量子理工学概論IV
講義1

ナノカーボンの調製と
エネルギー・環境デバイスへの応用

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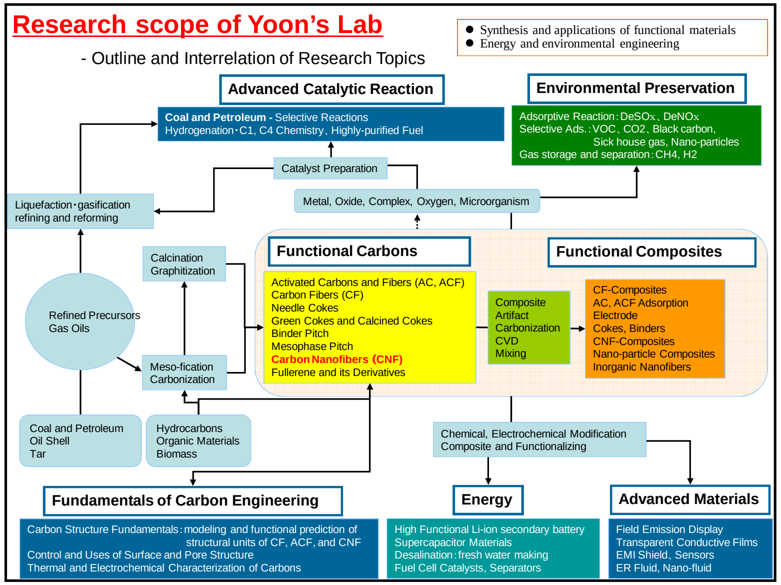
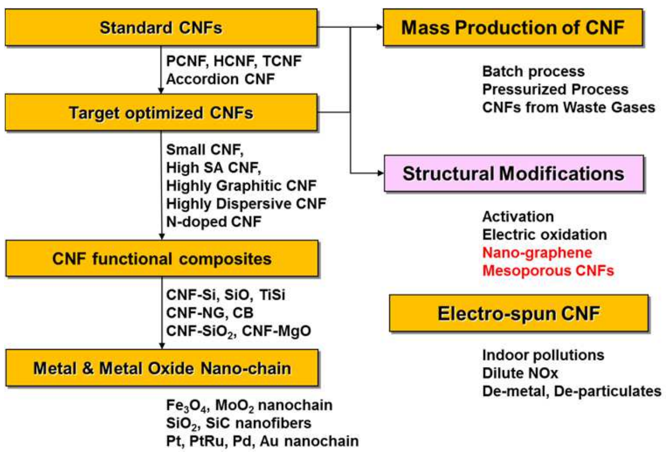


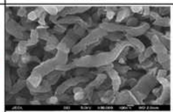
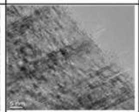
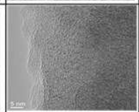
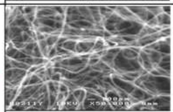
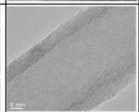
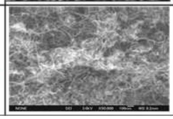
Flow chart of CNF studies in Yoon Lab



Short introduction of carbon nanofiber study in Yoon Lab

- Carbon nanofiber general
- Preparation and structural analysis of carbon nanofibers

Standard CNFs

Sample	SEM	TEM	Properties	Applications	Etc.
KNF-SPR Platelet Nano-rod			Platelet high grapht. deg. 80 ~ 400 nm, SA 90 m²/g d_{002} 3.36Å, Lc(002) 30 nm	Catalyst support	70 g//day
KNF-SH Herring-bone			Herringbone high surface area 70 ~ 500 nm, SA 150 m²/g d_{002} 3.45Å, Lc(002) 3 nm	Composite filler	100 g/day
KNF-ST Tubular Highly graphitic			Tubular thin walls, open tips high grapht.deg. 20 ~ 50 nm, SA 90 m²/g d_{002} 3.37Å, Lc(002) 13 nm	Composite filler	20 g//day
KNF-FM Tubular Small diameter			tubular, hollow 5~15 nm, 4 -7 walls	Composite filler Catalyst support	20 g/day

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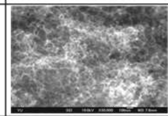
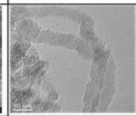
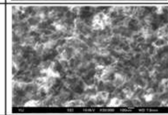
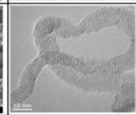
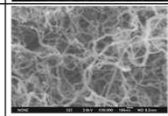
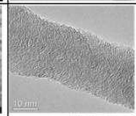
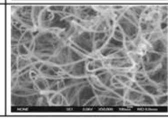
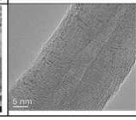
CNF (Small & Middle Diameters)

Sample	SEM	TEM	Properties	Applications	Product
KNF-CM Small Highly dispersive			**Herringbone, hollow** **7 ~ 20 nm**	**Composite Catalyst support FED**	**20-30 g/ day**
KNF-CC Small			**Herringbone** **7 ~ 15 nm**	**Composite Catalyst support**	**15-20 g/ day**
KNF-NM Middle			**Herringbone** **10~60 nm (30~40)**	**Composite Catalyst support**	**50-70 g/ day**
KNF-NF Middle linear			**Herringbone** **20 ~ 50 nm** **Straightness**	**Composite Catalyst support**	**50-70g/ day**

CARBON 42 (8-9): 1773-1781 2004

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Structural variety of CNFs

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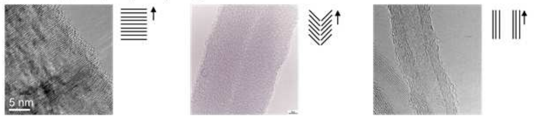
Typical classification of CNF Structure

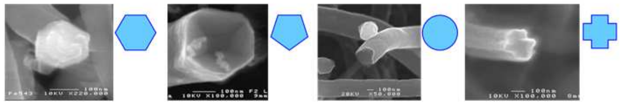
- graphene ((002) layers) alignment to the fiber axis, TEM observation



< 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

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Surfaces of PCNF

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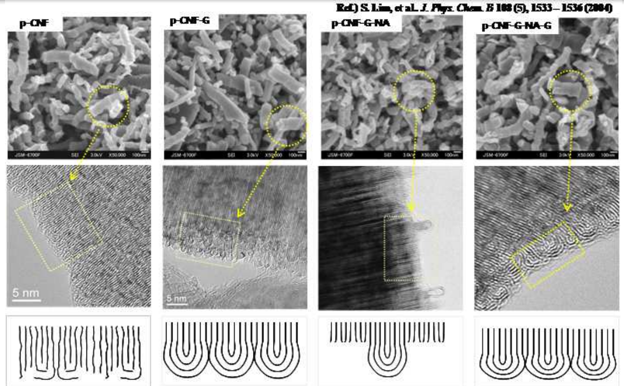
Ref.) S. Lim, et al. *J. Phys. Chem. B* 108 (5), 1533 – 1536 (2004)



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

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

Control of Graphitic Properties of TCNFs

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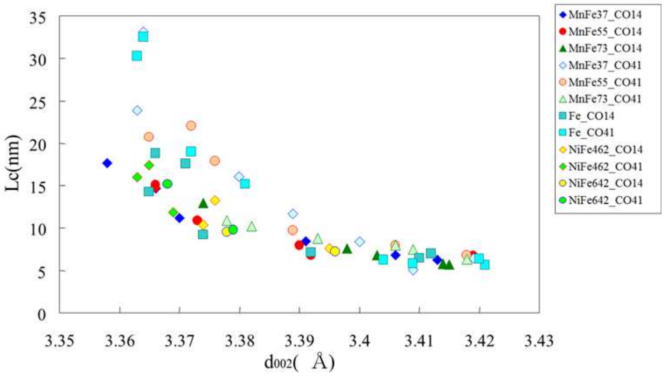

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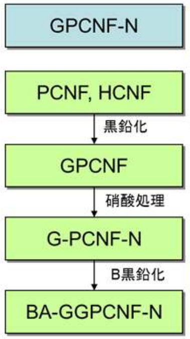
Carbon, 42, 1279-1283, 2004

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

J. Phy.Chem. C to be submitted

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Control of surface area

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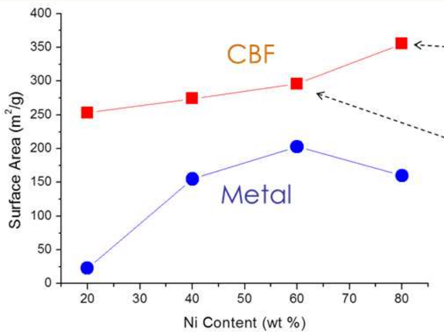

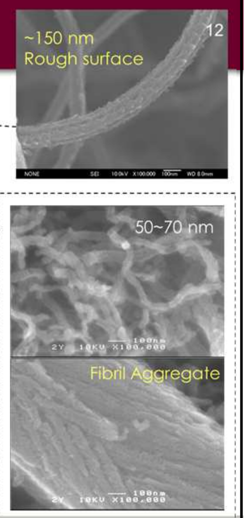

- CBF fibers 250 ~ 350m²/g, Metal fibers 20 ~ 200 m²/g
- CBF fibers shows 2~10 times higher SA than Metal fibers.
- SEM of CBF fibers with SA around 300 m²/g: small fibrils, fibril aggregate, and rough surface one like activated one.

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N-doped CNFs

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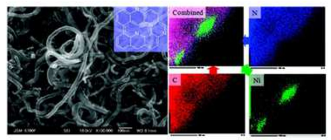
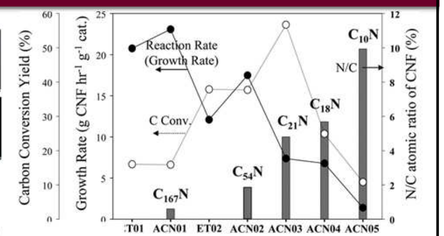
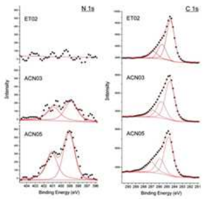




Synthesis Conditions Using Acetonitrile As the Nitrogen Source and Corresponding Sample Names

Conditions (at 530 ° C)

sample	C_2H_4 (g) mL/min	H_2 (g) mL/min	He (g) mL/min	N-source (liq.) μL/min	N/C (cal.) atom %
ET01	160	40	0	0	0.0
ET02	40	40	160	0	0.0
ACN01	160	40	0	35	4.6
ACN02	40	40	120	35	14.5
ACN03	0	40	160	35	50.0
ACN04	0	40	160	70	50.0
ACN05	0	0	200	35	50.0



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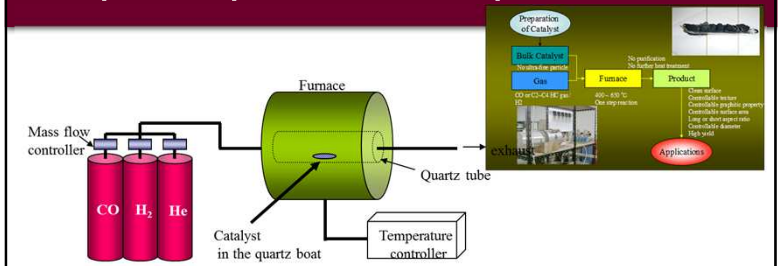
Langmuir, 25(14), pp. 8268-8278(2009)

Preparation (Fixed Bed Method)



Catalyst : Transition metals, Their alloys or supported catalyst
Catalyst preparation method : co-precipitation

1) Best, R. J. and Russell, W. W., J. Amer. Soc. 76, 838(1954)
2) Sinfelt, J. H., Carter, J. L. , and Yates, D. J. C., J. Catal. 24, 283(1972)

Reduction : H_2/He(1/9, 200sccm//4.5 cm diameter tubular furnace, 2h
Reaction : CO(C_2H_4)/H_2 (4/1 & 1/4v/v%), 200 sccm// 4.5 cm tubular furnace
Reaction Time & temperature : 1~4 hs, 400 ～ 680 ℃

Catalysts for CNF Preparation

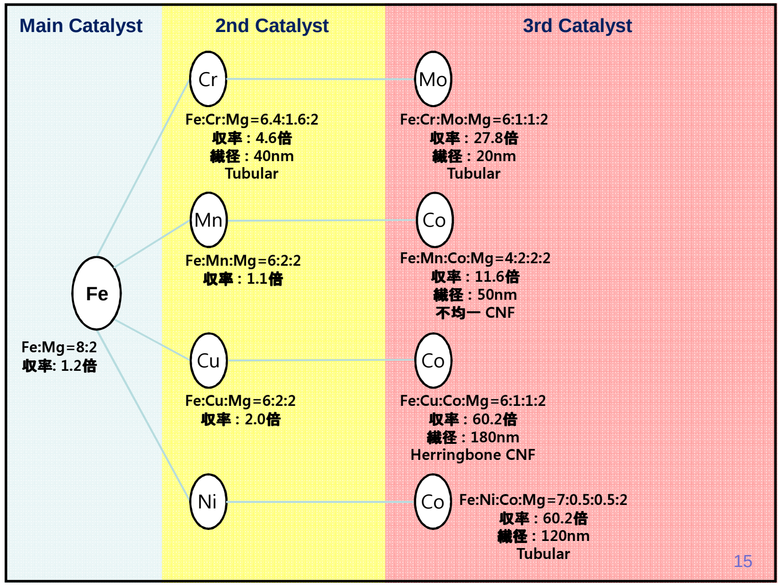
Mono-metal
- Fe, Co, Ni
- Fe, Co, Ni / Supports

Support: Alumina, Silica >>> MgO

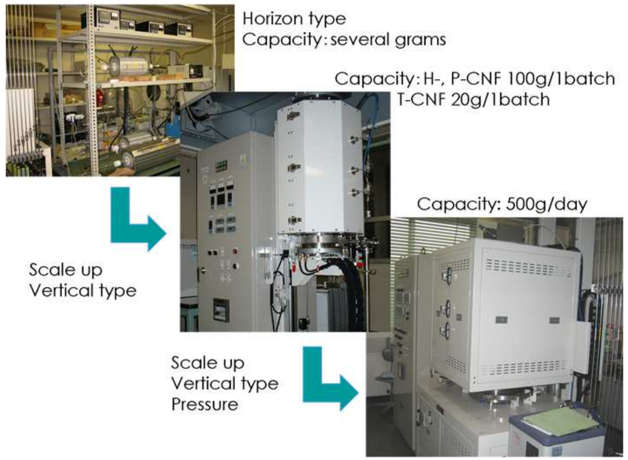
Bimetallic Catalyst
- Fe, Co, Ni / Fe, Ni, Mn, Cu, …/Supports

Trimetallic Catalyst
- Fe, Co, Ni / Fe, Ni, Cu, Mn / Cr, Al, …/Supports

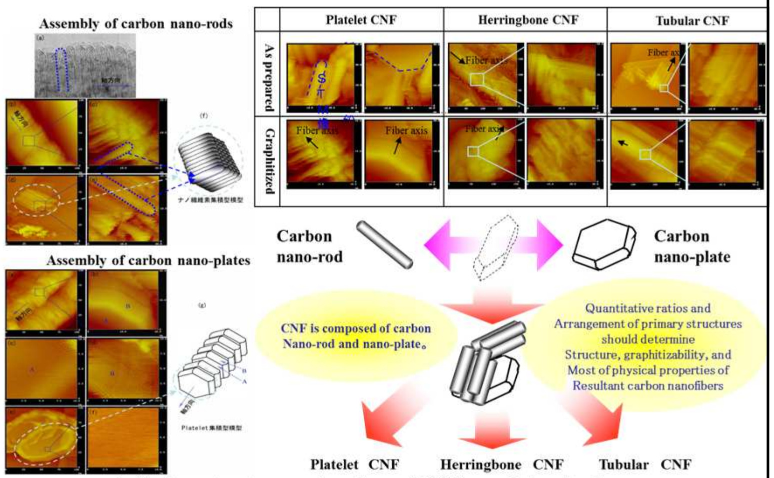
Functions of Second or Third Metals ?



Mass Production of CNFs

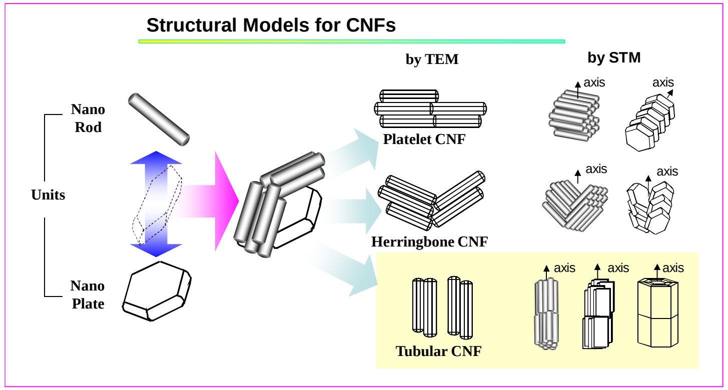


Primary Structures of Various CNFs



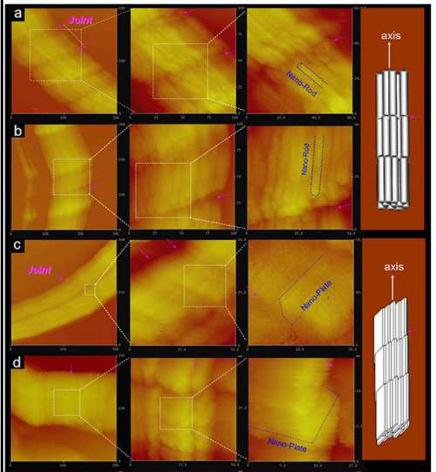
⇨ Various structures and surfaces of CNFs are determined by the arrangements of primary structural units

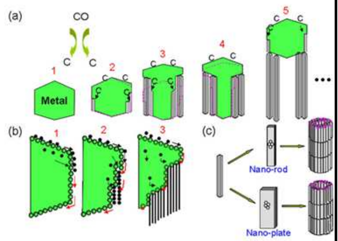
Recent new finding by us :
Platelet and herringbone CNFs are constructed by two types of structural units, a ***nano-rod*** type and a ***nano-plate*** type.



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

Schematic model of nucleation and growth process of CNTs



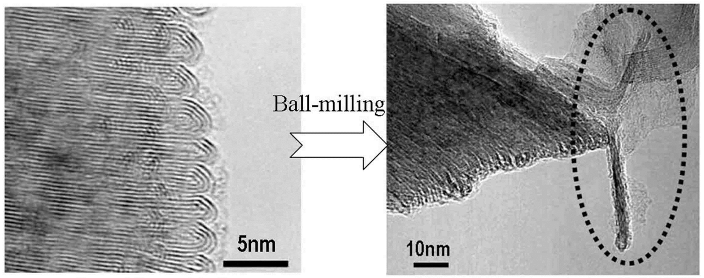


STM images of the pristine (a, c) and graphitized (b, d) carbon nanotubes, which indicate that both pristine and graphitized CNTs consist of rod (a, b) and plate (c, d) shape structural unit

Separation of structural units from CNFs
- From PCNF to Nano-graphene

Separation of structural unit (Nano-rod)

Graphitized platelet CNF

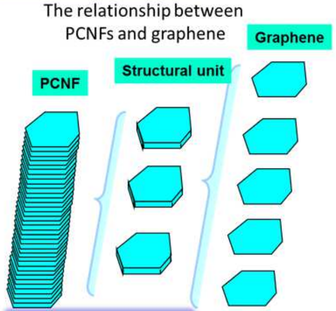


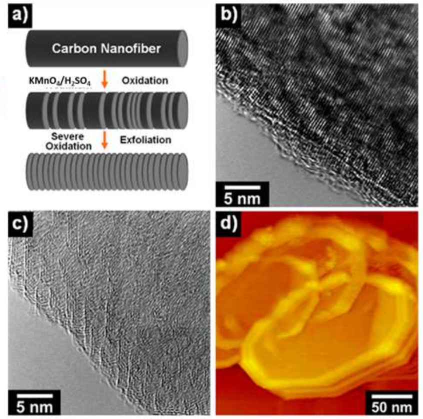
Closed Loop Ends — A Rod Unit Separated

Separation of structural unit (Nano-platelet)

Introduction

The relationship between PCNFs and graphene





Objective

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

ACS Nano **2011**, *5(8)*, 6254–6261.

CNF preparation using waste industrial gases

- Effect of poison gases: H_2S, COS
- Effect of oxidative gases: CO_2, H_2O
- Effect of different reactive gases
  - (a) C_2H_4
  - (b) CO
  - (c) CH_4

Carbon 2011 (Shanghai)

Waste Industrial Gases

Composition of gases (R.T.)

Gas	vol. %
H_2S	~ 1
CO_2	~ 8
H_2O	~ 2
(a) C_2H_4	~ 30
(b) CO	~ 24
(c) CH_4	~ 20
C_3H_6	~ 15
N-containing gases	trace

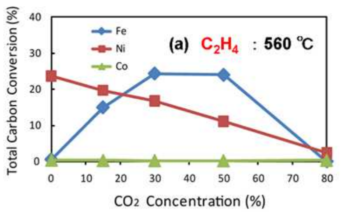
Problems

① H_2S …… Poison gas → Removal (1)

② CO_2, H_2O — Oxidative gases → CO_2 Effect on CNF growth

③ CH_4, C_2H_4, C_3H_6, CO — Different reactivity

(2) Effect of oxidative gas

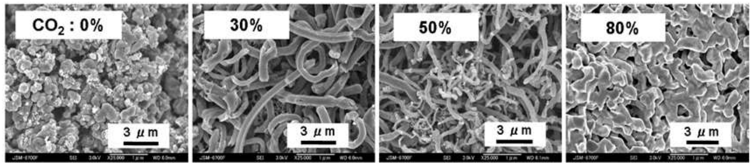


CO2 effect to carbon conversion on the various catalysts at 560 ℃

- Catalyst: Fe, Ni, Co
- Amount: 30 mg
- Gases: C_2H_4 / H_2 (1 / 1) + CO_2 (0 ~ 80%)

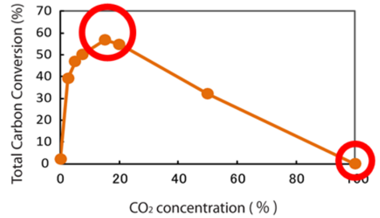
Total carbon conversion (%)

$$= \frac{\text{CNF weight (g)} \times 100}{\text{Carbon amounts of gases(g)}}$$



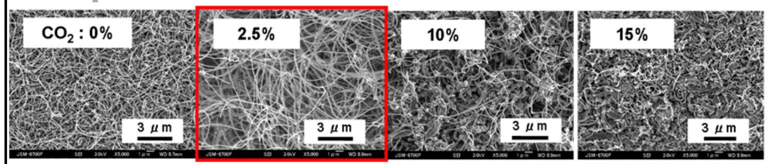
CNF images which are prepared at different amount of CO_2

Gas : C_2H_4, Catalyst : FN64, Temperature : 560℃



CO_2 Effect on the CNF preparation using FN64

- Catalyst: FN64
- Temperature: 560 ℃
- Amount: 100 mg
- Gases: C_2H_4 / H_2 (1 / 1) + CO_2 (0 ~ 100%)

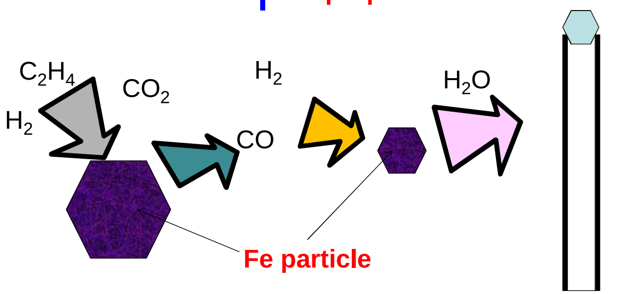


Conjectured reaction mechanism

1. Ethylene+H_2+CO_2
   → CO+CH_4+…
2. CO spillovers to Fe

1. CO+H2 to Fe surface
   → **Growth of CNF**

Disproportionation reaction



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CNFs for Battery Study

Concept of CNF composites

Selectively Grown CNF

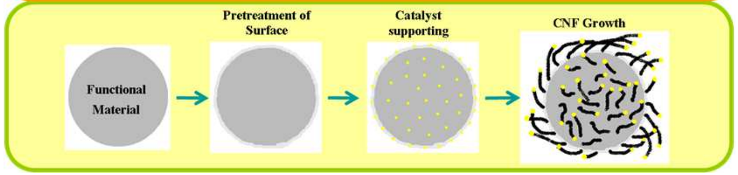
- Structure
- Dimensions
- Adhesion
- Amount
- etc.

Functional Material

- Adsorption
- Support
- Electrode
- Filler
- etc.

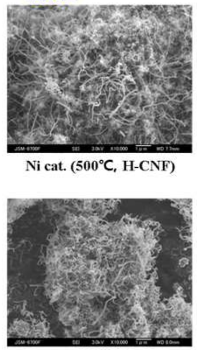
Function

- Improvement
- Hybridization
- Creation



Preparation and Analysis of SiO-CNF Composites

SEM

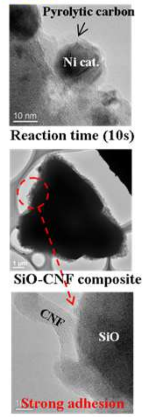


Ni cat. (500℃, H-CNF)

Fe cat. (600℃, P-CNF)

Ref: Yoon et al., Carbon 43 (9) (2005),1828-1838

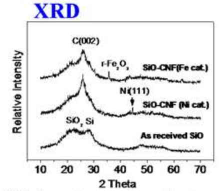
TEM



Reaction time (10s)

SiO-CNF composite

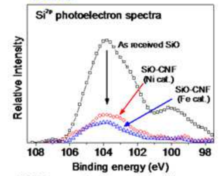
XRD



SiO showed amorphous structure

C(002) peak was observed by CNF growth

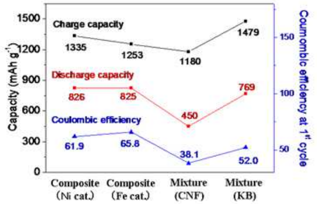
XPS



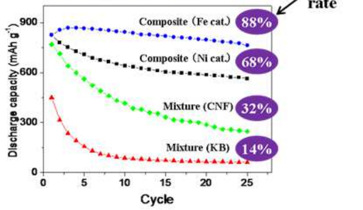
CNF growth decreases Si exposure.

Comparison *bet.* Composite *and* Mixture

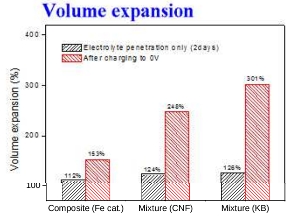
At 1st cycle



Cycle performance



Volume expansion



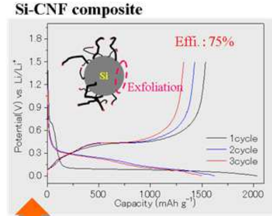
Superiority of the CNF composite

- High discharge capacity and coulombic efficiency at 1st cycle
- Excellent cycle performance
- Lower volume expansion

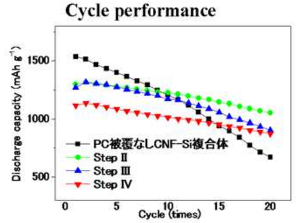
⇒ CNF growth provides spaces to relieve volume expansion and conductivities to improve performances

Cycle performances of PCSi-CNF composite

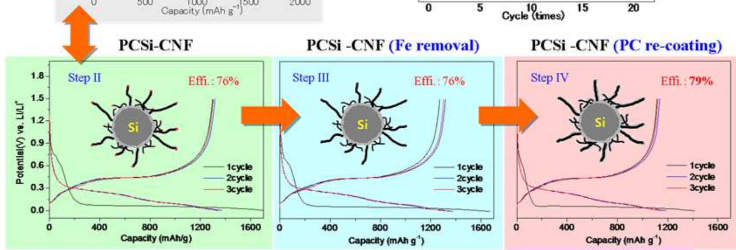
Si-CNF composite



Cycle performance

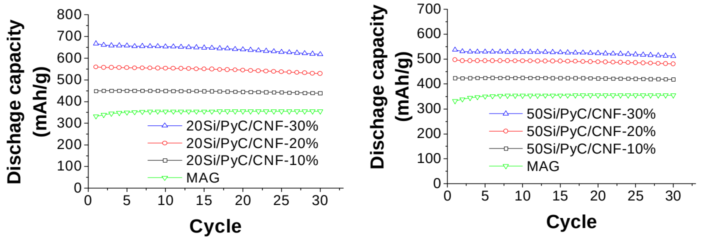


PCSi-CNF **PCSi -CNF (Fe removal)** **PCSi -CNF (PC re-coating)**



The decreased surface area

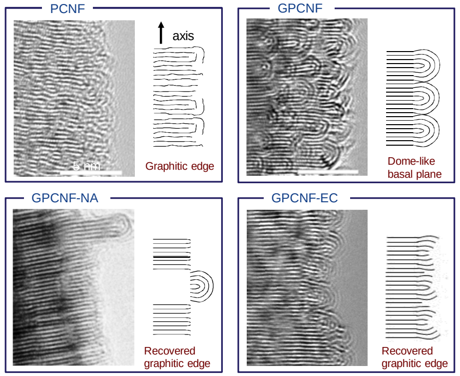
Si-CNF composite / Graphite Hybridization



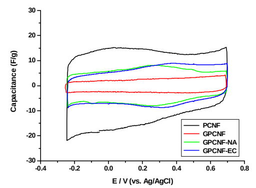
Carbon 2011 (Shanghai)

CNF for Capacitor Study

Surface-modified PCNF series



Cyclic voltammogram of GPCNF series



Elemental analysis of GPCNF series

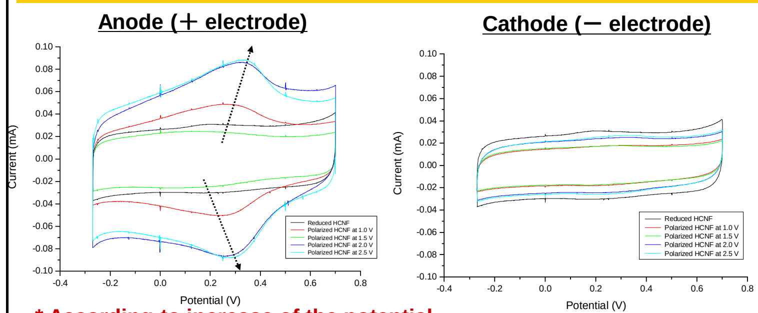
Samples	Elemental analysis (wt%)			
	H	C	N	O (diff.)
PCNF	0.33	98.15	0.05	1.47
GPCNF	0.10	99.90	0	0
GPCNF-NA	0.15	99.12	0.06	0.67
GPCNF-EC	0.13	98.50	0	1.37

Langmuir, 22 (22), 9086 -9088, 2006

Functional Groups vs. capacitance

Polarized anodic HCNF by binderless polarization condition in 30 wt% H2SO4

Polarized HCNF under binderless condition in 30 wt% H_2SO_4



*** According to increase of the potential,**

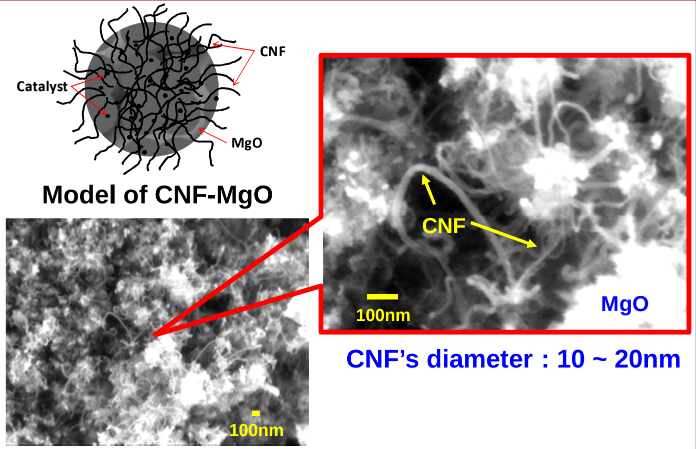
in anode, EDLC and psudocapacitane increased.
in cathode, capacitance decreased slightly.

Carbon 49 (1), pp. 96-105 (2011)

Ceramic applications

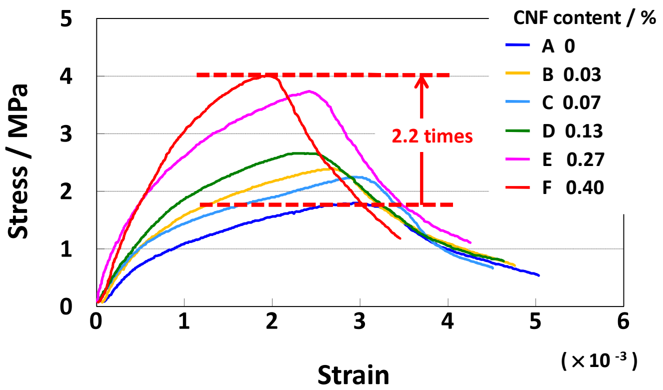
- Increasing the strength of refractory through the small amount addition of CNF-MgO composites

CNF coated MgO (CNF-MgO)



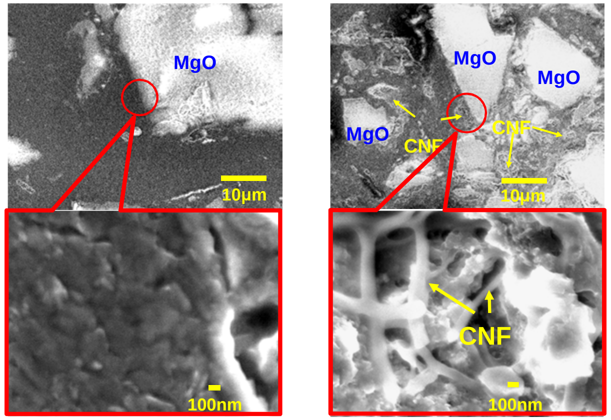
CNF's diameter : 10 ~ 20nm

Stress – strain curves



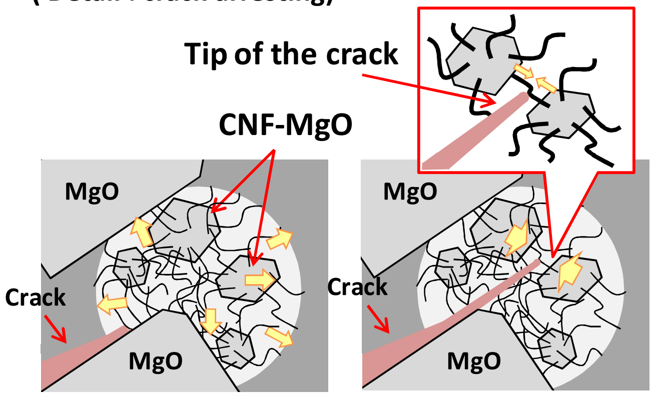
Scanning electron microscopy

Specimen A (CNF : 0%) F (CNF : 0.40%)



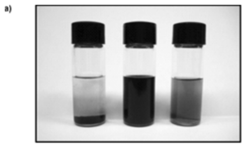
Mechanism of strengthening – Ⅱ

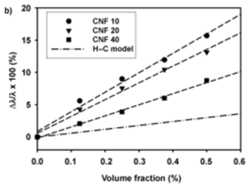
(Detail : crack arresting)



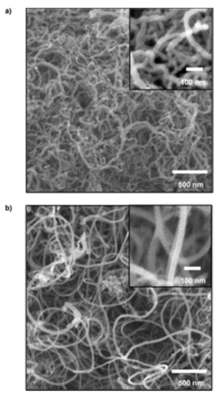
CNFs for Nanofluid

CNF AS A Novel Nanofiller for Nanofluid Applications





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

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

CNFs for Green Organic Chemistry

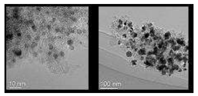
- *CHEMISTRY-AN ASIAN JOURNAL* 2 (12): 1524-1533 2007
- *JOURNAL OF SYNTHETIC ORGANIC CHEMISTRY JAPAN*, 67, 7, 724-734, JUL 2009
- *Organic Letters*, 11, 5042-5045 (2009)

Reduction Catalyst

[Organic Letters, 11, 5042-5045 (2009)]

Application for green catalyst supports

Commercial catalyst

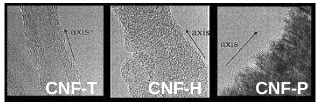


Problems of activity and selectivity

High dispersion
Size control

"Nano on nano approach

CNF: surface control

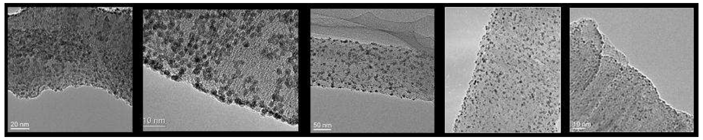


+

L_nM--CO (カルボニル錯体)

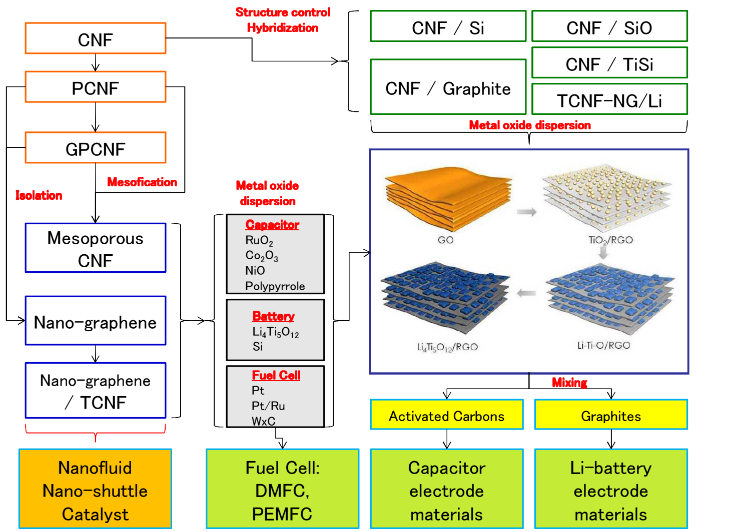
L_nM---‖ (オレフィン錯体)

Metal chelation: Thermal decomposition



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

Applications of Modified CNFs



Outline

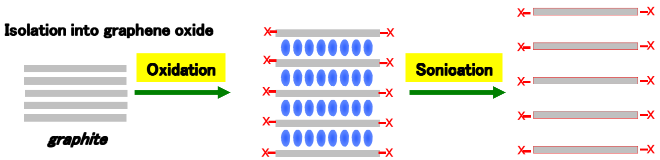
References

- Long, D.; Hong, J.Y.; Li, W.; Miyawaki, J.; Ling, L.; Mochida, I.; Yoon, S.-H.; Jang, J. *ACS Nano* **2011**, *5(8)*, 6254-6261.
- Long, D.; Li, W.; Qiao, W.; Miyawaki, J.; Yoon, S.-H.; Mochida, I.; Ling, L. *Chem. Commun.* **2011**, *47(33)*, 9429-9431.
- Long, D.; Li, W.; Qiao, W.; Miyawaki, J.; Yoon, S.-H.; Mochida, I.; Ling, L. *Nanoscale* **2011**, *3(9)* 3652-3656.
- Long, D.; Li, W.; Miyawaki, J.; Qiao, W.; Ling, L.; Mochida, I.; Yoon, S.-H. *Chem. Mater.* **2011**, *23(18)*, 4141-4148.

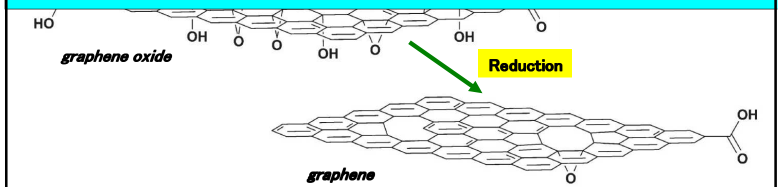
1. Preparation of graphene discs

Chemically derived graphene *via* exfoliation and reduction

(1) Isolation into graphene oxide

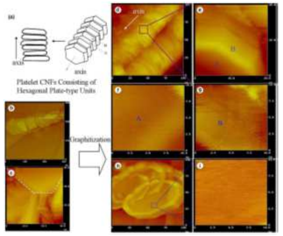


The chemical reduction method is a suitable approach to producing graphene sheets in bulk quantity at relatively low cost.
However, preparation of graphene with defined shape is still a challenging work.



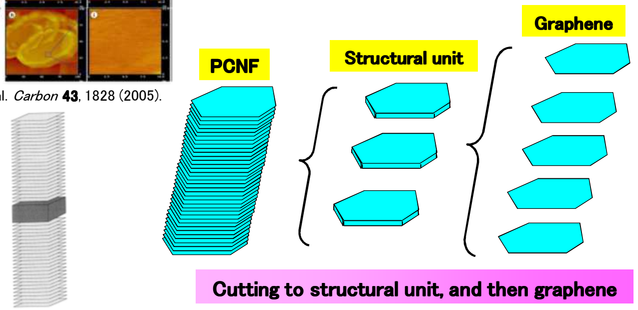
Preparation of uniform graphene disc

Step-by-step cutting of graphenes of platelet carbon nanofiber (PCNF)



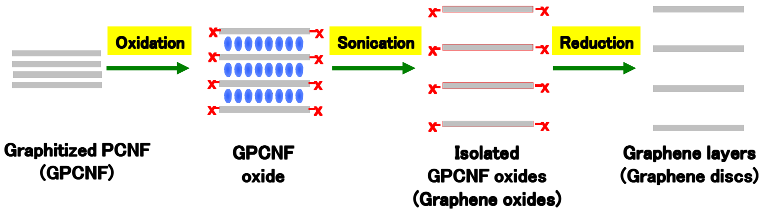
Yoon SH et al. *Carbon* **43**, 1828 (2005).

PCNF consists of nano-sized platelet structural units stacked perpendicular to fiber axis.
The plate unit has the thickness of 2-3 nm consisted of 6-10 graphene layers.



Cutting to structural unit, and then graphene

Oxidation, exfoliation and reduction of GPCNF



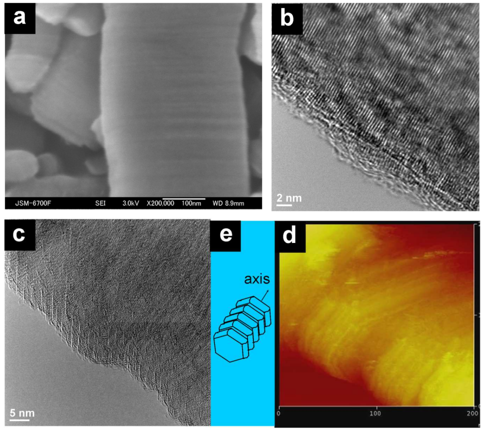
(1) Oxidation of GPCNF to PCNF oxide by the Hummer's method
Dispersion of 1g GPCNF in 100 mL of 98% H_2SO_4
Addition of 1～7 g $KMnO_4$
Stirring at 0°C for 30 min and then 40°C for 30 min

(2) Washing with assistant of centrifuge
Washing with water and H_2O_2
Centrifugation at 4800 rpm
Washing with HCl and acetone

(3) Exfoliation through strong sonication

(4) Reduction
Chemical reduction or Mechanical reduction

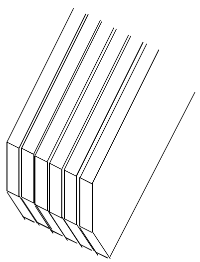
Structure of graphitized PCNFs



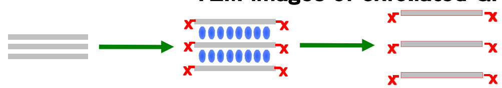
GPCNF (2800°C)

S_{BET} = 50 m^2/g

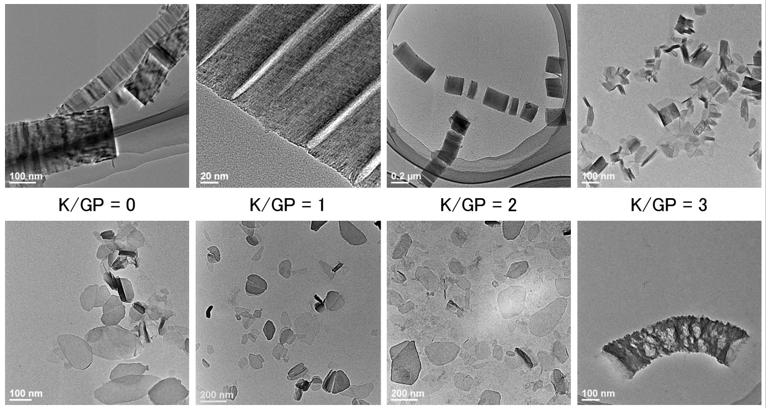
d_{002} = 0.3476 nm



TEM images of exfoliated GPCNFs

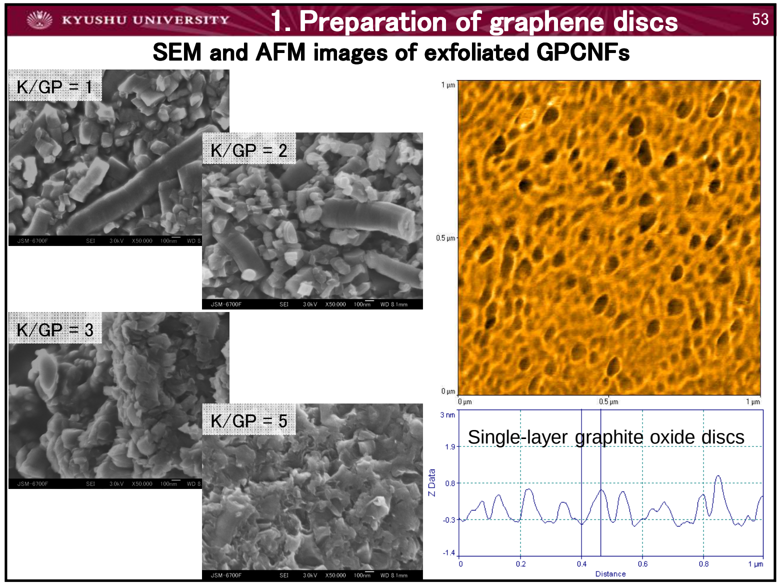


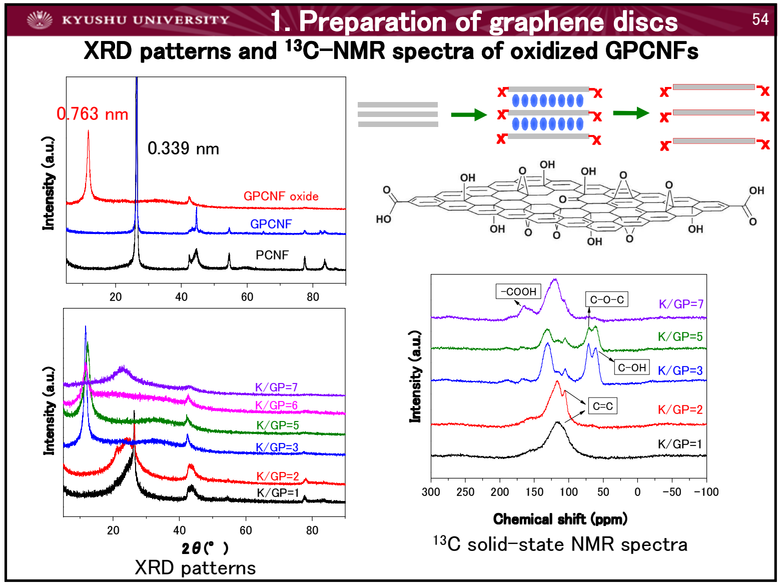
K/GP = $KMnO_4$/GPCNF ratio

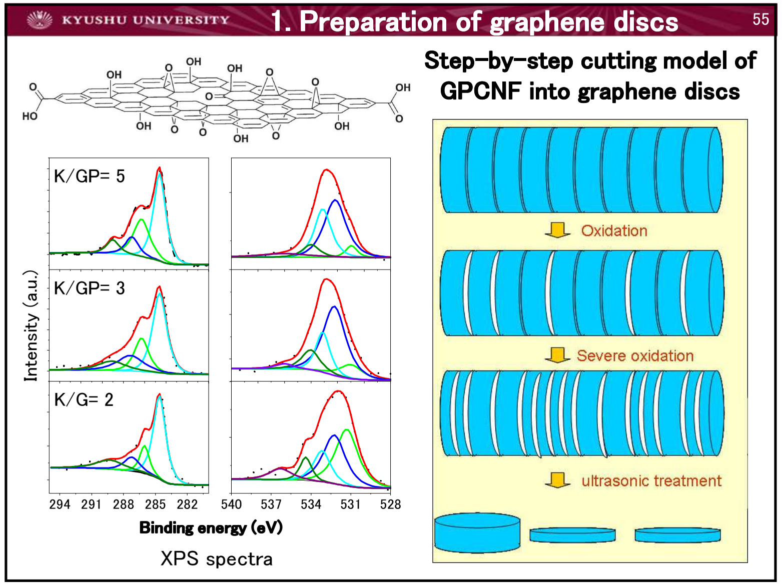


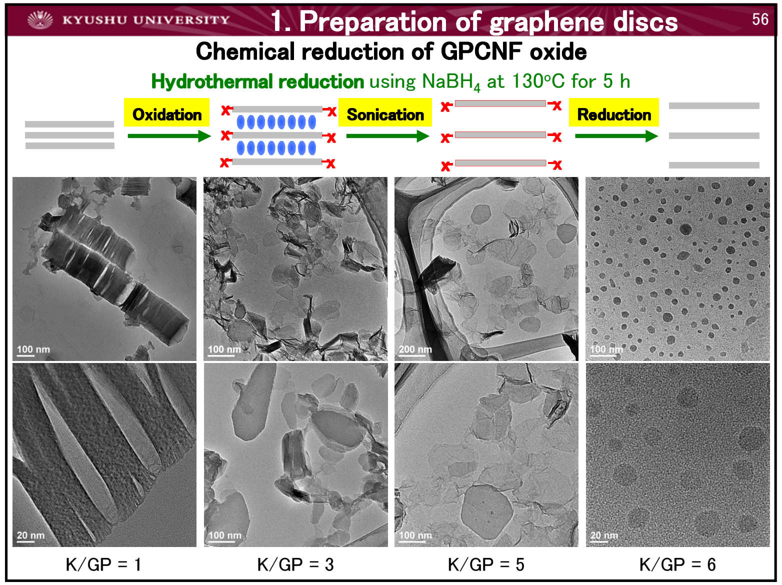
K/GP = 0 | K/GP = 1 | K/GP = 2 | K/GP = 3

K/GP = 4 | K/GP = 5 | K/GP = 6 | K/GP = 7


KYUSHU UNIVERSITY
1. Preparation of graphene discs
53
SEM and AFM images of exfoliated GPCNFs
K/GP = 1
K/GP = 2
K/GP = 3
K/GP = 5
Single-layer graphite oxide discs
Z Data
Distance

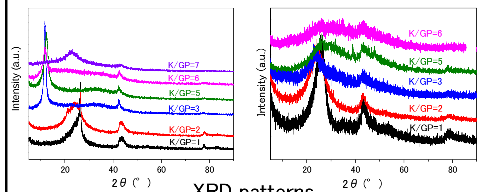

KYUSHU UNIVERSITY
1. Preparation of graphene discs
54
XRD patterns and 13C-NMR spectra of oxidized GPCNFs
0.763 nm
0.339 nm
Intensity (a.u.)
GPCNF oxide
GPCNF
PCNF
K/GP=7
K/GP=6
K/GP=5
K/GP=3
K/GP=2
K/GP=1
2θ(°)
XRD patterns
-COOH
C-O-C
C-OH
C=C
Chemical shift (ppm)
13C solid-state NMR spectra


KYUSHU UNIVERSITY
1. Preparation of graphene discs
55
Step-by-step cutting model of GPCNF into graphene discs
K/GP= 5
K/GP= 3
K/G= 2
Intensity (a.u.)
Binding energy (eV)
XPS spectra
Oxidation
Severe oxidation
ultrasonic treatment

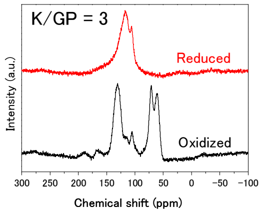

KYUSHU UNIVERSITY
1. Preparation of graphene discs
56
Chemical reduction of GPCNF oxide
Hydrothermal reduction using NaBH4 at 130°C for 5 h
Oxidation
Sonication
Reduction
K/GP = 1
K/GP = 3
K/GP = 5
K/GP = 6

Chemical reduction of GPCNF oxide

Hydrothermal reduction using $NaBH_4$ at 130°C for 5 h

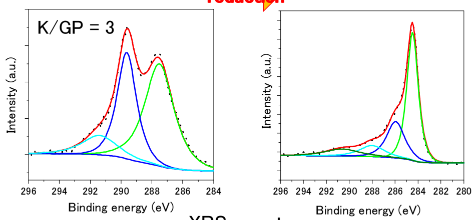


XRD patterns

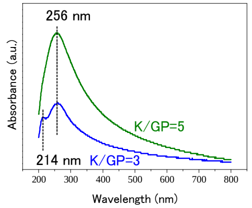


^{13}C solid-state NMR spectra

GPCNF oxide → Hydrothermal reduction → Graphene disks



XPS spectra

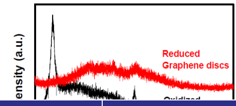


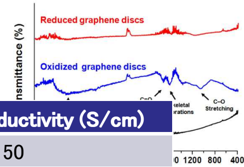
UVvis absorption spectra

Mechanical reduction of GPCNF oxide

Wet milling method using nano-dispersion machine

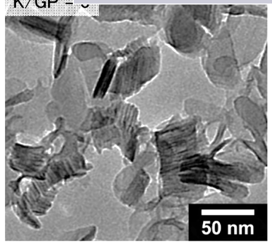
T.K.FILMIC (18400 rp

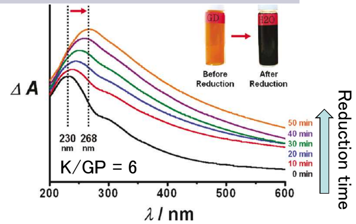




Sample	Electrical conductivity (S/cm)
GPCNF	150
GPCNF oxide (K/GP = 6)	7.4 × 10^{-4}
Graphene discs	14

K/GP =

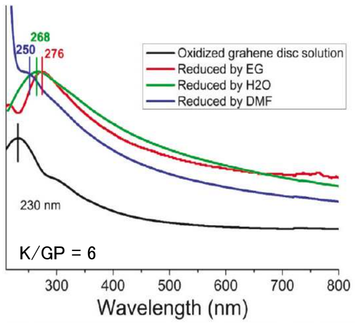




UVvis absorption spectra

Mechanical reduction of GPCNF oxide

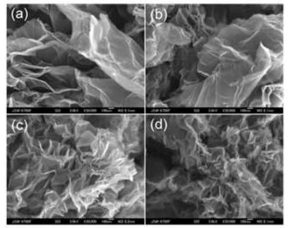
Influence of solvent during mechanical reduction

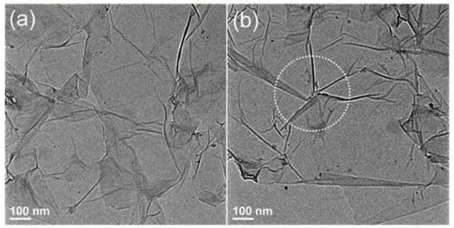


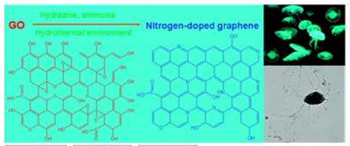
Concentration > 2.0 g/L

Nitrogen-Doped Graphenes by a Combined Chemical and Hydrothermal Reduction

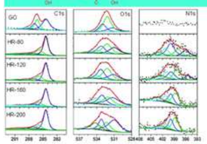
Langmuir, **2010**, *26* (20), pp 16096–16102



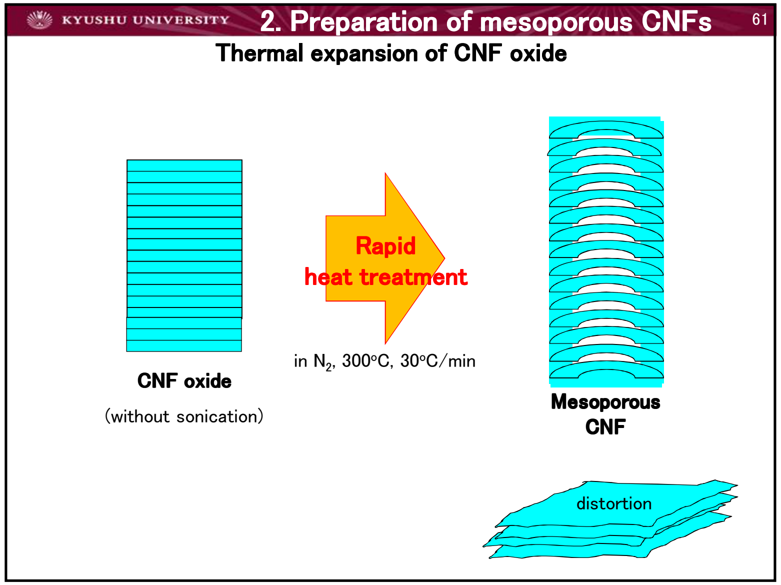


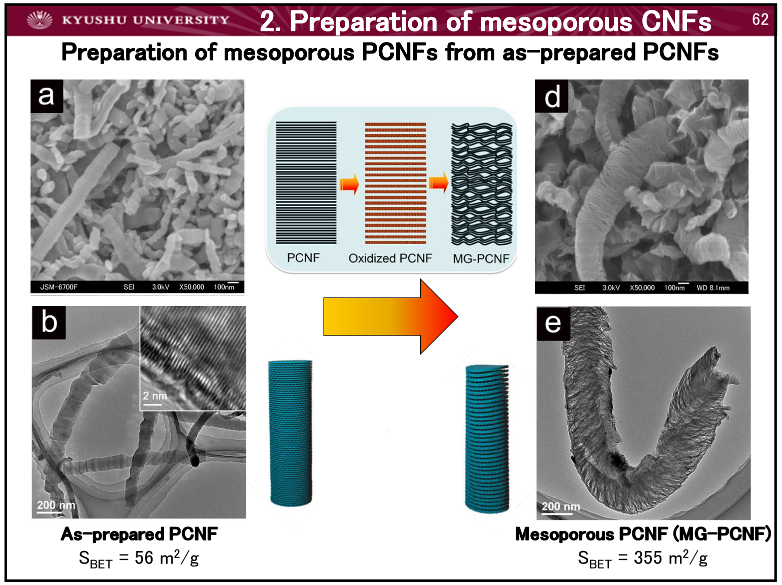


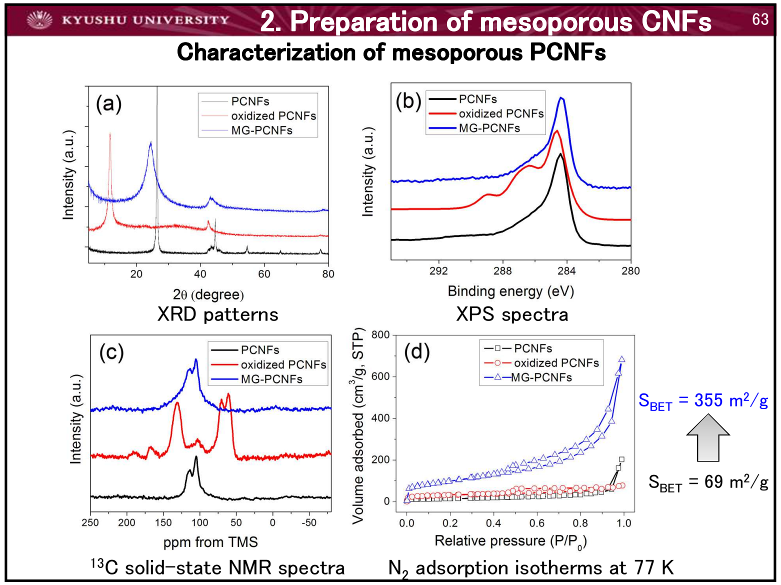
samples	C (wt %)	H (wt %)	N (wt %)	O[a] (wt %)	N/C (at./at.)	O/C (at./at.)
GO	49.59	2.28	0.03	48.05	0.0018	0.72
HR-80	80.43	1.23	5.21	13.13	0.074	0.12
HR-120	80.76	1.15	4.57	13.52	0.064	0.12
HR-160	84.15	1.15	4.09	10.61	0.055	0.091
HR-200	86.12	1.23	4.01	8.64	0.051	0.077

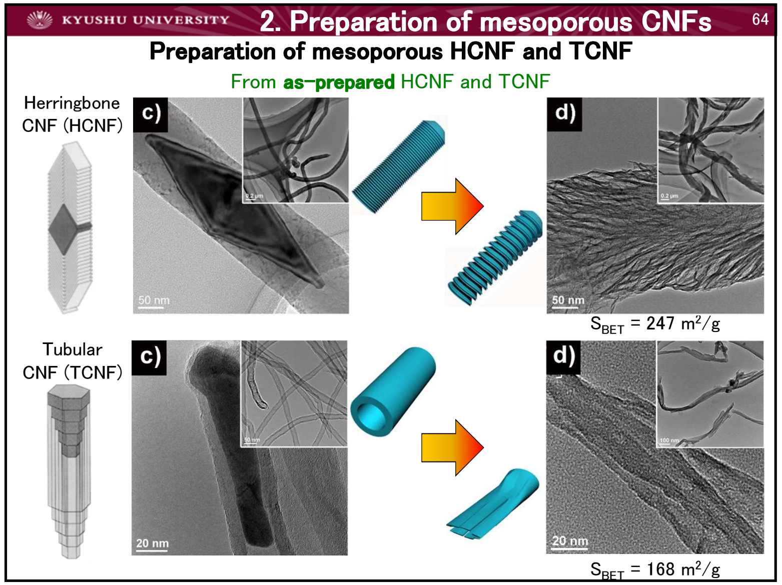


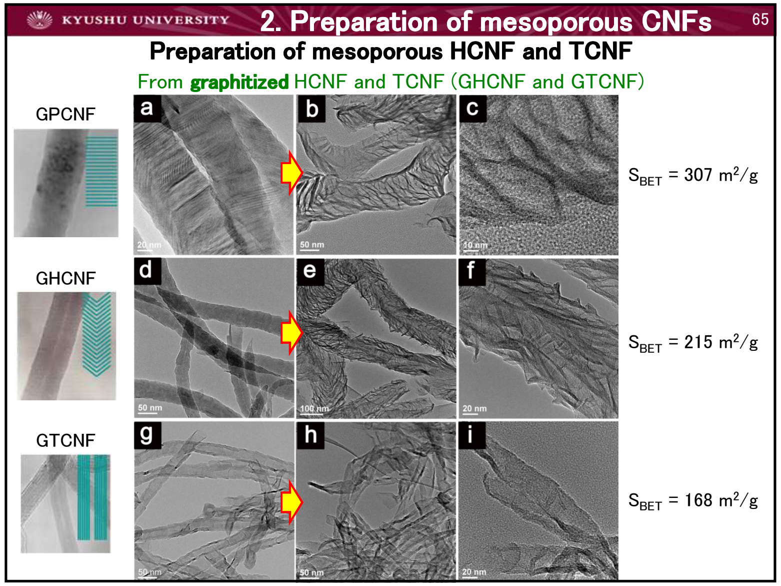
			N distribution (at. %)				
samples	N/C (at./at.)	O/C (at./at.)	395.7 ± 0.3 eV	398.7 ± 0.3 eV	400.3 ± 0.3 eV	401.4 ± 0.3 eV	402–405 eV
GO	0	0.45					
HR-80	0.11	0.16	16	18	37	18	11
HR-120	0.095	0.13	11	27	24	21	17
HR-160	0.071	0.13	0	39	25	17	19
HR-200	0.052	0.098	0	42	28	16	14


KYUSHU UNIVERSITY
2. Preparation of mesoporous CNFs
61
Thermal expansion of CNF oxide
Rapid
heat treatment
in N2, 300°C, 30°C/min
CNF oxide
(without sonication)
Mesoporous
CNF
distortion


KYUSHU UNIVERSITY
2. Preparation of mesoporous CNFs
62
Preparation of mesoporous PCNFs from as-prepared PCNFs
a
b
d
e
PCNF
Oxidized PCNF
MG-PCNF
2 nm
200 nm
200 nm
As-prepared PCNF
SBET = 56 m2/g
Mesoporous PCNF (MG-PCNF)
SBET = 355 m2/g


KYUSHU UNIVERSITY
2. Preparation of mesoporous CNFs
63
Characterization of mesoporous PCNFs
(a)
PCNFs
oxidized PCNFs
MG-PCNFs
Intensity (a.u.)
20
40
60
80
2θ (degree)
XRD patterns
(b)
PCNFs
oxidized PCNFs
MG-PCNFs
Intensity (a.u.)
292
288
284
280
Binding energy (eV)
XPS spectra
(c)
PCNFs
oxidized PCNFs
MG-PCNFs
Intensity (a.u.)
250
200
150
100
50
0
-50
ppm from TMS
13C solid-state NMR spectra
(d)
PCNFs
oxidized PCNFs
MG-PCNFs
Volume adsorbed (cm3/g, STP)
800
600
400
200
0
0.0
0.2
0.4
0.6
0.8
1.0
Relative pressure (P/P0)
N2 adsorption isotherms at 77 K
SBET = 355 m2/g
SBET = 69 m2/g


KYUSHU UNIVERSITY
2. Preparation of mesoporous CNFs
64
Preparation of mesoporous HCNF and TCNF
From as-prepared HCNF and TCNF
Herringbone
CNF (HCNF)
c)
d)
50 nm
50 nm
SBET = 247 m2/g
Tubular
CNF (TCNF)
c)
d)
20 nm
20 nm
SBET = 168 m2/g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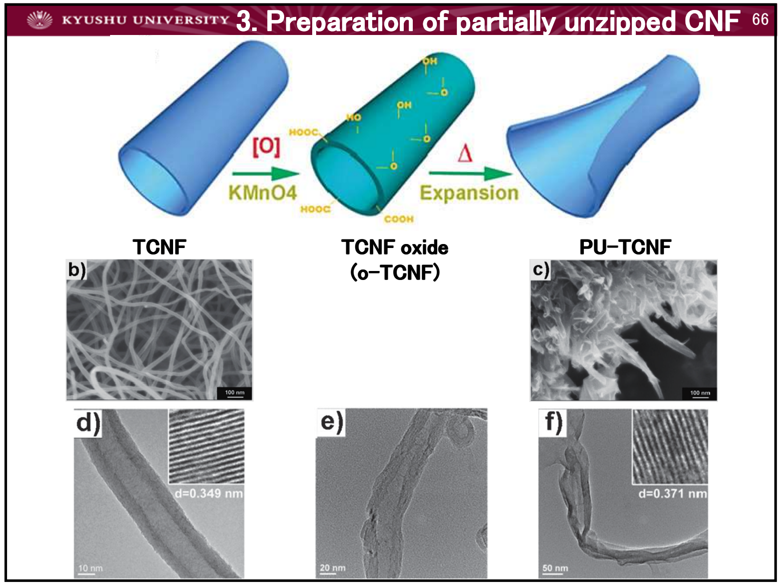
2. Preparation of mesoporous CNFs
65
Preparation of mesoporous HCNF and TCNF
From graphitized HCNF and TCNF (GHCNF and GTCNF)
GPCNF
GHCNF
GTCNF
a
b
c
d
e
f
g
h
i
S_{BET} = 307 m^2/g
S_{BET} = 215 m^2/g
S_{BET} = 168 m^2/g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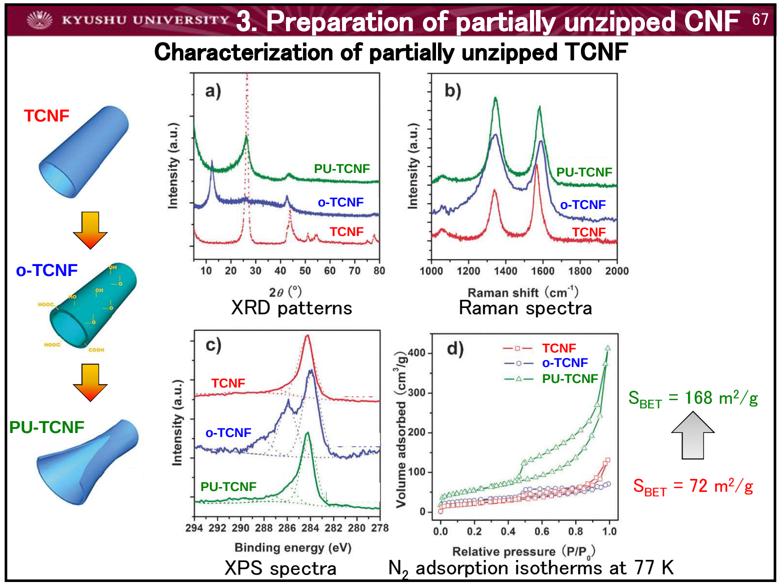
3. Preparation of partially unzipped CNF
66
[O]
KMnO4
Δ
Expansion
TCNF
TCNF oxide
(o-TCNF)
PU-TCNF
b)
c)
d)
e)
f)
d=0.349 nm
d=0.371 nm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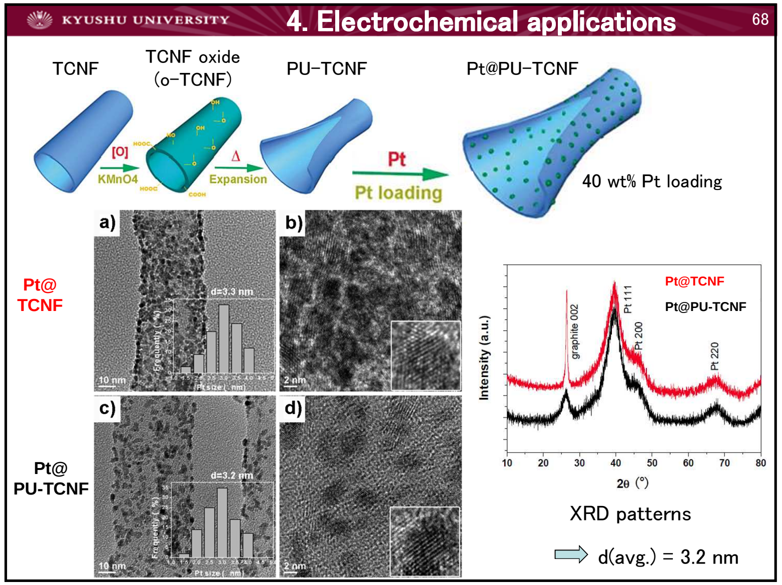
3. Preparation of partially unzipped CNF
67
Characterization of partially unzipped TCNF
TCNF
o-TCNF
PU-TCNF
a)
b)
XRD patterns
Raman spectra
c)
d)
XPS spectra
N$_2$ adsorption isotherms at 77 K
S_{BET} = 168 m^2/g
S_{BET} = 72 m^2/g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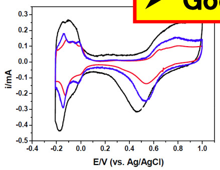
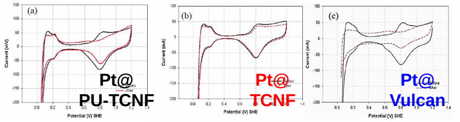
4. Electrochemical applications
68
TCNF
TCNF oxide
(o-TCNF)
PU-TCNF
Pt@PU-TCNF
Pt
Pt loading
40 wt% Pt loading
Pt@
TCNF
Pt@
PU-TCNF
a)
b)
c)
d)
d=3.3 nm
d=3.2 nm
Pt@TCNF
Pt@PU-TCNF
XRD patterns
d(avg.) = 3.2 nm

4. Electrochemical applications

- Improved electrocatalytic performance
- Good durability

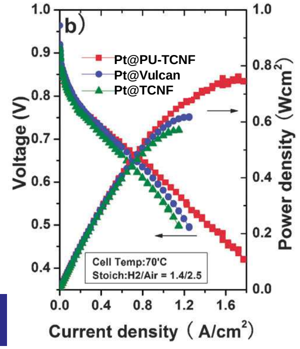


Cyclic voltammograms in 0.5 M H_2SO_4



Durability tests

Sample	Electrochemically active surface area, ESA (m^2/g)	Decay rate of ESA (%)
Pt@PU-TCNF	129	**38**
Pt@TCNF	64	**11**
Pt@Vulcan	71	**65**



Proton exchange membrane fuel cell (PEMFC) single-cell profiles

Conclusion

1. Special properties of CNFs are still promising for their commercial applications through the innovation of the performances of conventional carbons.
2. Very homogeneous nano-graphene and special fibrous mesoporous carbon can be obtained using CNFs as an effective precursor
3. We have to solve the problems of CNFs for the effective applications to the real market.

- From science to engineering
- Full understanding of the performances and costs of the conventional functional carbons

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- ✓ **Jin Miyawaki: Assistant Professor**
- ✓ **1 Guest Professor**
- ✓ **2 Post-doctorates**
- ✓ **2 Researcher for Analyses**
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Thank you for attentions!