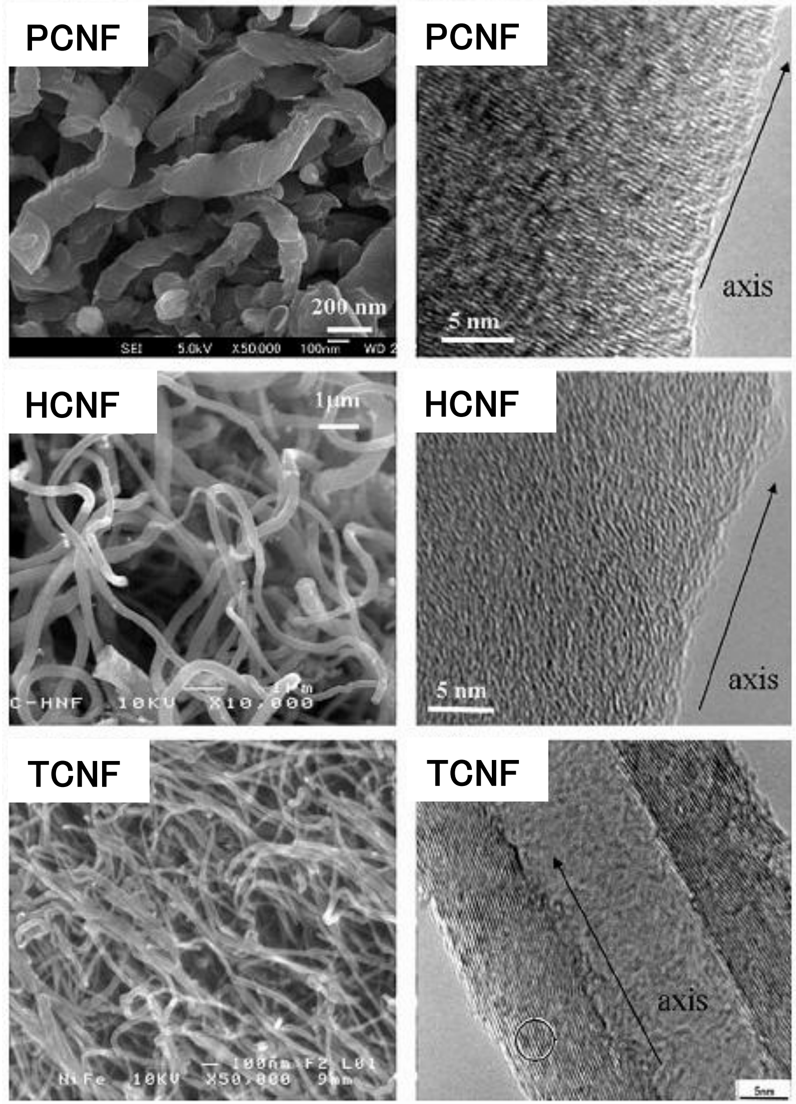
Lean against fiber axis

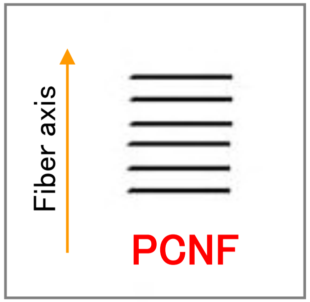
Tubular CNF

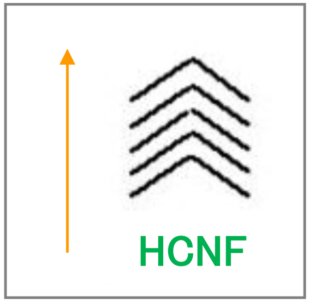
Basal plane surface

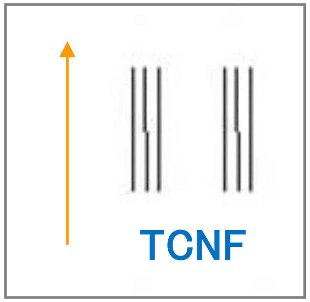
Graphene layer alignment :

Parallel to fiber axis









Langmuir, 2006, **22(22)**, 9086.

Mass Production of CNFs

Horizon type
Capacity : several grams

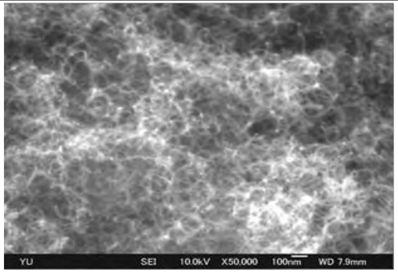
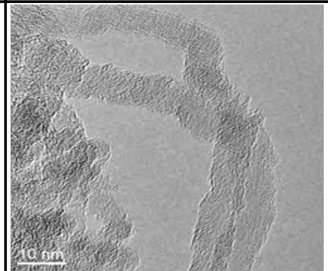
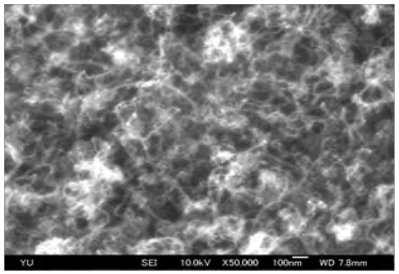
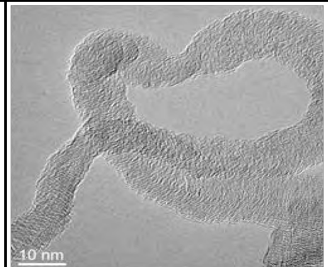
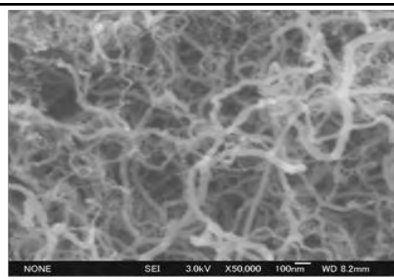
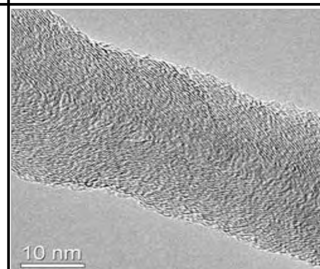
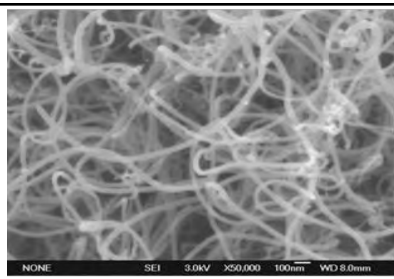
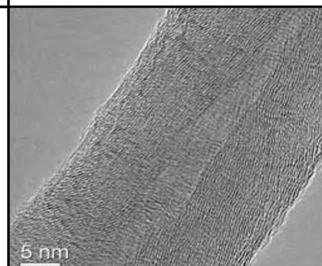
Capacity : H-, P-CNF 100g/1batch
T-CNF 20g/1batch

Scale up
Vertical type

Capacity: 500g/day

Scale up
Vertical type
Pressure

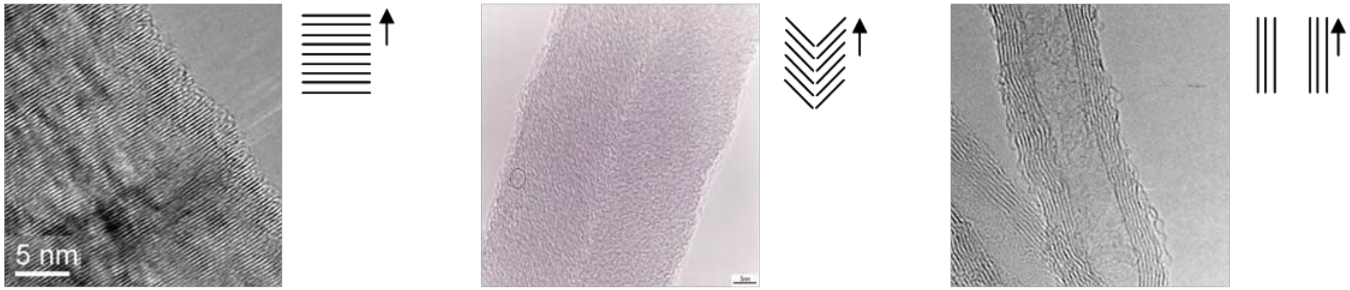
CNF (Variety of diameters)

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**

CNF (Variety of textures and shapes)

Typical classification of CNF Structure

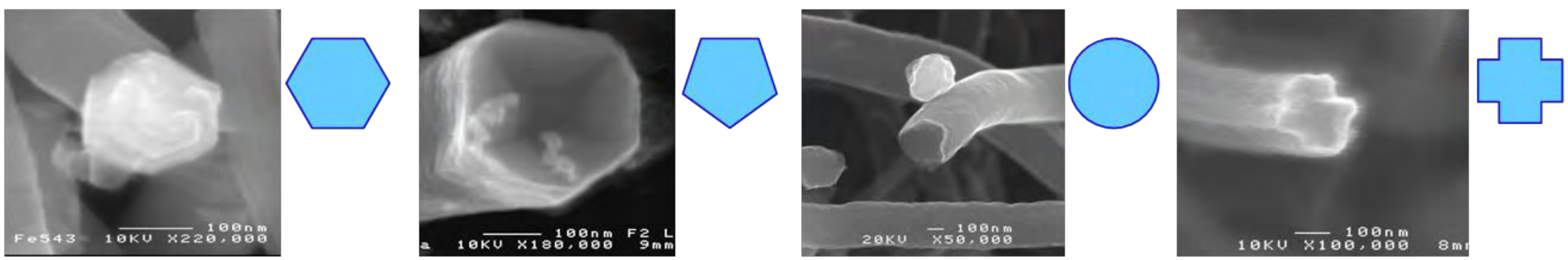
- graphene ((002) layers) alignment to the fiber axis, TEM observation



< 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.

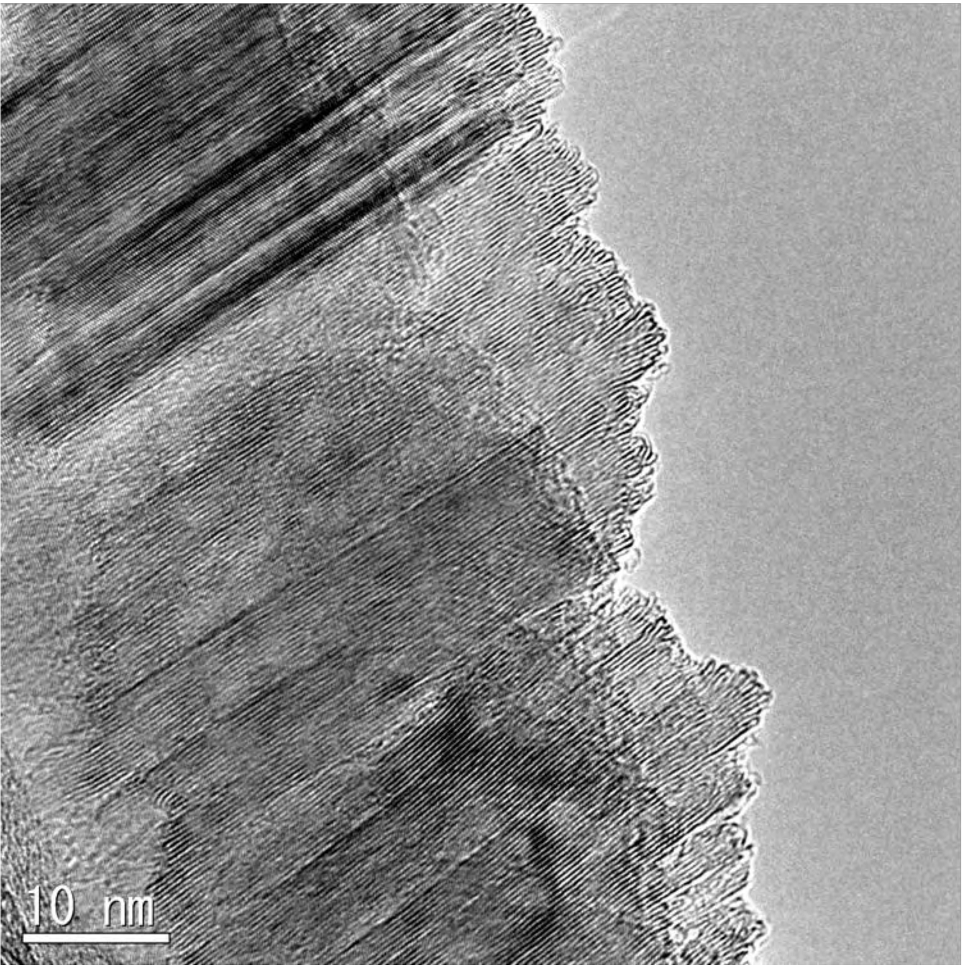
Various cross sections of CNFs

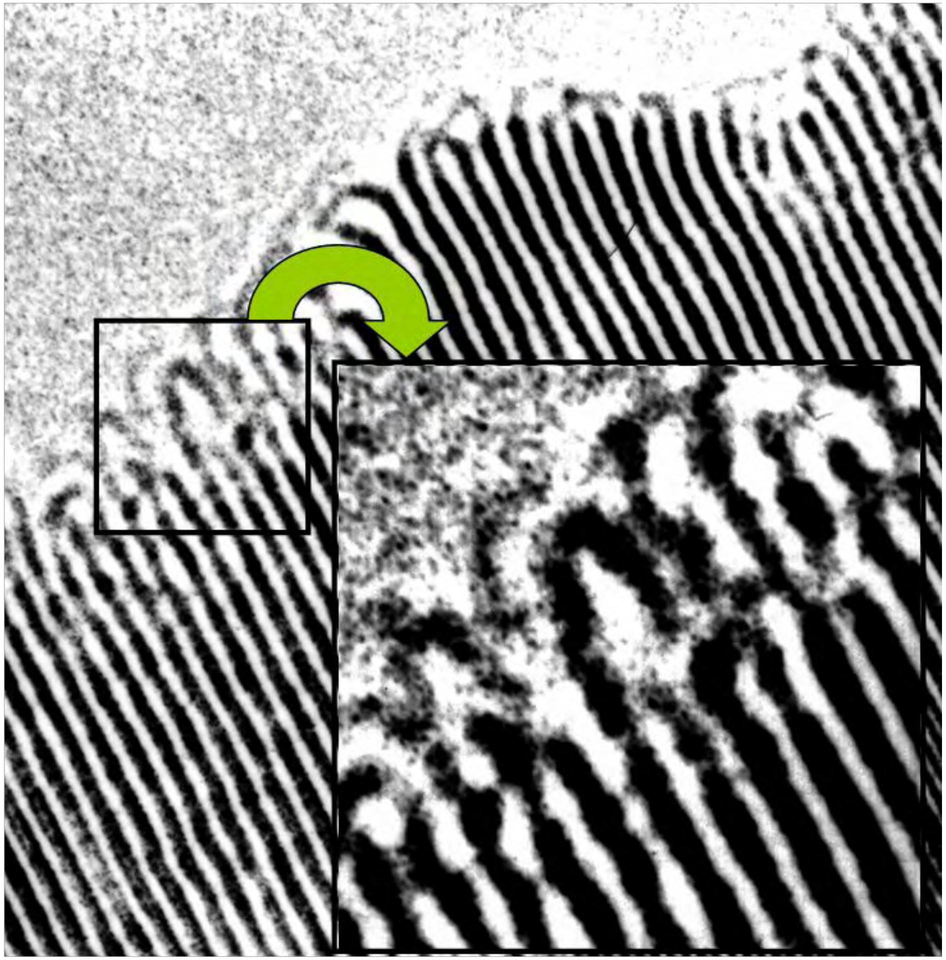


Polygonal Circle Cross

Different Surface Characteristics

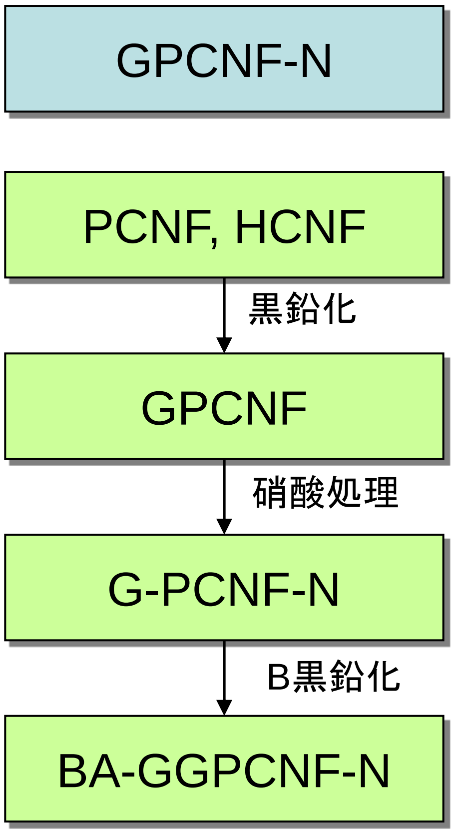
CNF (Variety of surfaces)





Highly graphitic CNFs

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

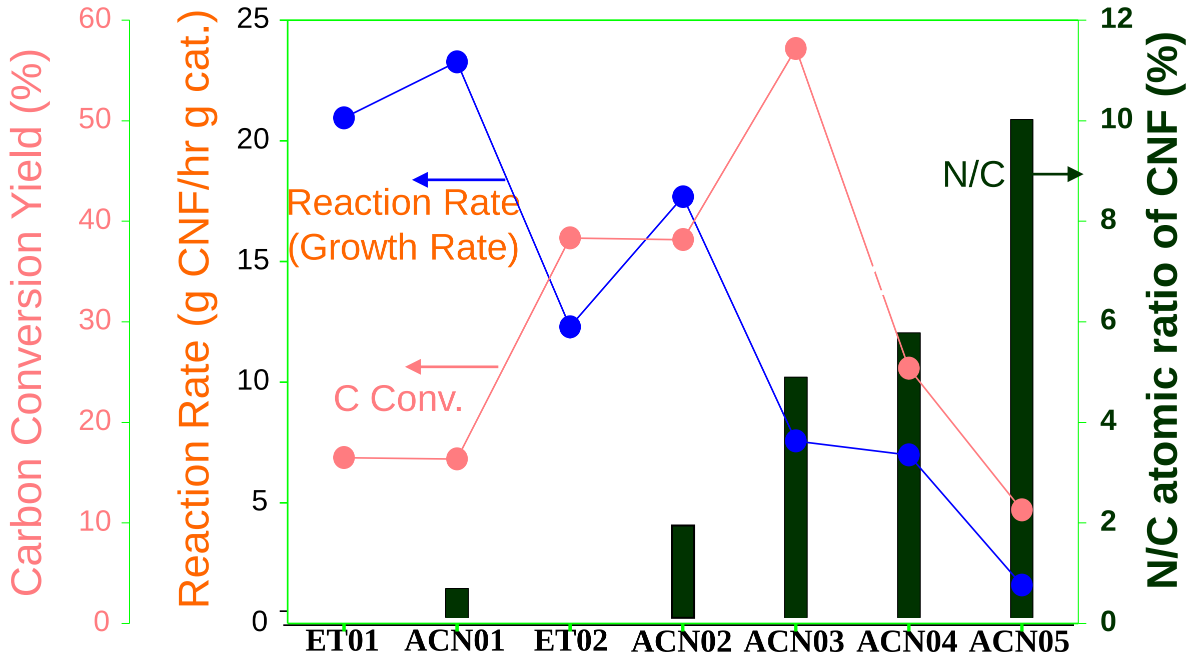


	Preparation conditions	d_{002} (nm)	Lc(002) (nm)
PCNF	Fe catalyst, 620, CO/H2 : 4/1	0.3365	72
G-PCNF	2800℃ heat treatment of PCNF	0.3364	83
G-PCNF-N	30% HNO3 treatment of GPCNF for 50℃, 8hs	0.3362	152
GG-PCNF-N	2800℃ heat treatment of GPCNFN	0.3362	106
BA-G-PCNF	Boric acid added heat treatment of PCNF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

N-doped CNFs

N-Source
: Acetonitrile

Reaction Temp.
530°C

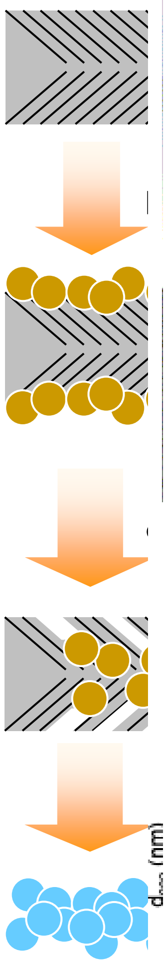


		ET01	ACN01	ET02	ACN02	ACN03	ACN04	ACN05	
Ethylene	ml/m (*g*)	**160**	**160**	**40**	**40**	**0**	**0**	**0**	Total 200 ml/m
Hydrogen		**40**	**40**	**40**	**40**	**40**	**40**	**0**	
He		**0**	**0**	**120**	**120**	**160**	**160**	**200**	
Acetonitrile (*liq.*)	μl/m	**0**	**35**	**0**	**35**	**35**	**70**	**35**	
Input N/C	at.%	0	4.6	0	14.5	50	50	50	

Modifications of CNFs

- Syn

Ca

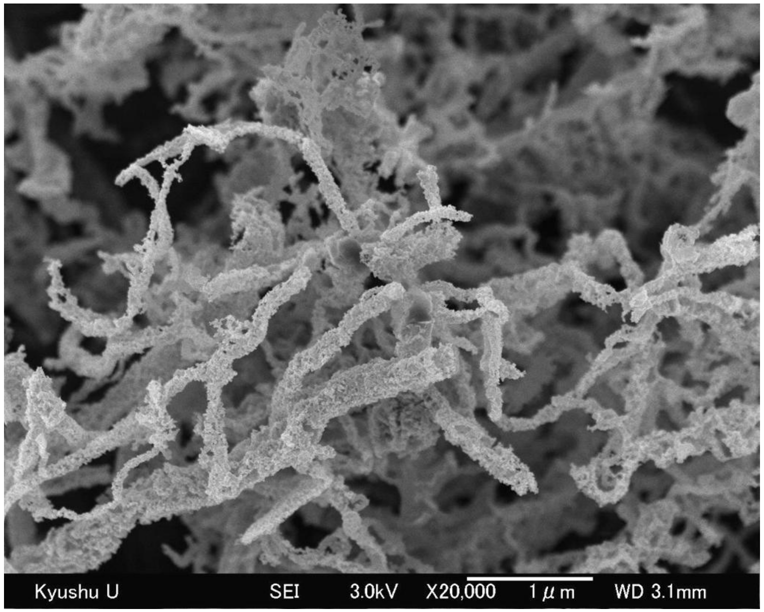


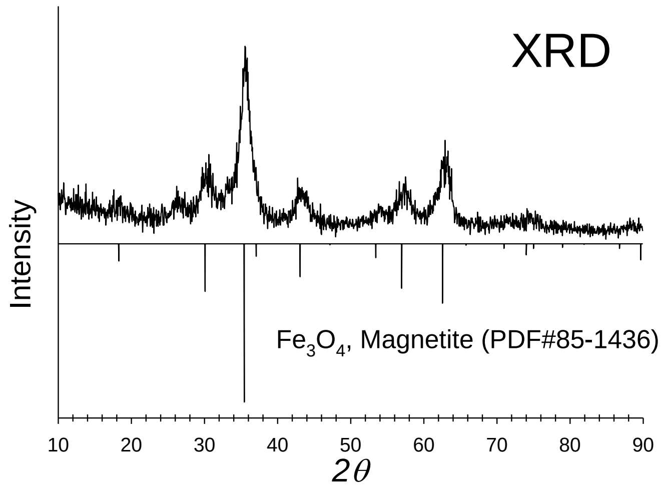
Meta

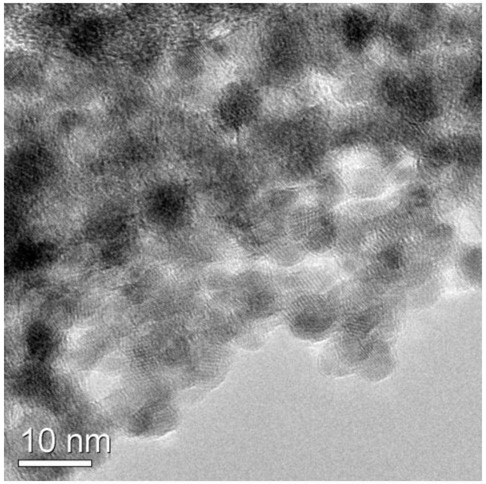
KYUS

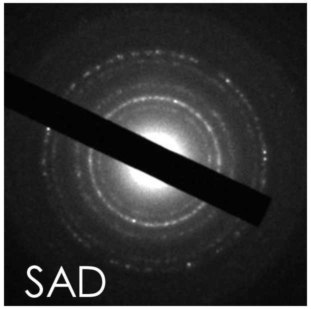
Synthesis of Magnetite Nanoparticle-Chain

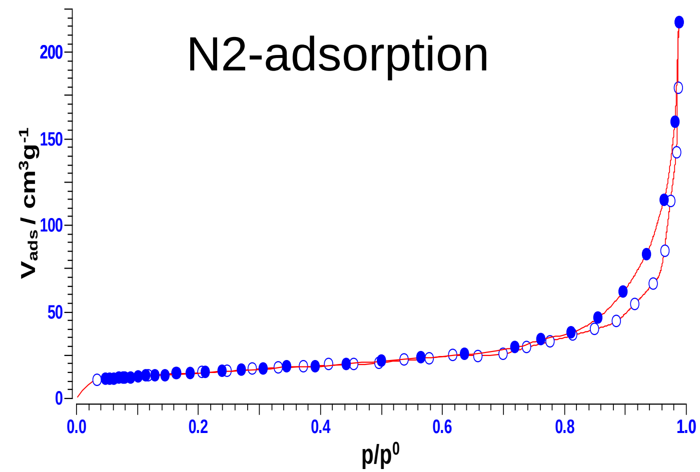
Ref.) S.Y. Lim, et al. *Carbon 2006: International Conference on Carbon, Robert Gordon College, Scotland (2006)*











New finding by us:

Platelet and herringbone CNFs are constructed by two types of sub-structural units, a ***nano-rod*** type and a ***nano-plate*** type.

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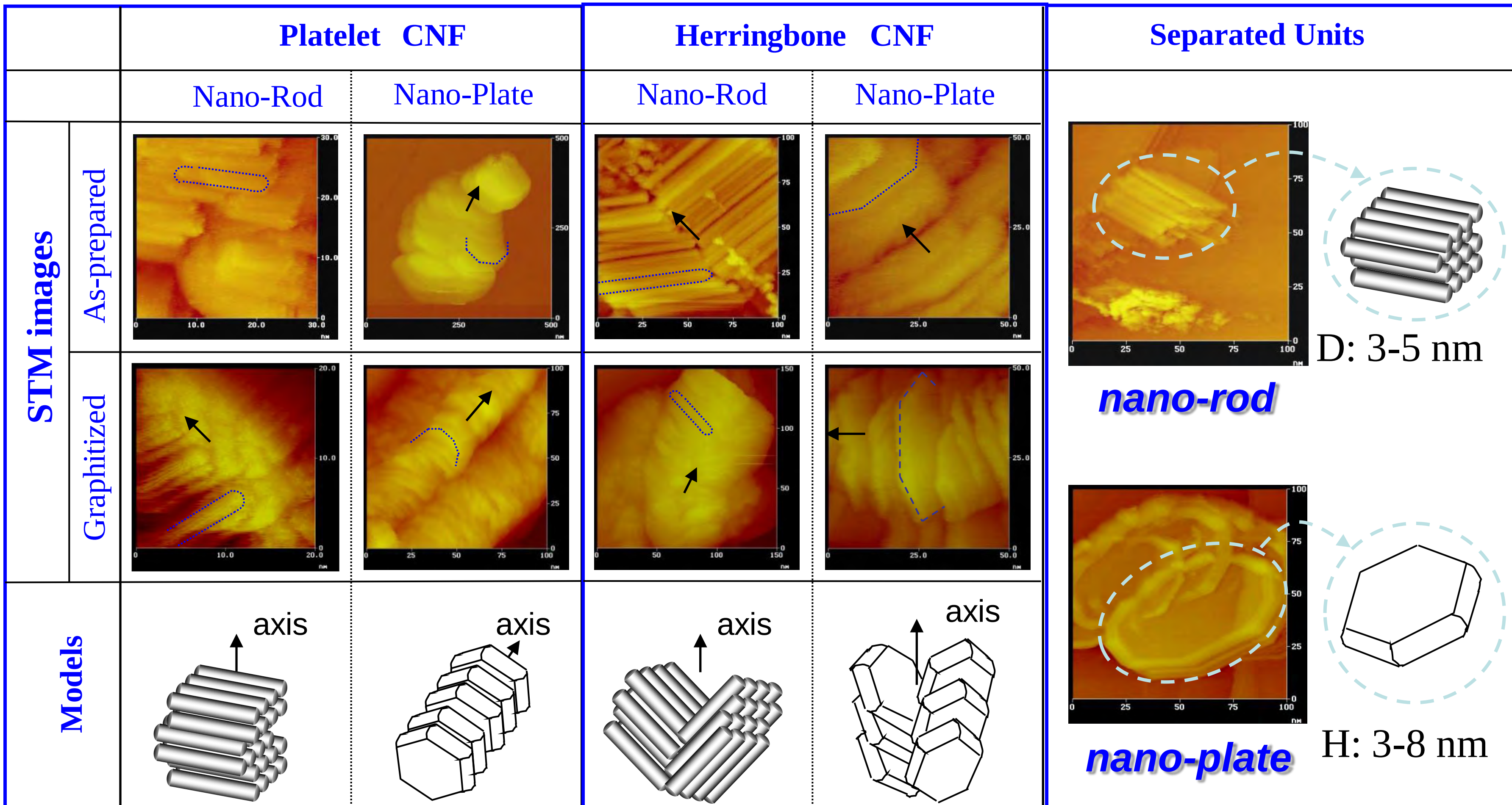


*S-H. Yoon et al., Carbon **42** (2004),3087.*
*Carbon **43** (2005),1828.*

Basic carbon nanofibers

System (Conditions)

Additives

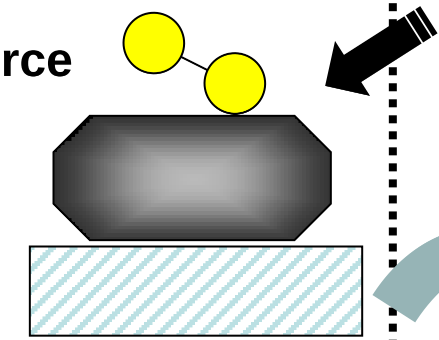
Carbon source

Interaction ↕

Catalyst

Interaction ↕

Support

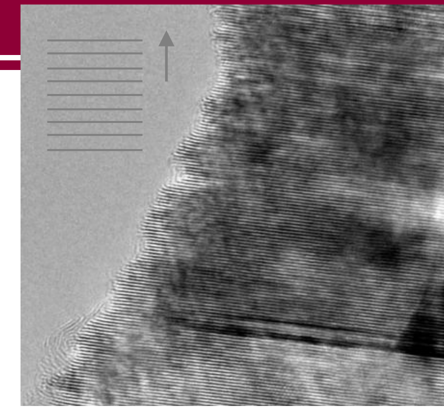


Structural Diversity of Carbon Nanofibers

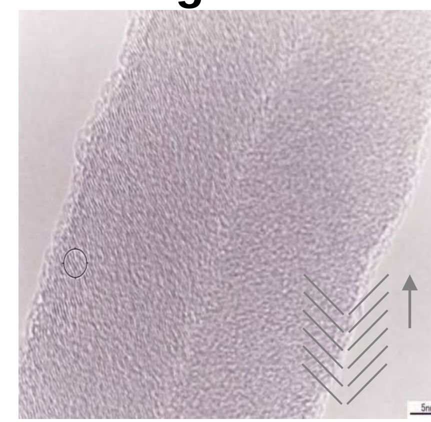
- Alignment of Graphene Layers to the Fiber Axis
- Diameter, Length
- 3-Dimensional Shape – Cross Section

Physical, Chemical, Electrical, Electronic, Surface Properties

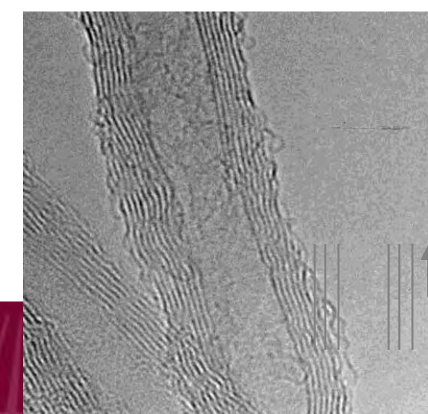
Platelet



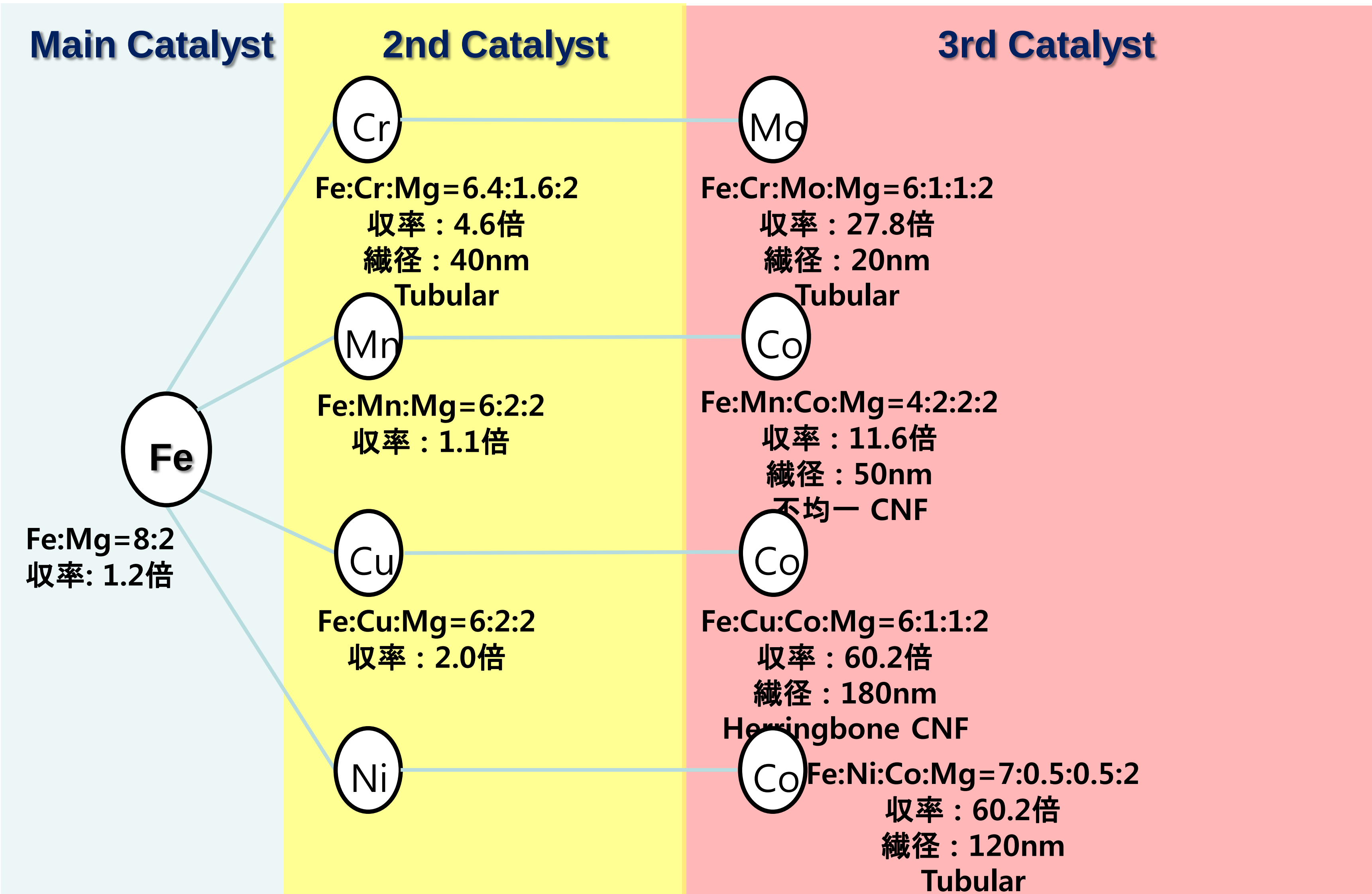
Herringbone



Tubular

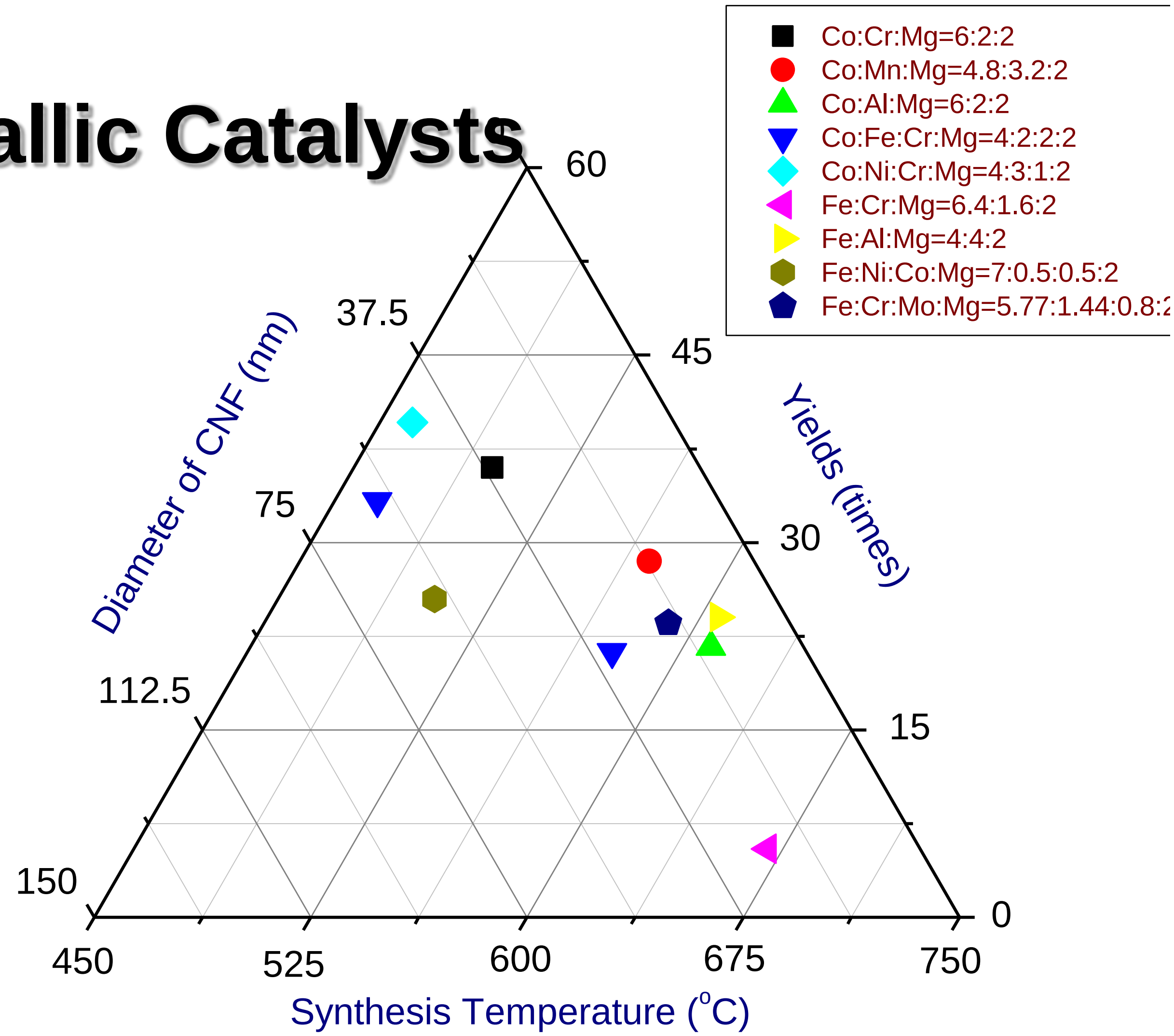


CNF (Control of structures and properties)



CNF (Catalysts)

Tri Metallic Catalysts



Background and Objective

- During last 3 decades, nano-carbons such as fullerene, CNT and graphene are important key materials in the advanced sciences and Engineerings.
- Big market based on such nano-carbons was very expected, but was hard to find.

⇒ What is the reason and how to develop a novel market?

- **For the development of nano carbon market, we suggest here the CNT or CNF composites of functional materials as an effective route for developing novel or conventional functional materials through improving the unsatisfied property of the functional material for special application.**

Concept of CNF composites

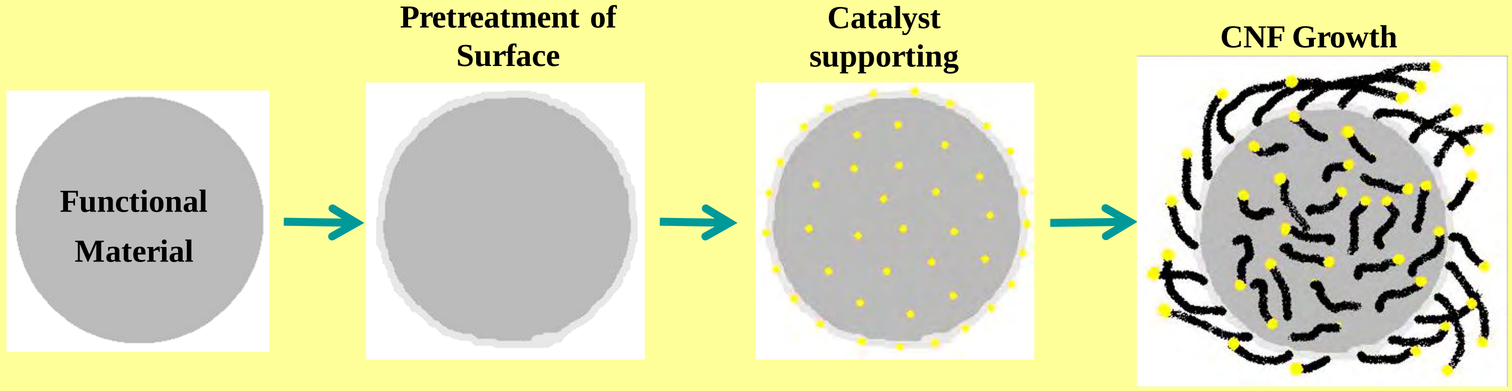
Functional Material

- Adsorption
- Support
- Electrode
- Filler
- etc.

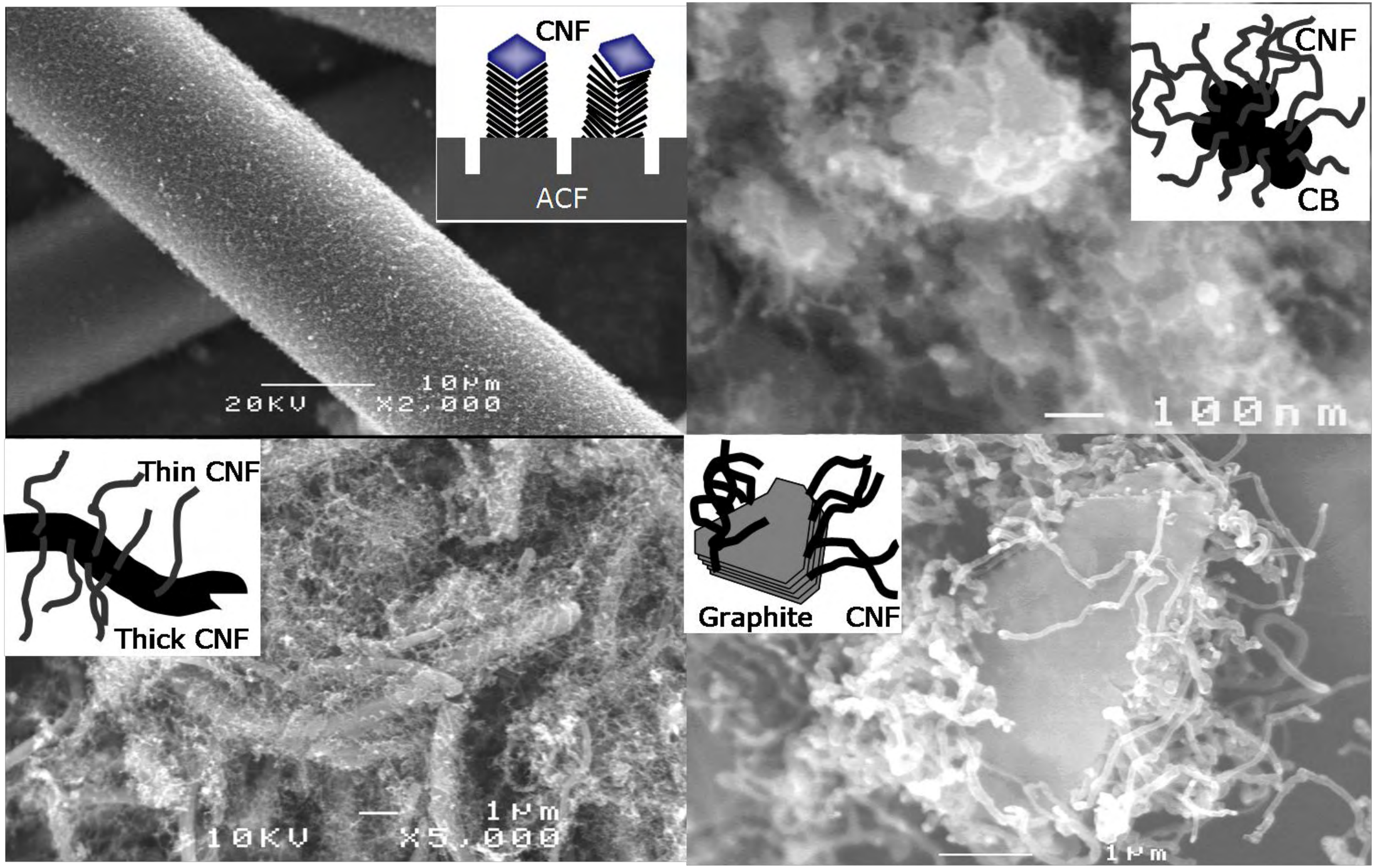
Improvement of Functions by Growing CNFs

CNF
複合化

Function improvement
Function Hybridization
Novel Function Creation



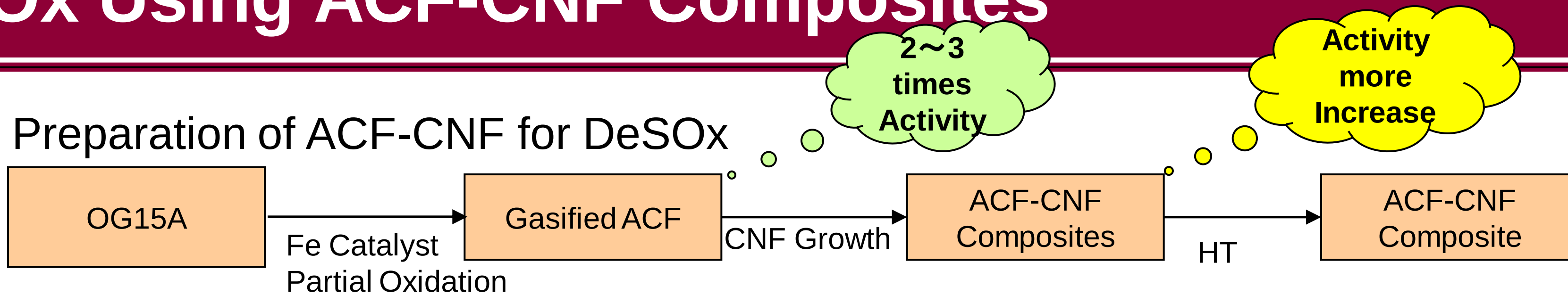
Various CNF Composites



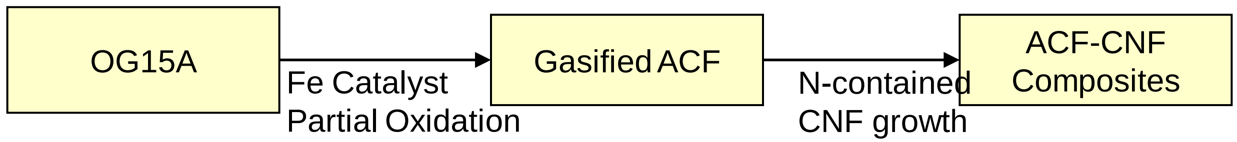
"Surface Control of Activated Carbon Fiber by Growth of Carbon Nanofiber"
Seongyop Lim, Seong-Ho Yoon, Yoshiki Shimizu, Hangi Jung, and Isao Mochida
Langmuir; 2004; *20*(13) pp 5559 – 5563

DeSOx Using ACF-CNF Composites

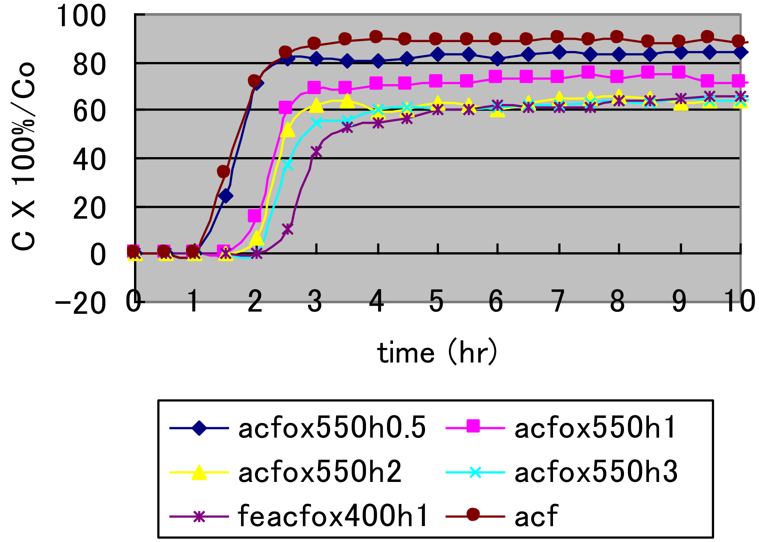
Preparation of ACF-CNF for DeSOx



Preparation of ACF-CNF for DeNOx



1.Heat treatment→ in Progress
2.MnO2→ Patent
3.CNF→ in Progress
4.Urea → Patent



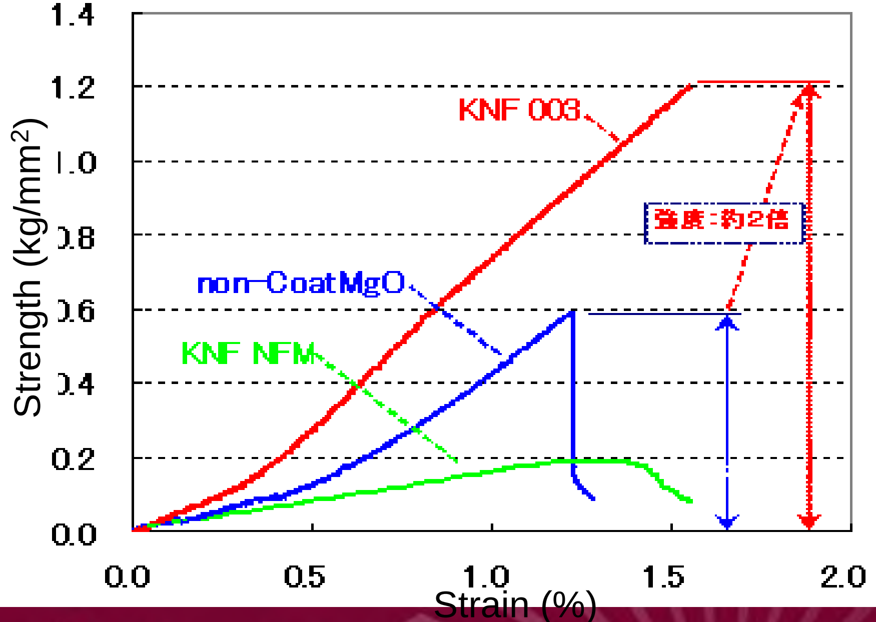
SO2 =1000ppm, acf= 100 mg. All samples were heat treated at 1100oC

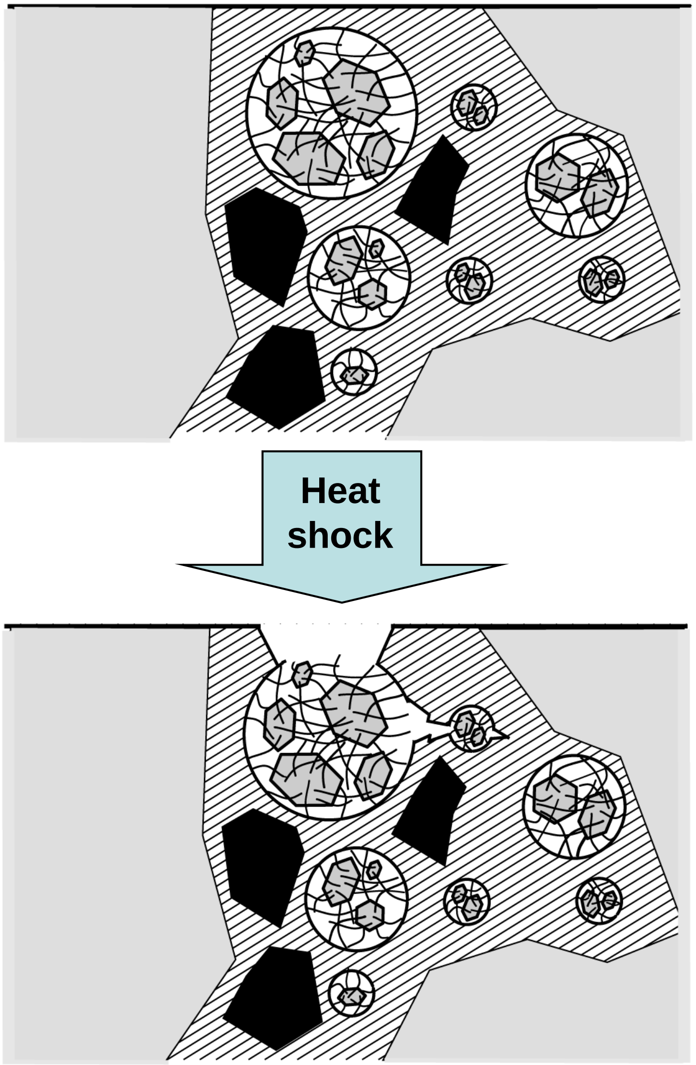
Table Surface area of CNF ACF and Yields of CNF

sample no.	reaction temp (℃)	reaction time (min)	CNF/ metal (g/g)	surface area (m^2/g)
ACF (OG15A)		–	–	1530
1% FN28 nitrate	600	5	1.6	1290
	600	20	2.5	1130
0.5% FN28 nitrate	600	5	2.4	1610
		–	–	
1% Nickelo Ferro28	600	5	6.4	1120
	600	20	8.5	840
0.5% Nickelo Ferro28	600	5	6.4	1780
	600	20	8.8	1210

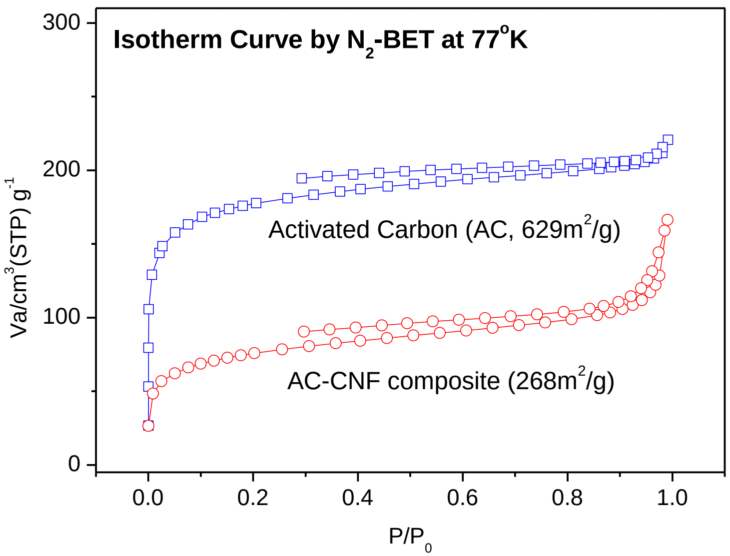
Strength of MgO refractory for blust furnace

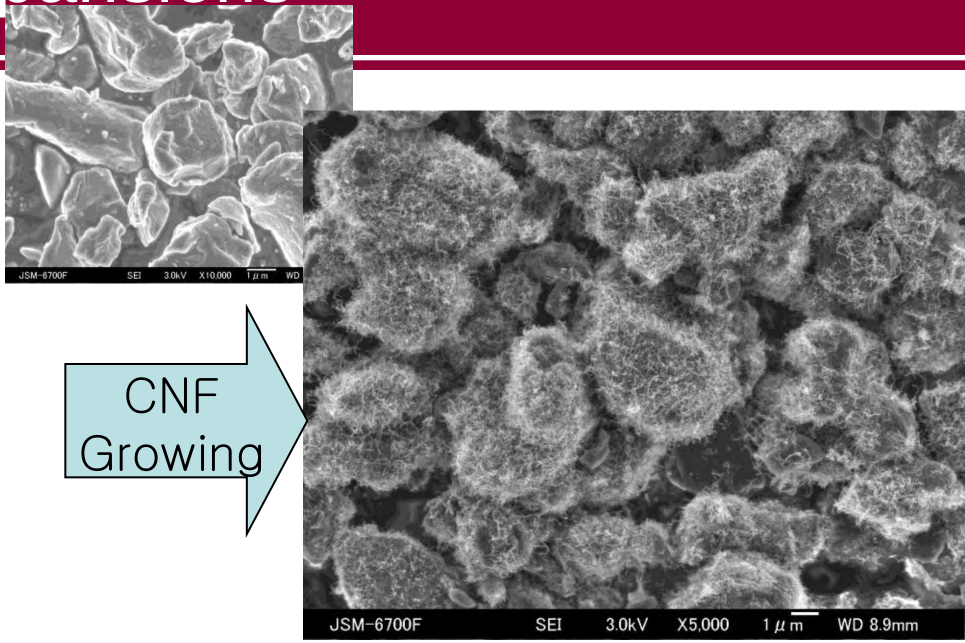
	Sample weight (g)	CNF amount (wt%)	Compositions
KNF003	70	2~5%	CNF-MgO composites
KNF NFM	70	5%	Herringbone type CNF (Diameter 5-10nm)

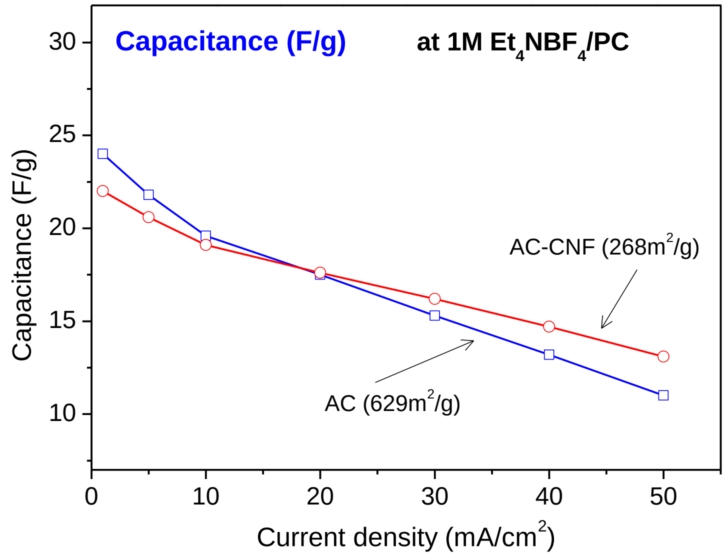




Decreasing the electrode expansions







	SA(㎡/g)	Density (g/cc)	Vol. Change(%)
AC	662	0.91	38~48
AC-CNF	271	0.92	5~9

CNF-composites for Li-ion Batteries

- **SiO, Si and Sn (SiO 2100, Si 4200, Sn 931 mAh/g) are very promising materials as anodic materials of LIB for their large theoretical capacities, however, they have poor cycle performances because of internal crack in particles caused by large volumetric expansion in charge process.**

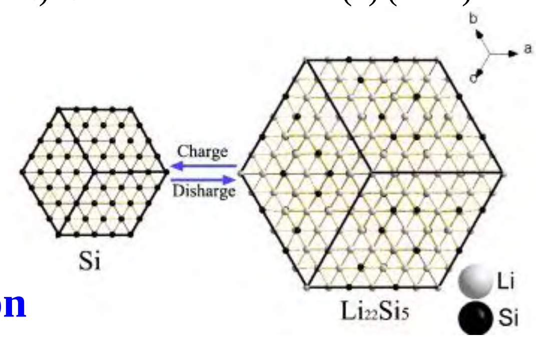
Li-Si system

Compound	Structure	Unit cell vol. (A^3)	Vol. / Si atom (A^3)
Si	Cubic	160.2	20.0
$Li_{12}Si_7$	Orthorhombic	243.6	58.0
$Li_{14}Si_6$	Rhombohedral	308.9	51.5
$Li_{13}Si_4$	Orthorhombic	538.4	67.3
$Li_{22}Si_5$	Cubic	659.2	82.4

Volume expansion (over 400%)

Ref. : A. John Appleby and et al., J Power Sources 163 (2007) 1003-1039

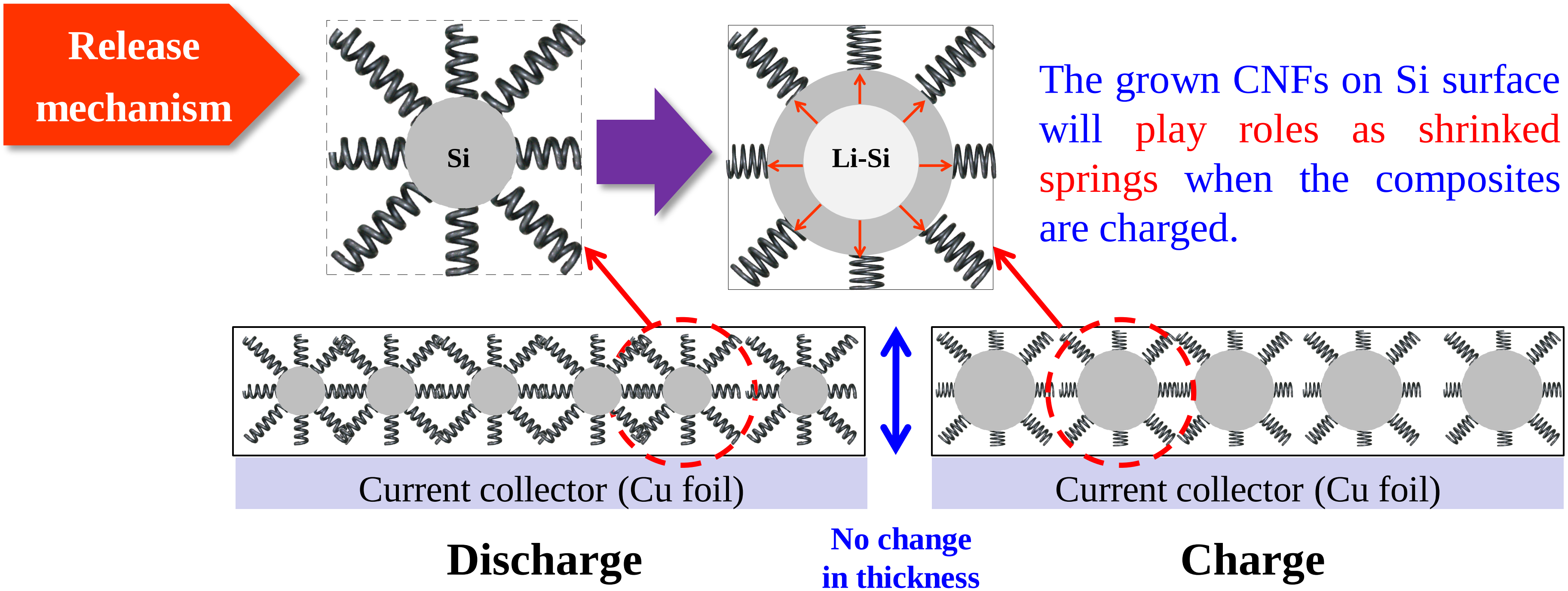
Ref.) J. Power Sources 192 (2) (2009) 644-651



Objective & principle

- **Objective, in this study, is a development of high performance anodic material using SiO, Si and Graphites for LIB.**

- **Composite with carbon nanofiber (CNF) is suggested as a solution to relieve volumetric expansion and improve cycle performance.**



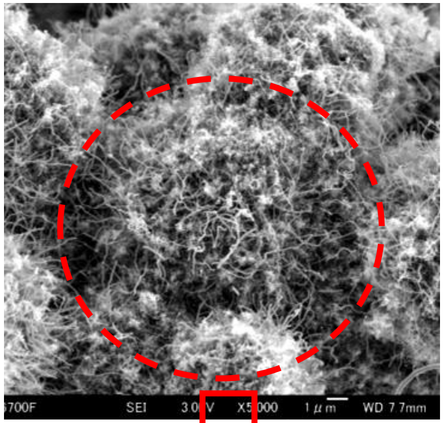
The grown CNFs on Si surface will play roles as shrinked springs when the composites are charged.

SiO-CNF composite

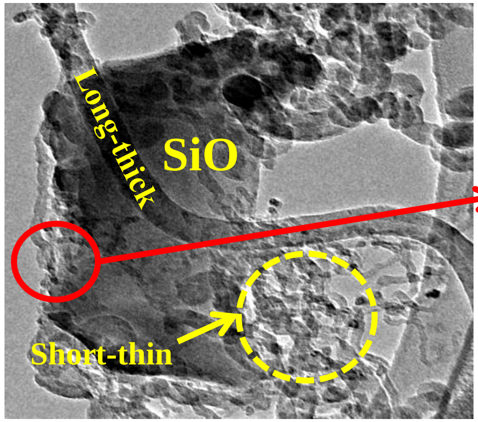
Preparation process of SiO-CNF Composite

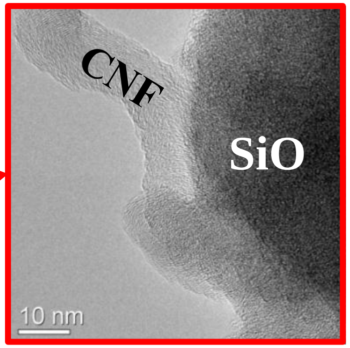
SiO particles	▪ 8 um SiO was used as a starting material. ▪ Received from Matsushita denchi kogyo.
Catalyst deposition on SiO	▪ Ni or Fe was used as a catalyst. ▪ Precursor：$Ni[(NO)_3]_2 \cdot 6H_2O$, $Fe[(NO)_3]_3 \cdot 9H_2O$
CNF growth (SiO-CNF Composite)	▪ React at 450～600℃ with C_2H_4 or CO gas ▪ Amounts of CNF : 19～128wt%
Analysis & evaluation	▪ SEM、TEM、XRD ▪ Performance test

SEM



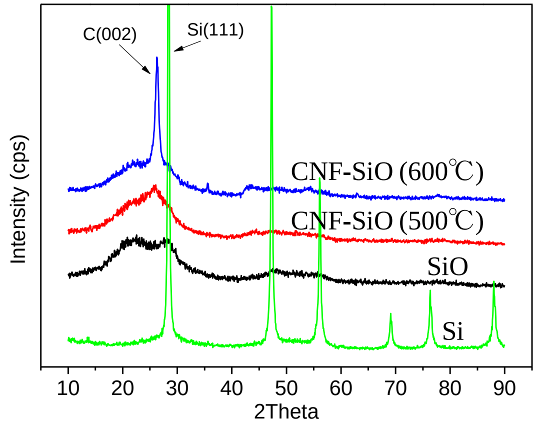
TEM



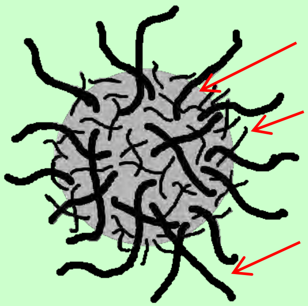


Strong adhesion bet. SiO and CNF.

XRD



Model of SiO-CNF composite



SiO particle

Short/thin CNF
（Supply conductivity to SiO surface）

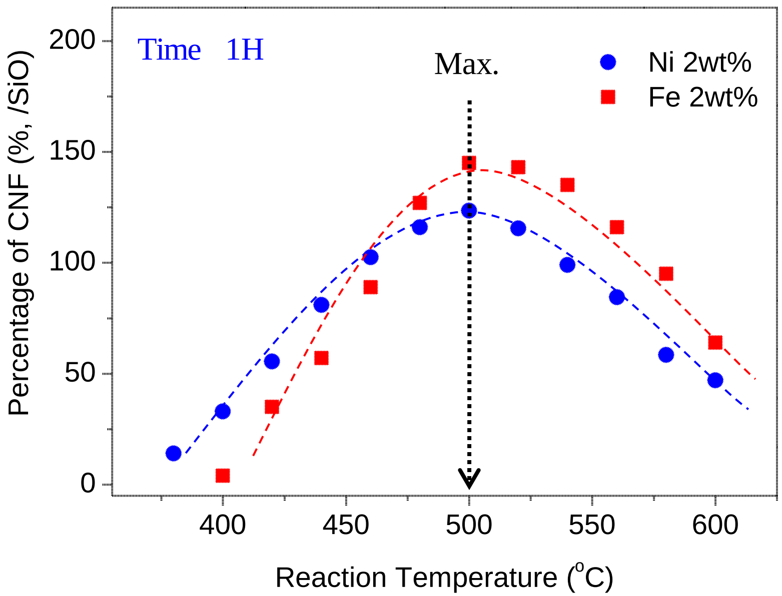
Long/thick CNF
（Supply conductivity bet. SiO particles）

- SiO showed amorphous structure.
- The higher reacting temperature increased the graphitization degree of SiO-CNF composite.
- CNF structure according to reacting temp.
  ⇒ 500℃(H-CNF), 600 ℃ (P-CNF)

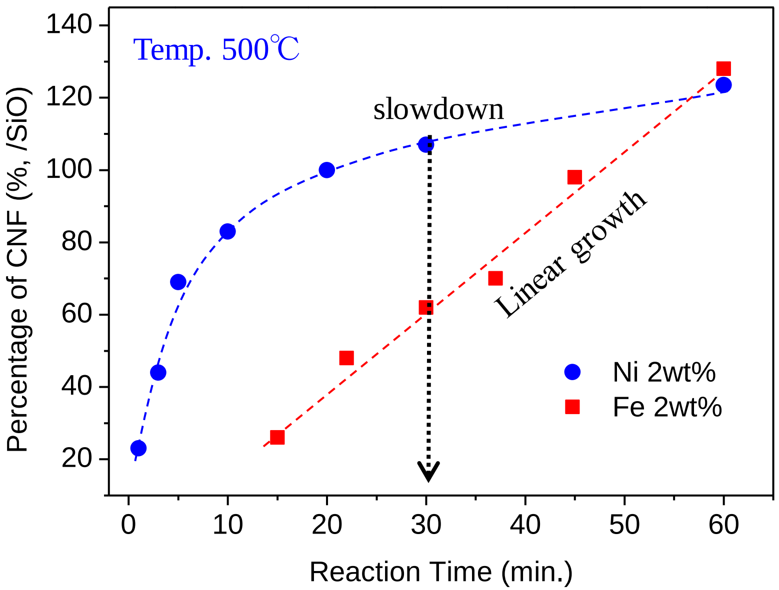
Reaction condition for CNF compositeness

$$\frac{\text{Total weight of Output}}{\text{Total weight of Input}} \text{ X } 100(\%)$$

Temp. and CNF amounts



Time and CNF amounts



- Both of Ni and Fe catalysts showed maximum amount of CNF at 500℃.

- Ni catalyst was slow down of CNF growth after 30 min.
- Fe catalyst showed a tendency of linear growth.

Cycle performance of SiO-CNF Composite

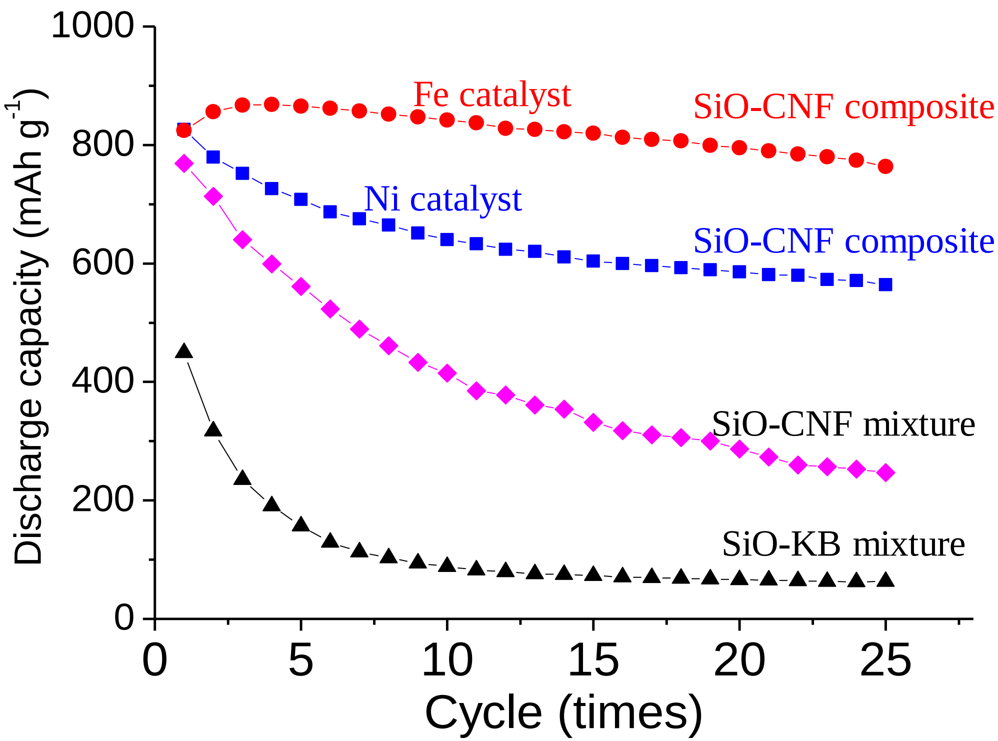
Growth & Mixing ratios

- SiO-CNF composite or mixture
  : SiO/CNF = 100/93 (wt%)
- Si-KB mixture
  : SiO/KB = 100/100 (wt%)

Test condition

- Coin cell : CR2032
- 1M $LiPF_6$/(EC:DEC, 1:1 vol%)
- Counter : Li foil (thick 0.3mm)
- Sep. : PE film (thick 16um)
- CC method at 100 mA/g

$$\frac{\text{Dcap. at 25cycle}}{\text{Maximum Dcap.}} \times 100(\%)$$



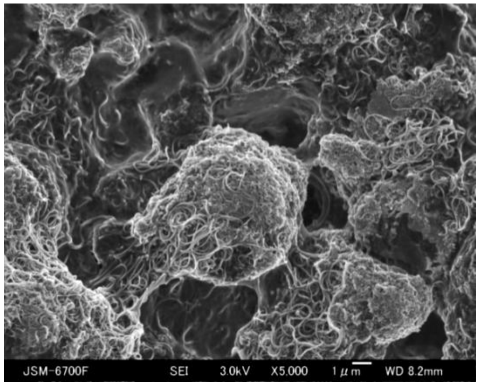
Retention ratio (%)
88%
68%
14%
32%

SiO-CNF composite showed the better discharge capacity, cycle performance and retention ratio than mixtures.

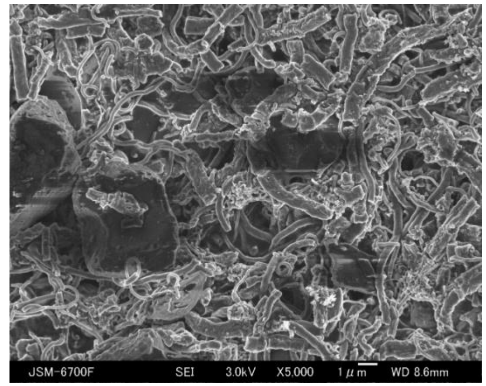
SEM of electrodes of composite and mixtures

SiO-CNF composite | **SiO-CNF mixture** | **SiO-KB mixture**

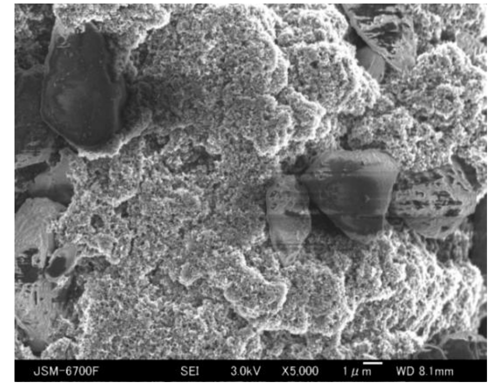
Before Cycle test



CNF covered well SiO particles

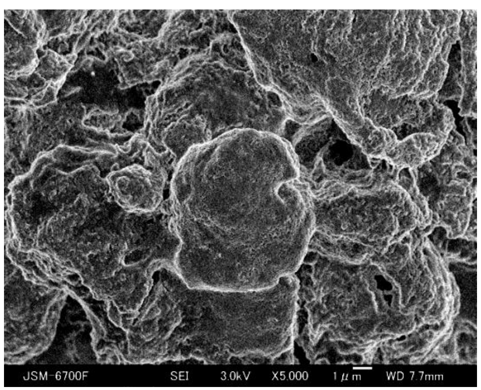


CNF & SiO were separated

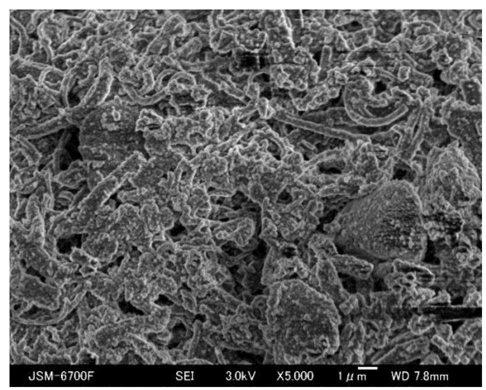


KB & SiO were separated

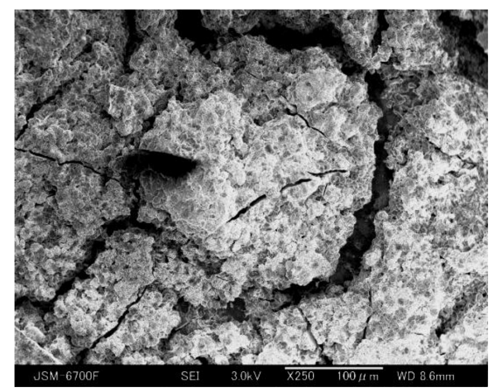
After 25 cycle



No change before and after test



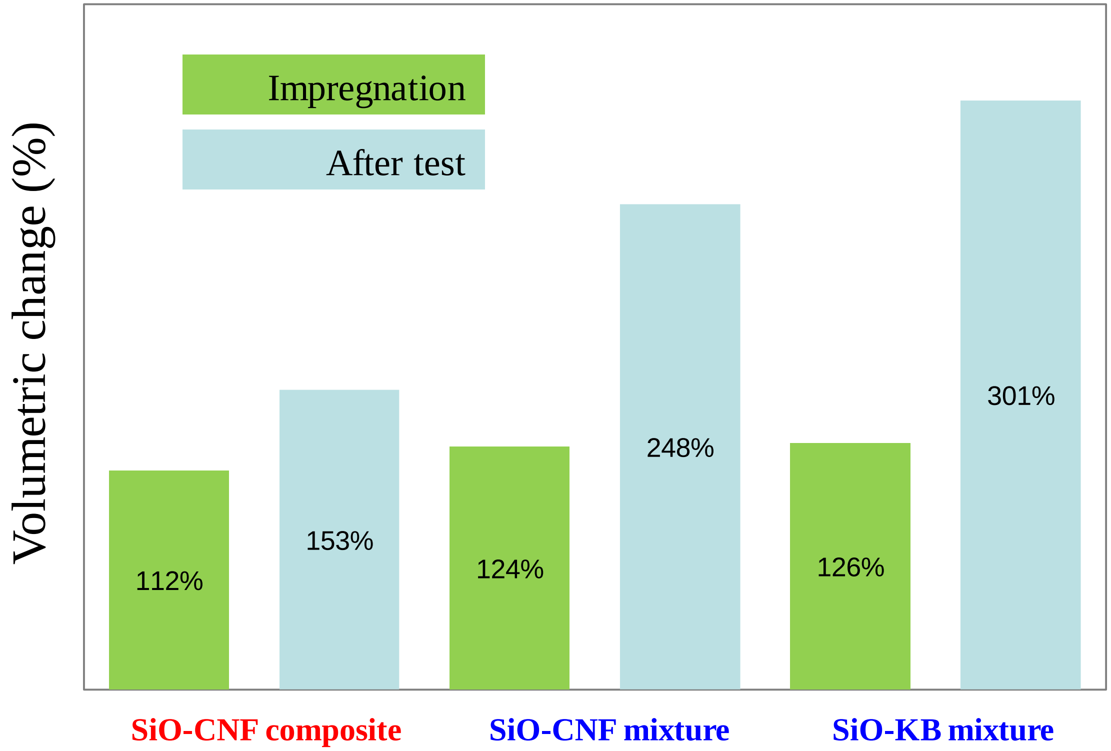
No change before and after test



Large crack was observed by cycles

Volumetric expansions of composite and mixtures

Volumetric expansion ratio was calculated from the thickness change before and after test.



Test condition

- Initial thickness of electrode
  : 46~49 um
- Coin cell : CR2032

Volume expansion

✓Impregnated in electrolyte for 3 days without ch./dis.

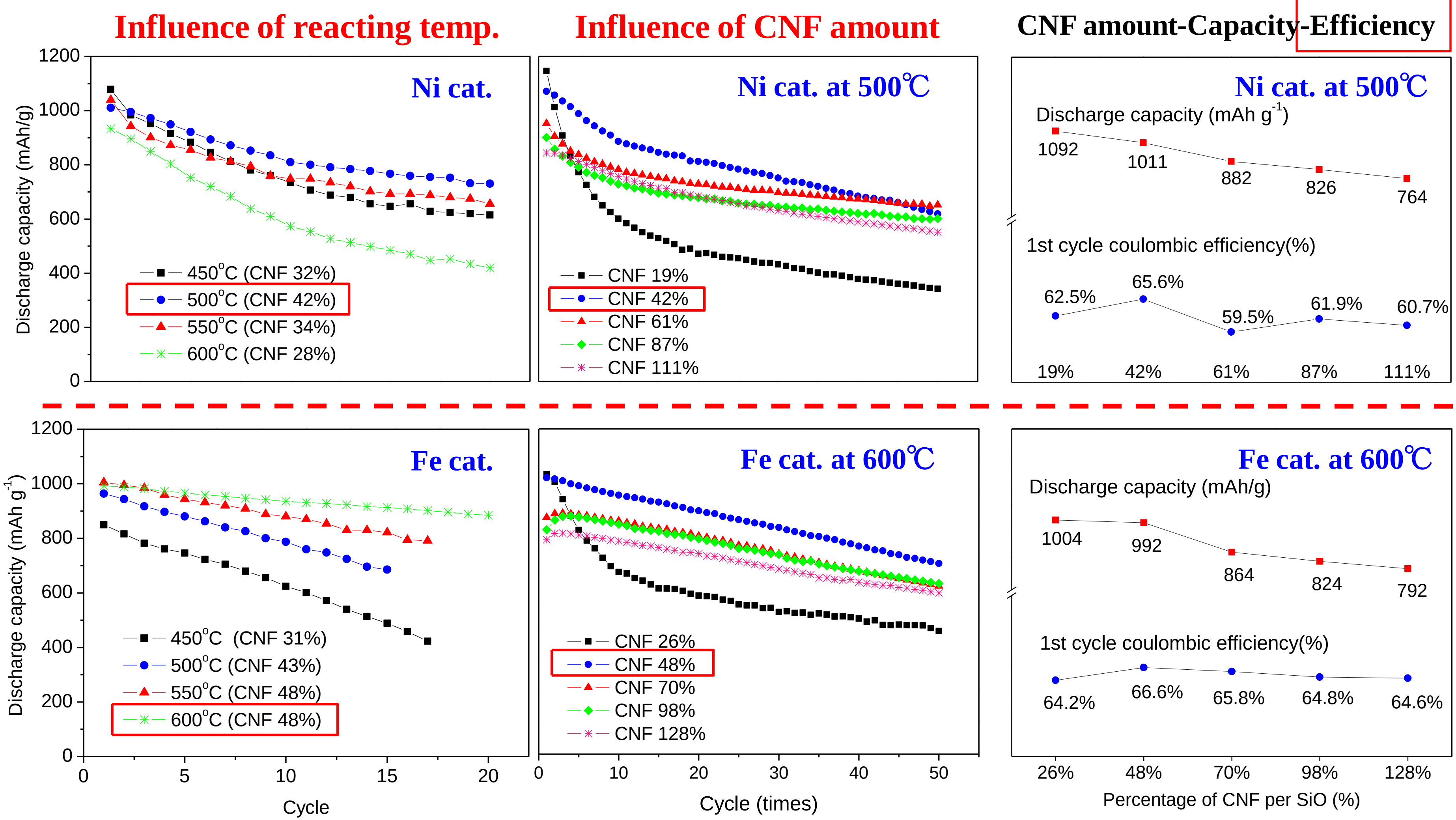
✓After test (3 cycles)

Impregnation showed almost same volumetric change in all cases, where as SiO-CNF composite was lower volumetric change than mixtures after 3 cycle test.

Cycle performances of SiO-CNF composite

Optimization of SiO-CNF composite

Dis cap. / Ch cap. x 100(%) at 1st cycle



SiO-CNF composite

◆ SiO-CNF composite showed the improved cycle performances because the grown CNF on SiO relieved volumetric expansion of electrode.

◆ The influences of prepared SiO-CNF composite

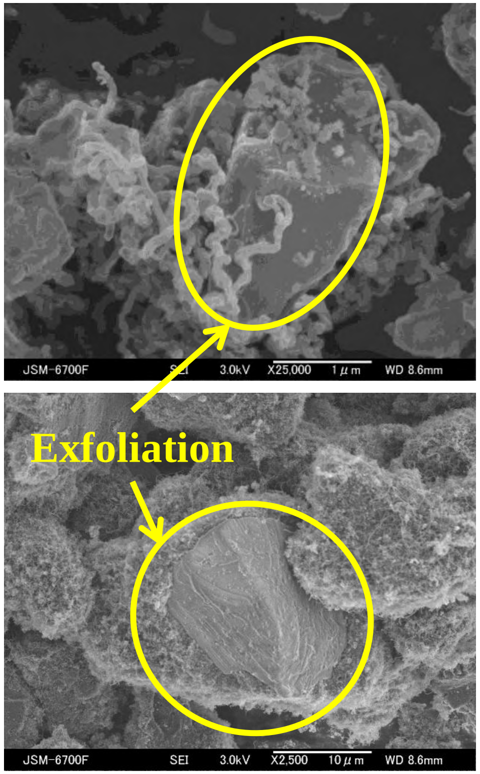
・Discharge capacities were 764～1092 mAh/g when the amounts of CNF were 40~100wt% compared with the weight ratio of SiO.

・However, initial efficiency was under 70% because of the increased surface area caused by CNF growth.

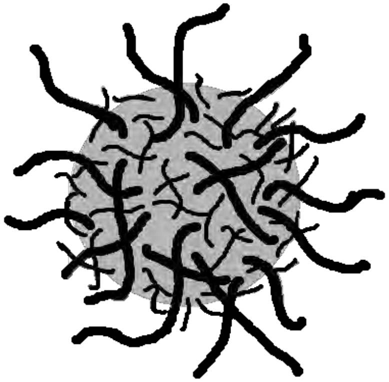
Si-CNF composite

Si-CNF composite

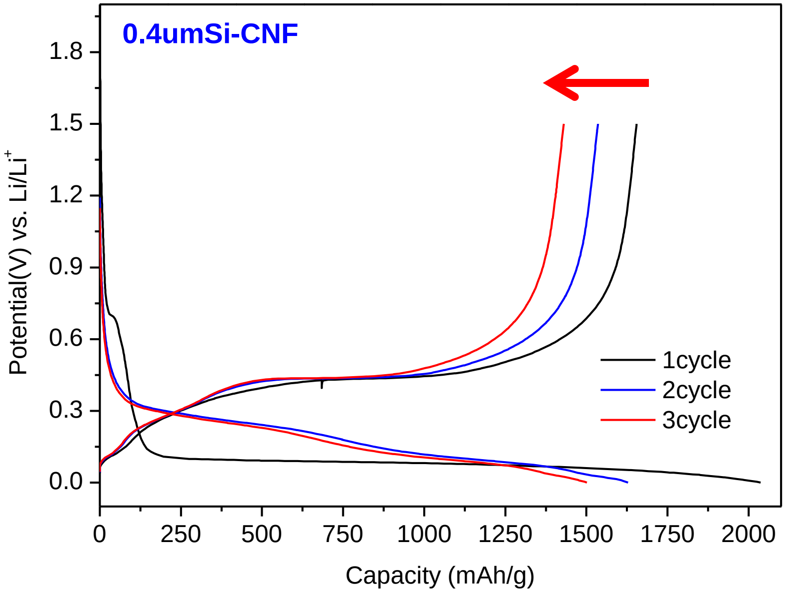
SEM



Schematic model of Si-CNF composite



Cycle performance

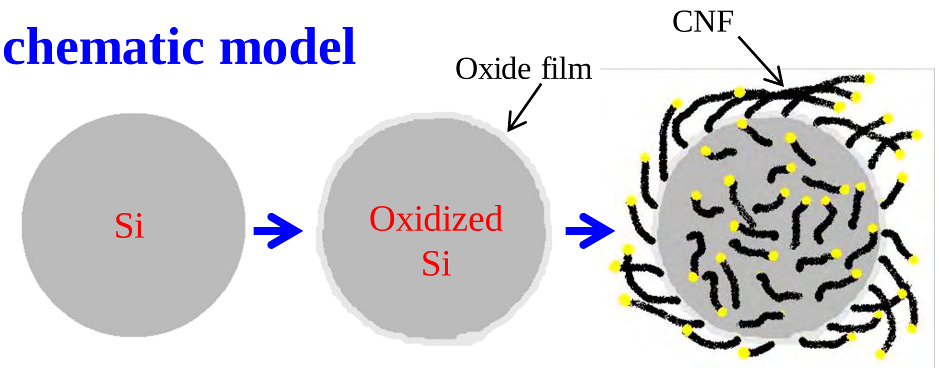


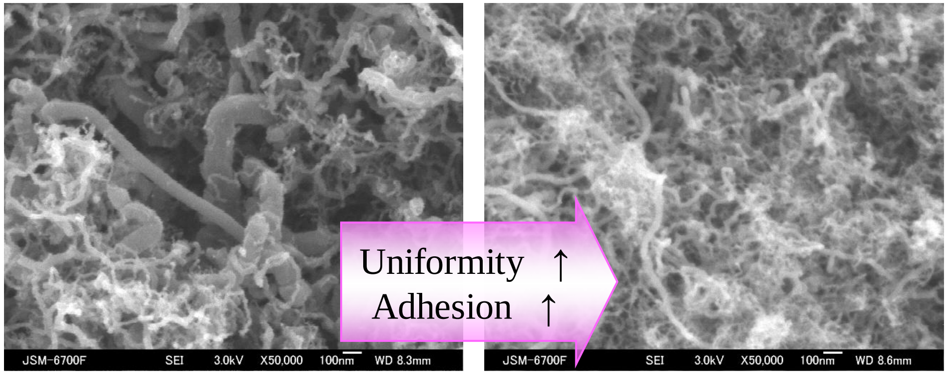
- Although CNF grown on Si particle (Si-CNF composite), Si-CNF composite didn't show improved cycle performance because CNF exfoliated from Si which had no surface acidity.

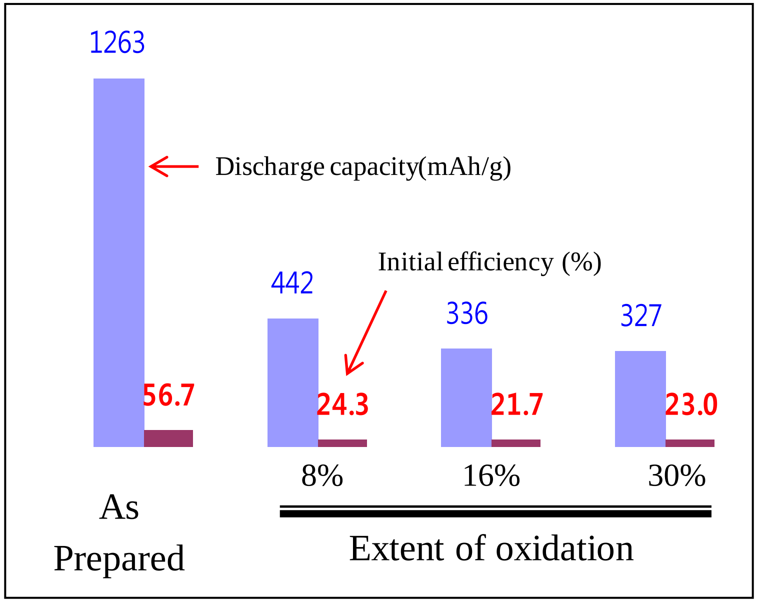
Oxidized Si-CNF composite

- To improve surface acidity, Si particle was oxidized at 700~900℃ for 3 hrs with H_2O_g.

Schematic model







Adhesive power and uniformity of CNF was improved by surface oxidized Si, where as charge-discharge performance became poor.

Composite of PC coated Si and CNF

Background

- Si is more cheap and has higher capacity.
- Si-CNF composite couldn't improve cycle performance because Si has no surface acidity such as SiO.
- Oxidized Si-CNF couldn't improve cycle performance because oxidized Si has no conductivity.

Solution

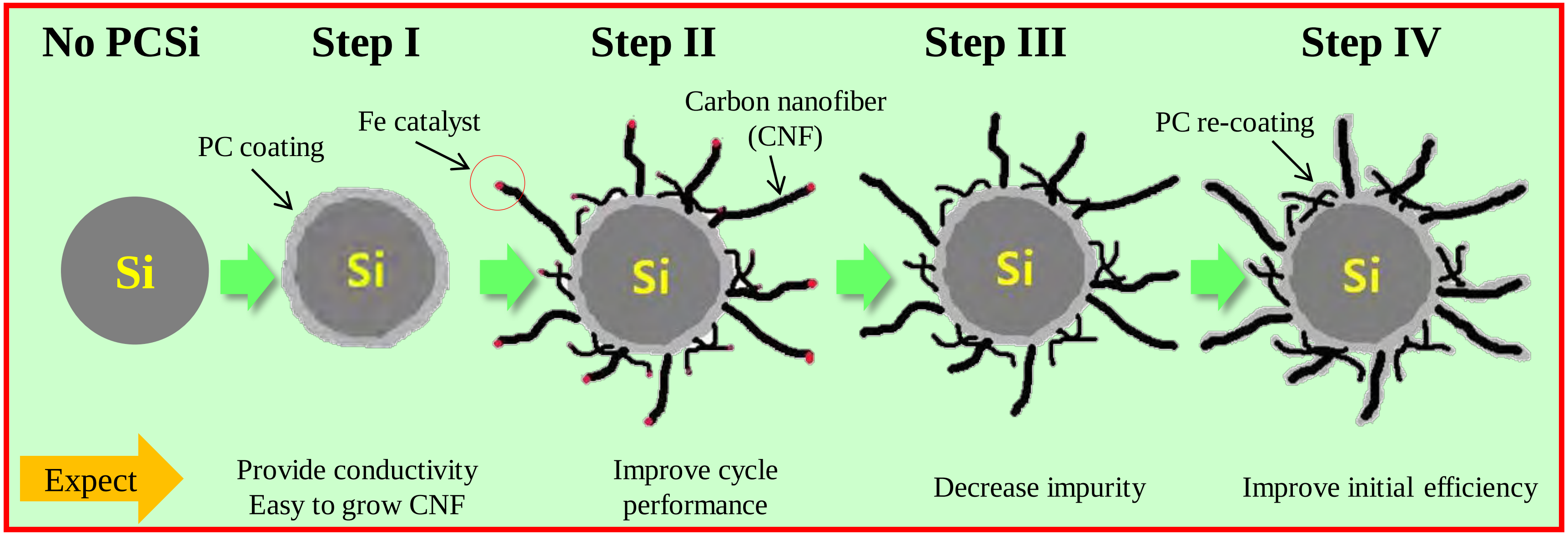
① Pyrolytic Carbon(PC) is coated on Si particle to improve Adhesion between Si and CNF (PCSi).

⇒ The coated PC provide conductivity with Si particles as well as Adhesion strength.

② CNF is grown on PCSi to improve cycle performance

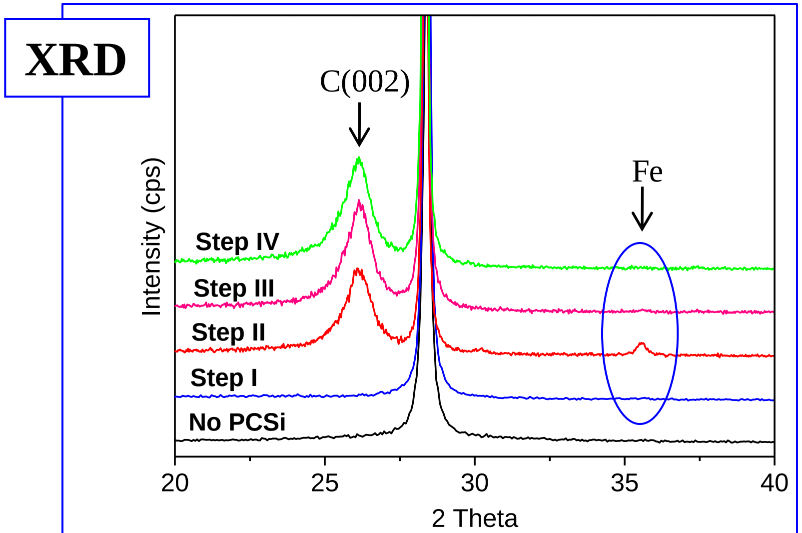
③ PC is re-coated on PCSi-CNF composite to improve initial efficiency by decreasing surface area.

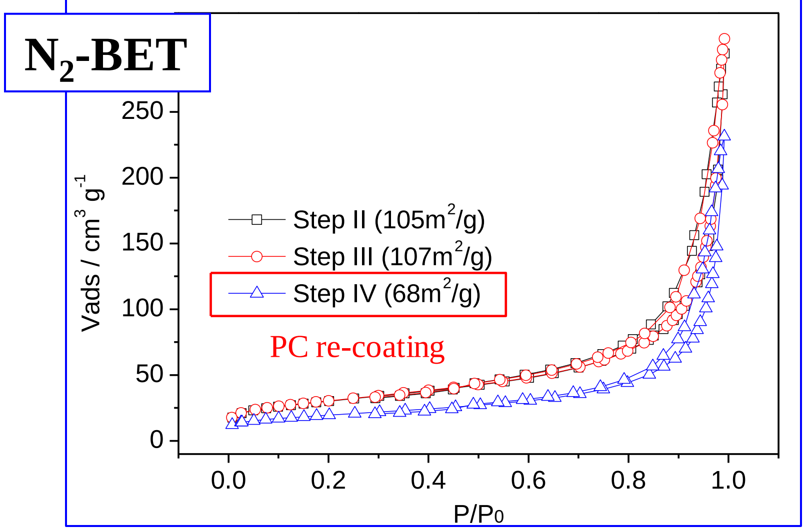
Schematic model of PCSi-CNF composite



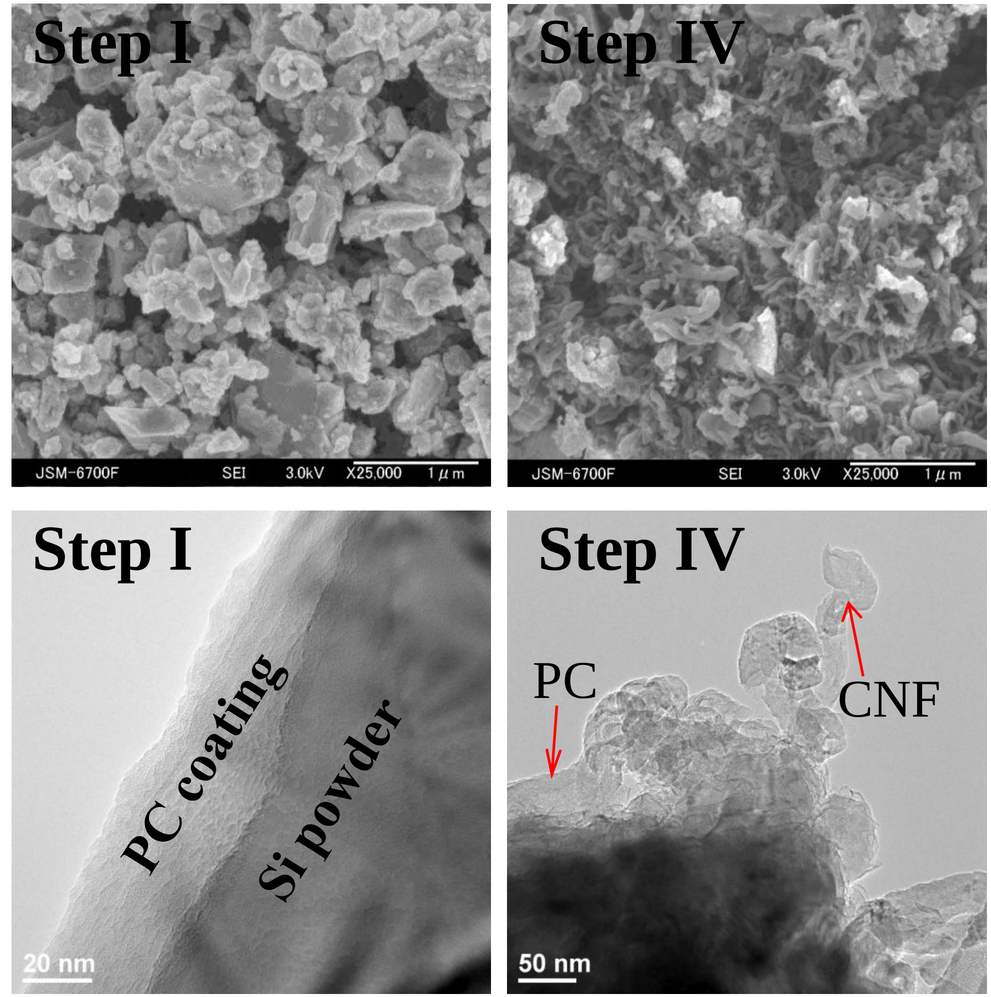
	Conditions	Results
No PCSi	0.4 um, Matsushita denchi kogyo	
Step-I	$CH_4 : H_2$, 900℃, 30 min	PC 6%
Step-II	Fe catalyst, $CO : H_2$, 600℃	CNF 93%
Step-III	10% HCl -24hr	-
Step-IV	$CH_4 : H_2$, 900℃, 30 min	PC 8%

Analysis of PCSi-CNF composite



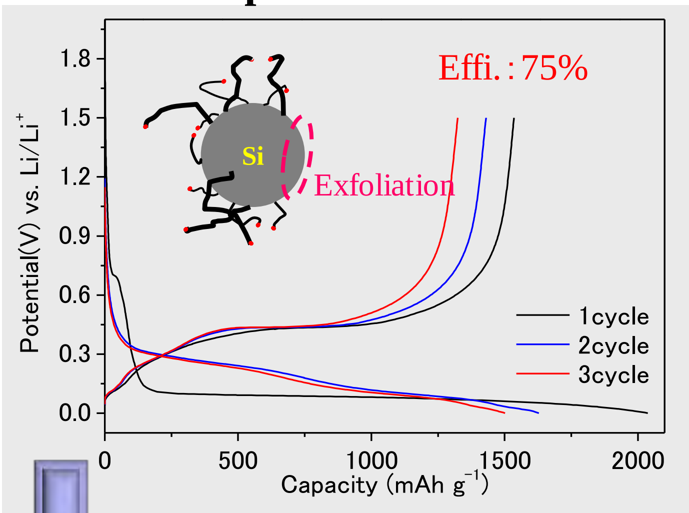


SEM &TEM

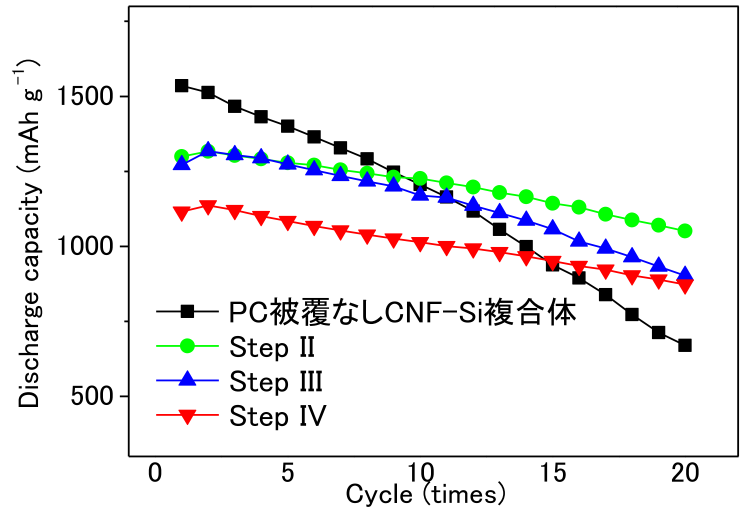


Cycle performances of PCSi-CNF composite

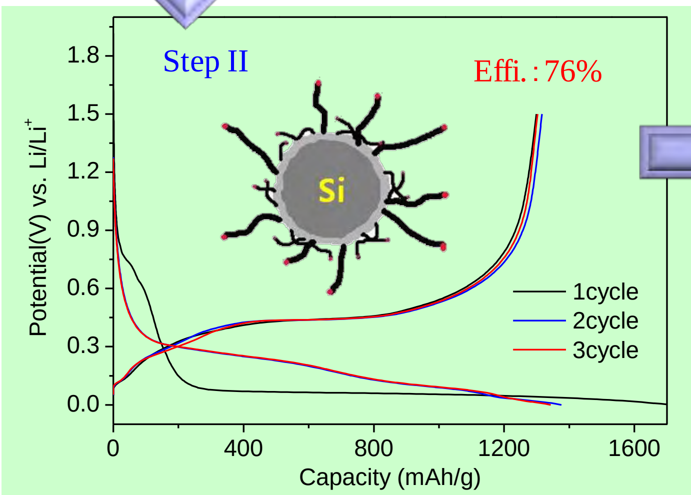
Si-CNF composite

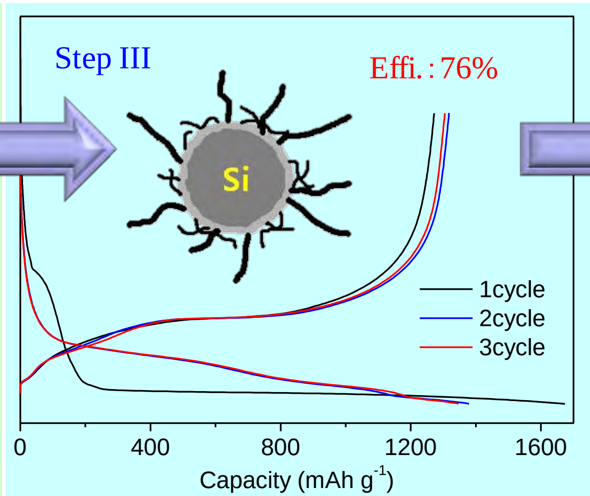


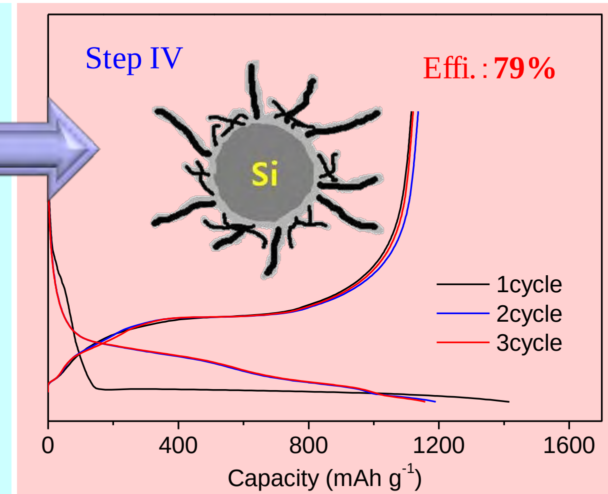
Cycle performance



PCSi-CNF | **PCSi -CNF (Fe removal)** | **PCSi -CNF (PC re-coating)**







The decreased surface area

Summary

● PC coating on Si and composite with CNF could improve cycle performance.

● PC coating on Si provide conductivity as well as Adhesion strength bet. Si and CNF.

● Cycle performance became poor by removing Fe catalyst.

● PC re-coating improved initial efficiency by decreasing surface area.

Conclusions

- CNF composites is a novel concept materials which can broaden the applications of fibrous nano-carbons.
- Conductivity and expansion properties of electrodes in battery can largely improved by the controlled growth of CNFs on the surface of electrode materials.

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Thank you for your attentions !