November 21st , 2012
Lecture

Functional Carbon Materials for Energy and Environmental Devices

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Application of carbon materials

Electric and Heat Conductions

- Conductor and Semi-conductor

Energy Storage

- Battery anode
- Super capacitor
- Gas storage

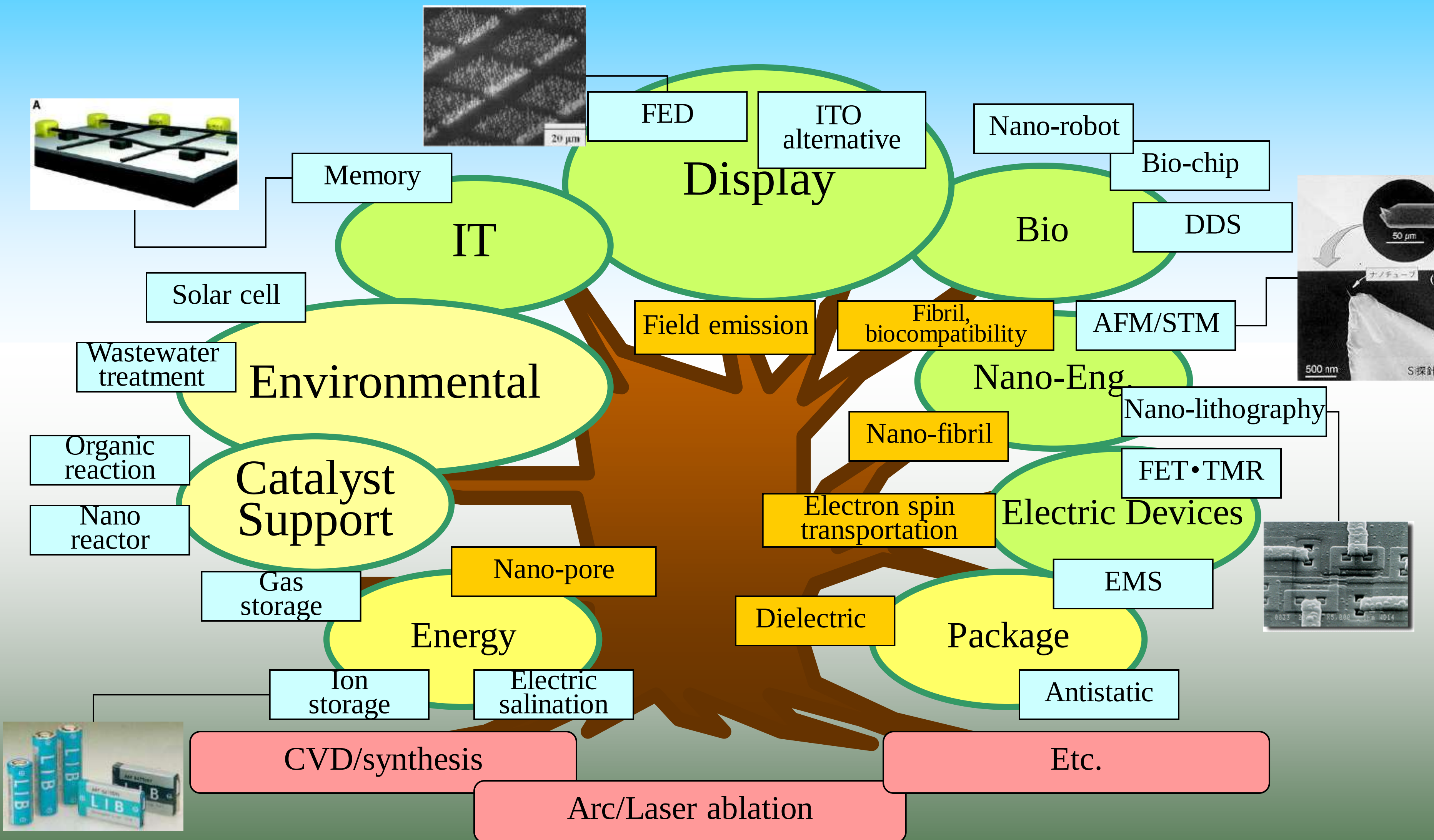
Environmental Protection

- Activated surface

Mechanical Reinforcement

High Temperature Materials

Applications of Carbons

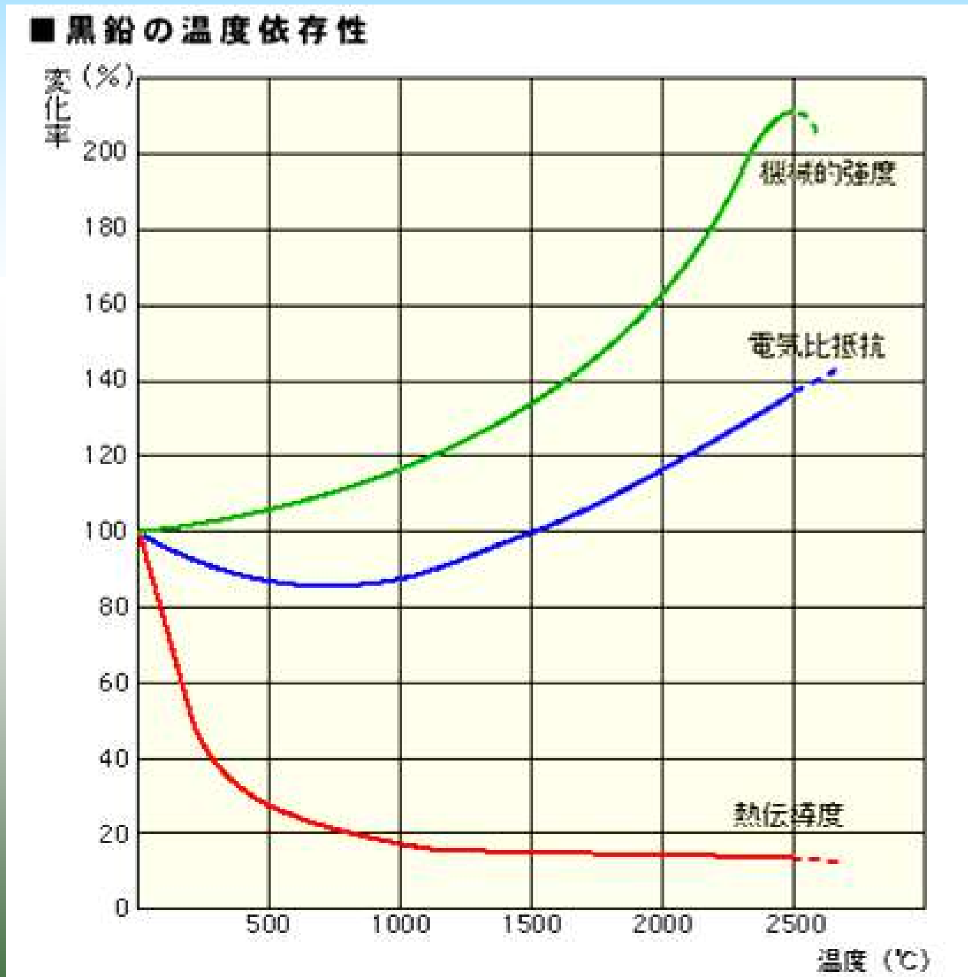


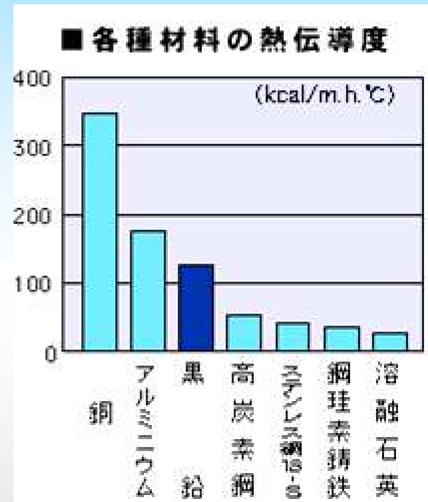
Characteristics of carbons

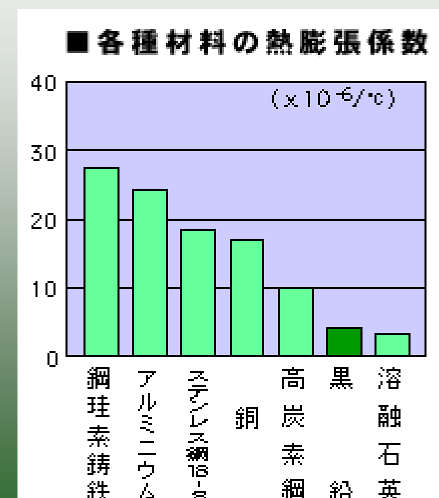
- **Thermal stability**
- **High thermal and electric conductivities**

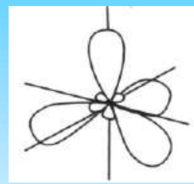
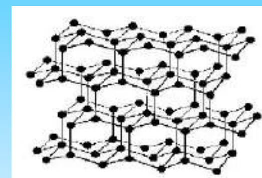
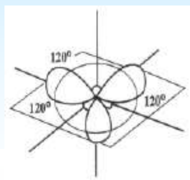
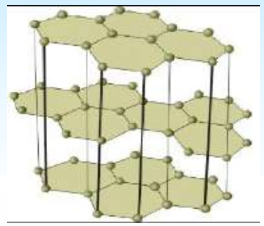
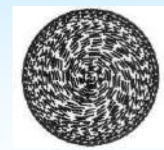
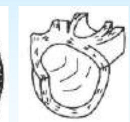
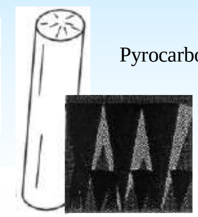
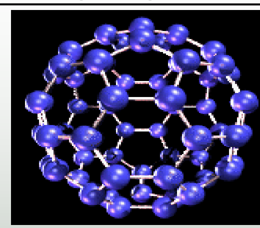
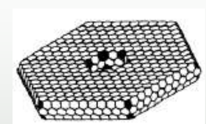
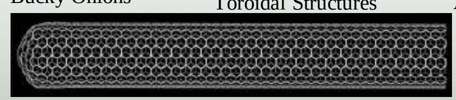
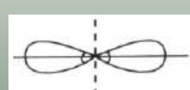
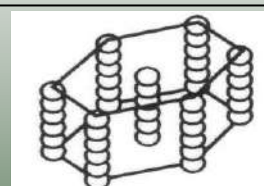
  SWNT, Diamond : 4000 W/mK, K-11 carbon fiber: 1100 W/mK
- **Small heat expansion**
- **High thermal shock properties**
- **High chemical stability**
- **Abrasion and lubricant properties**
- **High mechanical properties**

Thermal characteristics of carbons







Bonding Hybridization	Allotropes	Derived and Defective Forms
 **SP³**	 **Cubic diamond**	 Diamond-like Carbon
 SP²	 **Hexagonal graphite**	Poly-crystalline Graphite    Carbon Black  Cokes and Activated Carbons  Pyrocarbons Carbon Fibers
 SP$^{2+\varepsilon}$ rehybridization	 **Fullerene**	 Bucky Onions  Toroidal Structures  Acetylene Blacks  Nanotubes
 SP¹	 **Carbyne**	Ref.) Bourrat, X. Structure in Carbons and Carbon Artifacts. In: *Sciences of Carbon Materials*. Marsh, H.; Rodriguez-Reinoso, F., Eds., Universidad de Alicante, **2000**. pp1-97.

Carbon Allotropes

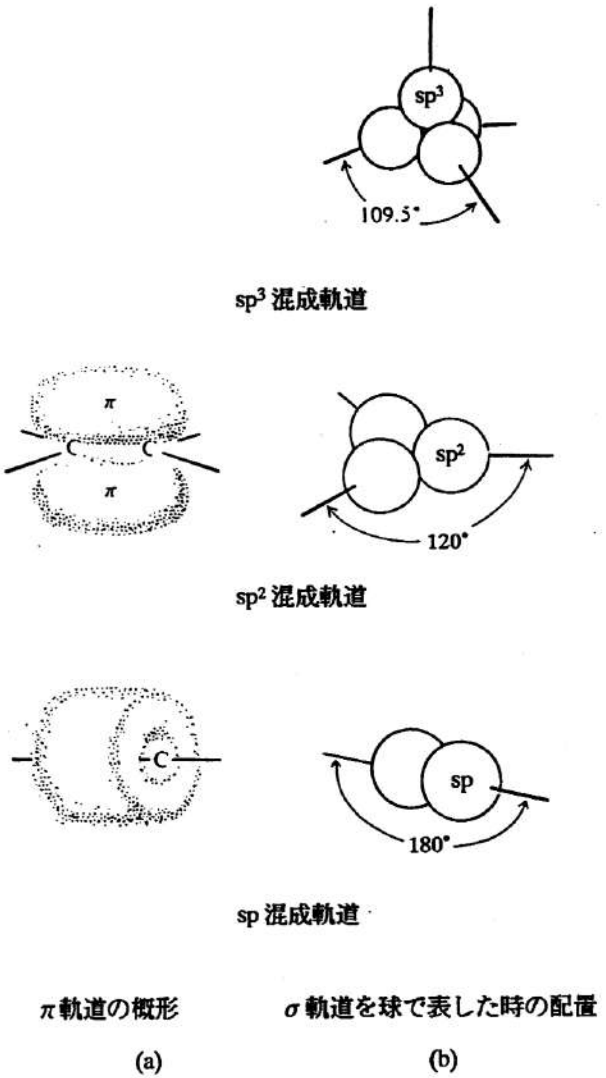


図-1　炭素の混成軌道

表-1　各種炭素ー炭素結合の結合解離エネルギーと結合距離[1)]

化合物	結合解離エネルギー (kcal/mol)	結合距離 (Å)
$H_3C\text{-}C_3H$	88	1.53
$H_2C{=}C_2H$	163	1.34
$HC{\equiv}CH$	198	1.21

表-2　炭素同素体の種類[3)]

結合の種類	配位数	炭素同素体
sp	2	カルビン（ポリイン, クムレン）
sp²	3	グラファイト（六方晶, 菱面体晶）
		フラーレン（C_{60}, C_{70}, バッキイチューブなど）
sp³	4	ダイヤモンド（立方晶, 六方晶, 菱面体晶*）
		ダイヤモンド多形体（6H, bc-8*など）
		ダイヤモンドライクカーボン（DLC）, i-カーボン
イオンまたは	6	単純立方晶*, β-スズ型*
金属的	8	体心立方晶*
	12	面心立方晶*, 六方最密充填*

* 実

表-4　IV族sp³立方晶体の性質[6)]

性　質	ダイヤモンド	β-SiC	Si
格子定数（Å）	3.567	4.358	5.430
密度（g/cm³）	3.515	3.216	2.328
熱膨張率（×10⁻⁶/℃）	1.1	4.7	2.6
融点（℃）	4000	2540	1420
バンドギャップ（eV）	5.45	3.0	1.1
キャリア移動度（cm²/(V・S)）			
電　子	2200	400	1500
ホール	1600	50	600
熱伝導率（W/(cm・K)）	20	5	1.5
硬度（kg/mm²）	10000	3500	1000

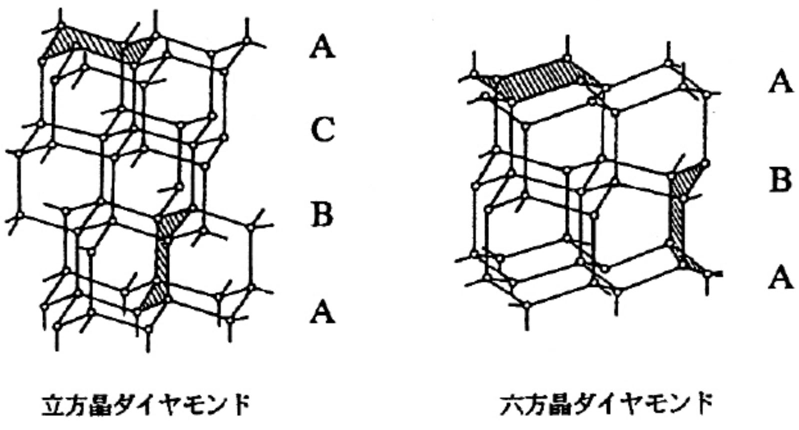


図-2　ダイヤモンドの構造[5)]

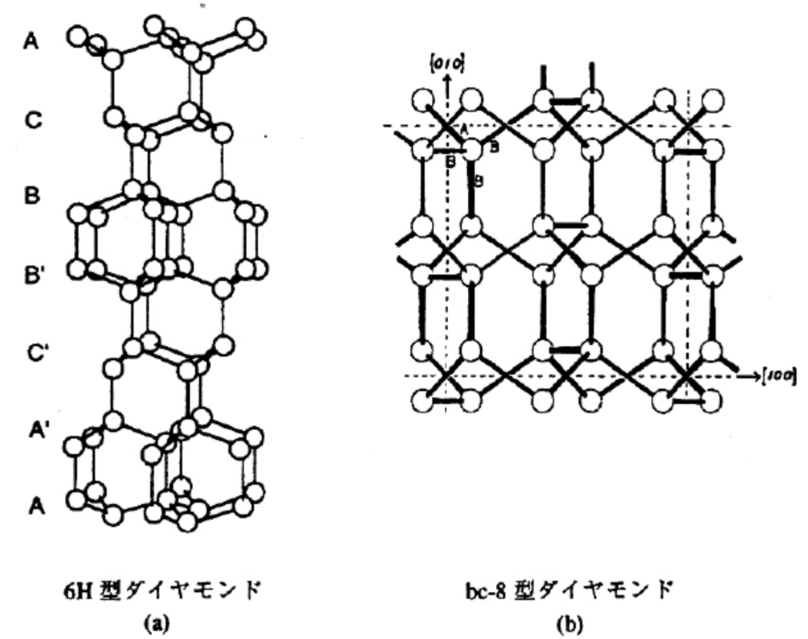
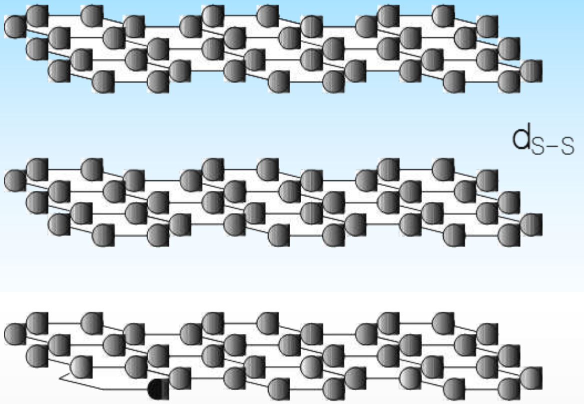
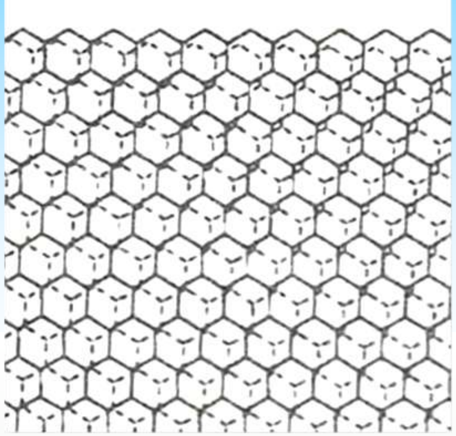


図-3　6H型およびbc-8型ダイヤモンド多形体の構造[5), 8)]

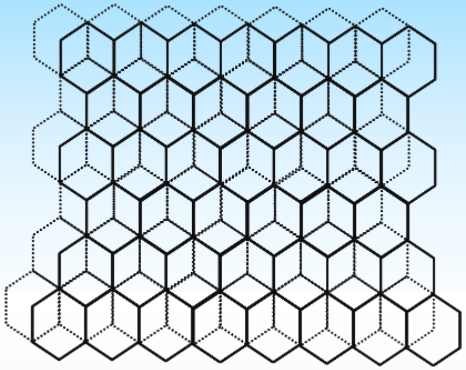
Molecular structures of graphite



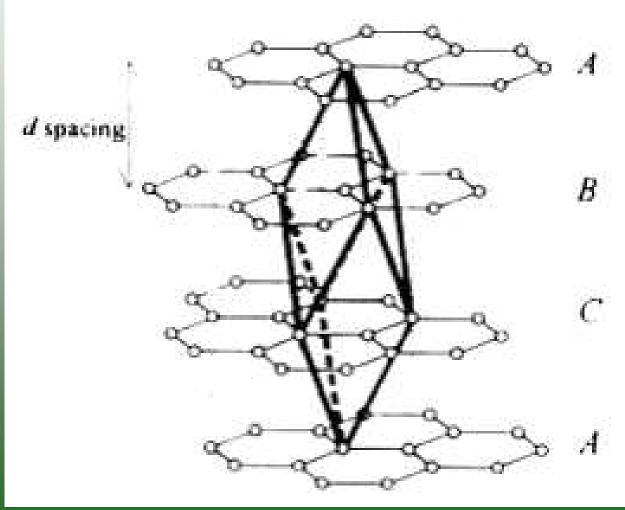
(a) Basic Structure of Graphite

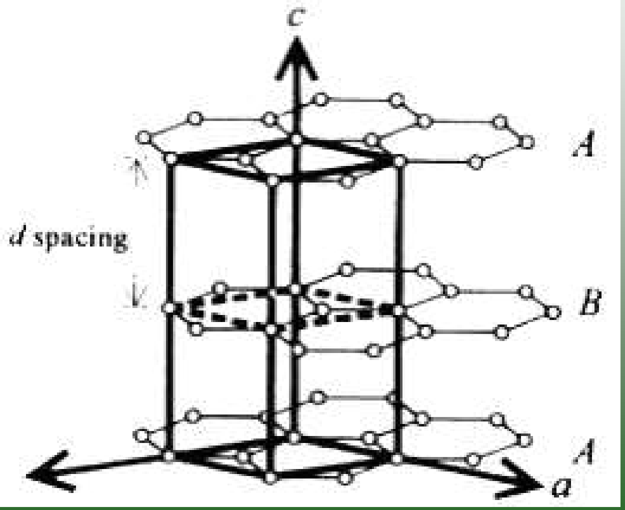


(b) Turbostratic structure (low crystallinity)



(C) Graphitic structure (high crystallinity)





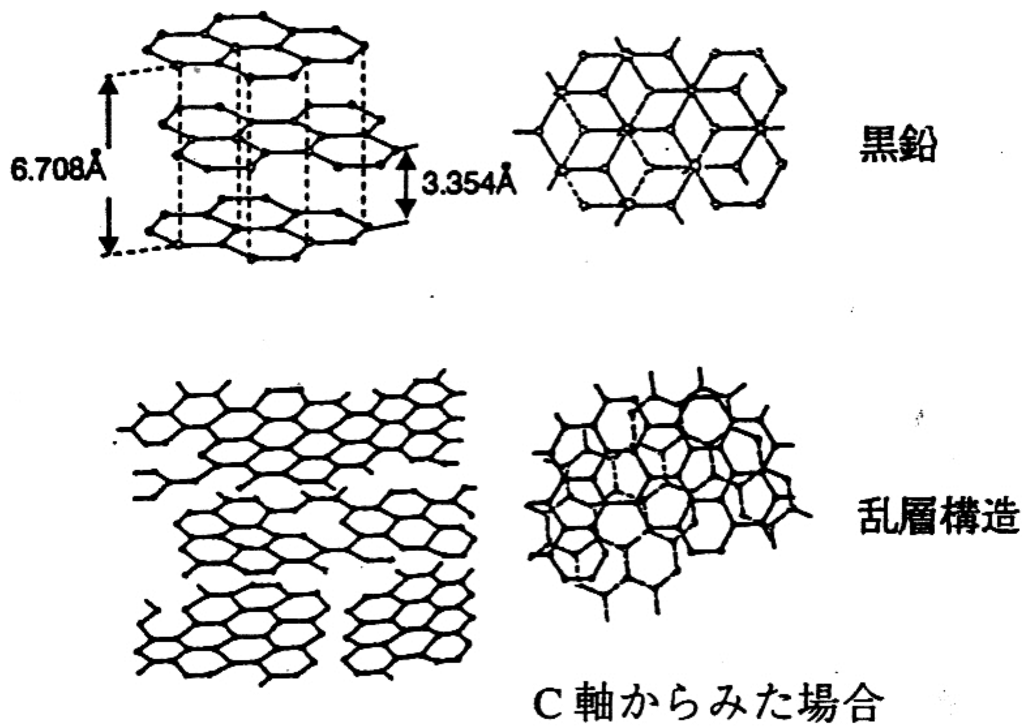


図-3　黒鉛と乱層構造の積層状態の違い

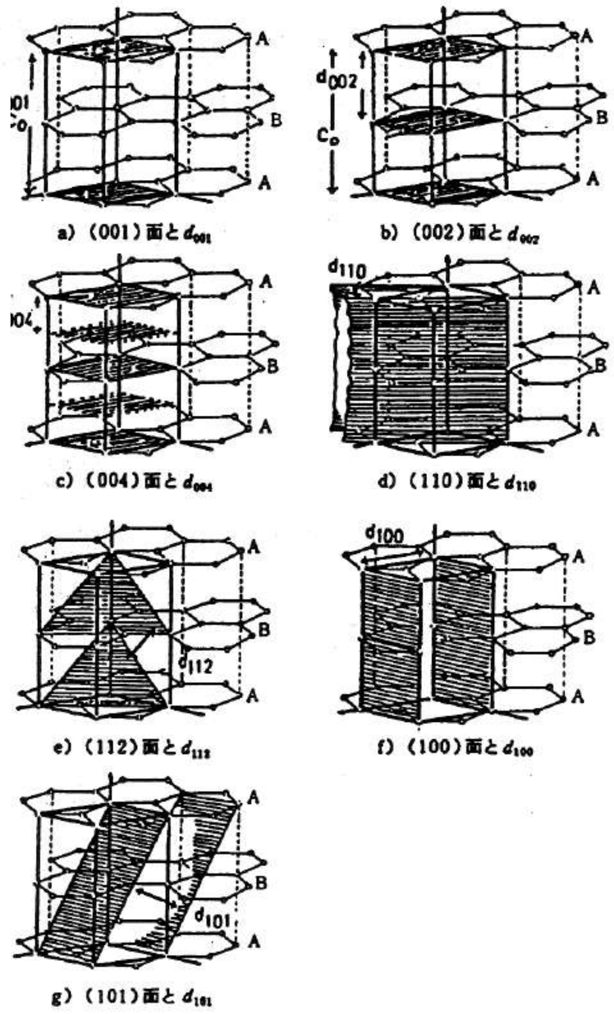


図-2　六方晶系黒鉛の格子面

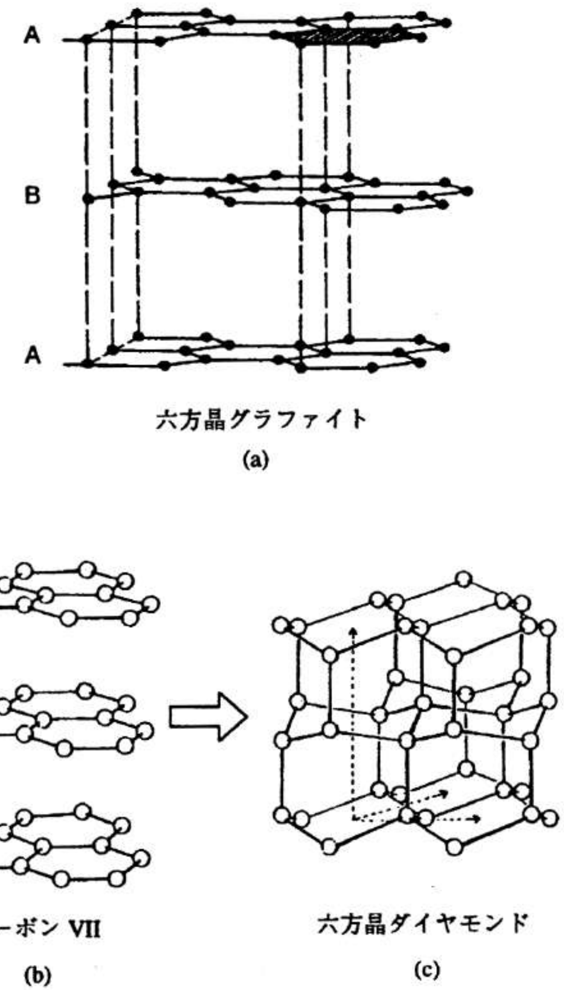
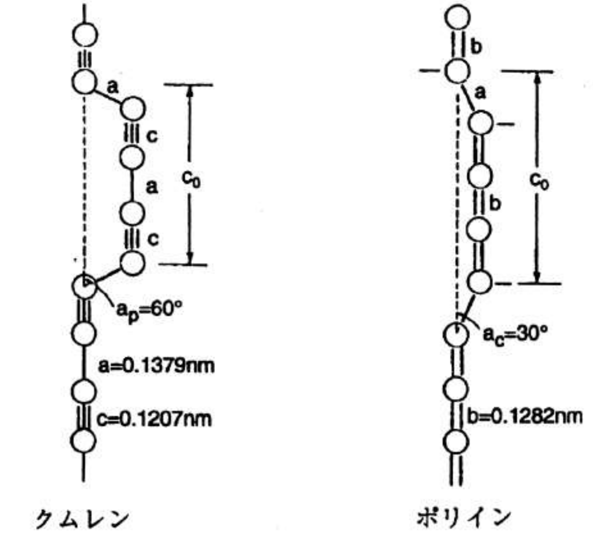
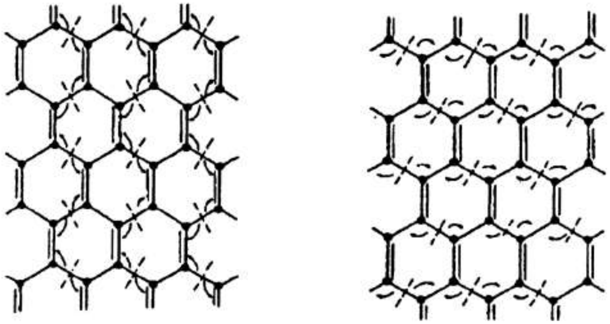


図-4　グラファイトの構造およびダイヤモンドへの転換イメージ[12)]



(a)



グラファイト面内の一重結合の開裂イメージ

(b)

図-6　カルビンの構造およびグラファイト面内一重結合開裂イメージ[2)]

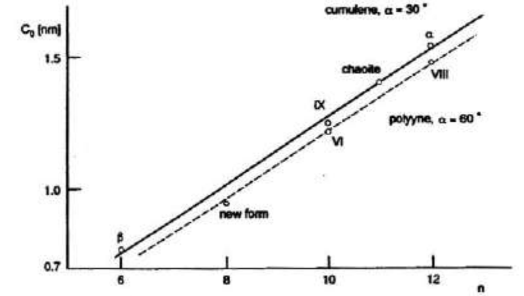
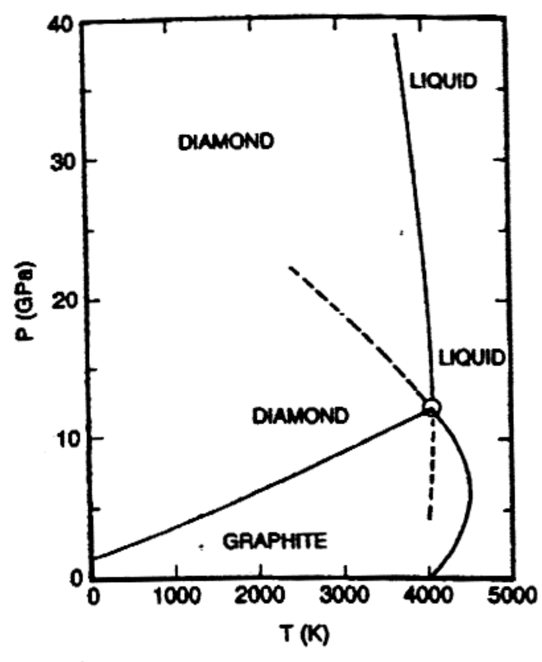
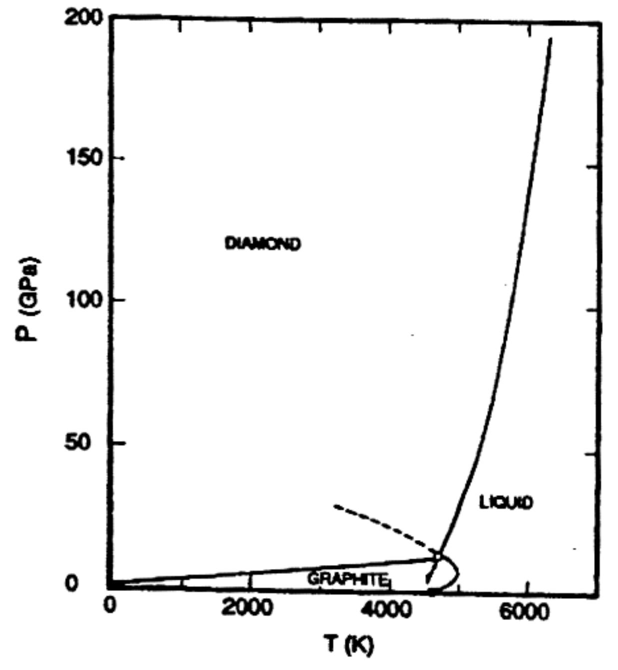


図-7　カルビン同族体の鎖内炭素数nとC_0パラメータ（図-6参照）との関係[2)]





(a) 1964年に提案された相図

(b) 1989年に提案された相図

図-8 Bundyによって提案された炭素の相図[27]

Conventional Fossil Fuels

Petroleum — **Exploration and Production, Refining of Heavy Fraction to Very Clean Fuel**

Coal — **Clean Coal Technologies**

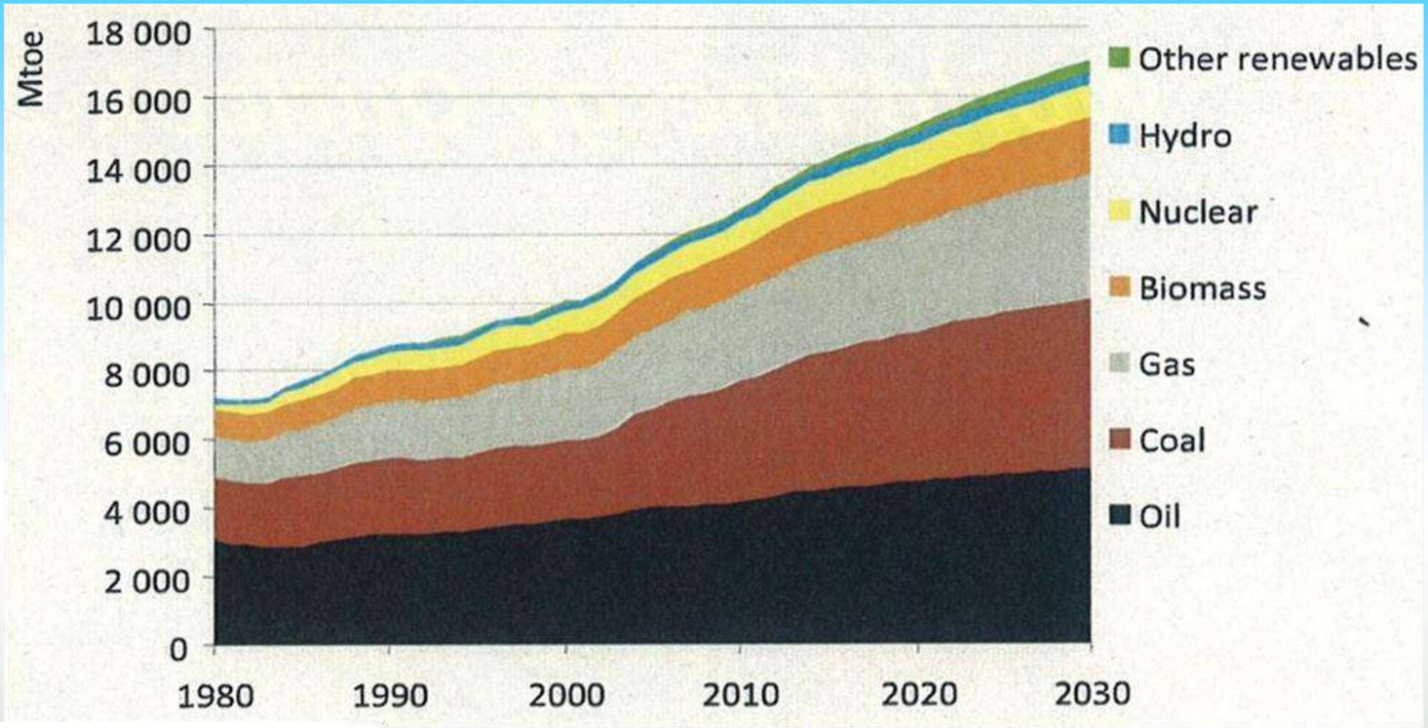
- **Efficient Combustion**
- **Gasification**
- **Liquefaction**

Natural Gas — **Transportation**

- LNG or Pipe Line
- GTL: Small Resources

Price and Cost : Ultimate Recoverable Quantity

化石燃料の将来



	1980	2000	2006	2015	2030	Annual average increase rate 2006-30
Coal	1788	2295	3053	4023	4908	2.0%
(US)			551	580	633	0.6%
(China)			1214	1898	2441	4.0%
(India)			223	315	579	6.0%
Petroleum Oil	3107	3649	4029	4525	5109	1.0%
Gas	1235	2088	2407	2903	3670	1.8%
Nuclear Power	186	675	728	817	901	0.9%
Hydraulic Power	148	225	261	321	414	1.9%
Biomass	748	1045	1186	1375	1662	1.4%
Other Renewables	12	55	66	158	350	7.2%
Total	7223	10034	11730	14121	17014	1.6%

Approx. 45% increase

Three countries - U.S., China, and India - account for 75% in 2030

炭素材料原料

Raw materials

Coal tar
Polymer: Thermosetting and thermoplastic
Heavy oil and residues
Biomass

Precursor

- Pitches: CF, ACF, MCMB, Ball type AC, Binder pitch, Additives
- Polymer: AC, ACF, Glassy carbon, CF
- Cokes: Electrode, Capacitor, Battery anode, AC, Additives
- Char: AC, Additives, Reducer for Solar cell

From fossil fuel to functional carbons

Carbonaceous resources	Side products	Advanced Carbon Materials for Energy Saving, Storing, And Environmental Protections and Improvements		

Effective conversion and utilization of fossil fuels and their residues

Carbonaceous resources: Petroleum, Natural Gas, Coal, Biomass

Side products: Heavy residues, C10+, Syngas, Coke, COG, Tar, Char

Energy Saving	Energy Storing	Environmental Protections
Fuel Cell	Battery	Water
Catalyst	**Li-ion battery**	**Purification**
Separator	**Na-S battery**	**Water conversion**
Bipolar Plate	**Air battery**	**NO_3^-, PO_4^{-3} removal**
Advanced Generation	Super capacitor	Atmosphere
Structural Materials For IGCC, IGFC	**EDLC for EV, FV**	**AC, ACF for DeSOx, DeNOx, deVOCs**
Structural Materials For Atomic Reactor	Hydrogen	**AC, ACF for Sick-house gases**
	H-storing Bombe	**CO_2 separation & Concentration**
Light Weight	Methane	
Carbon Fibers	**Methane storage**	
Synthetic Carbon		

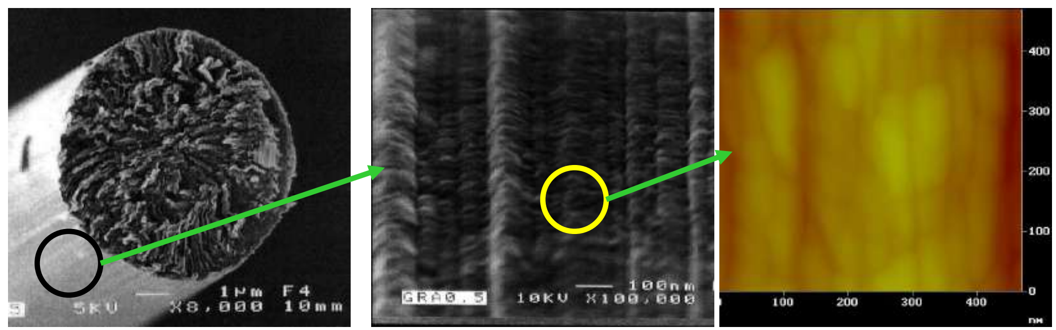
ピッチ系高性能炭素繊維

メゾフェーズピッチ → 紡糸 → 不融化 → 炭化・黒鉛化

高弾性、高引張強度、高熱・電気伝導度

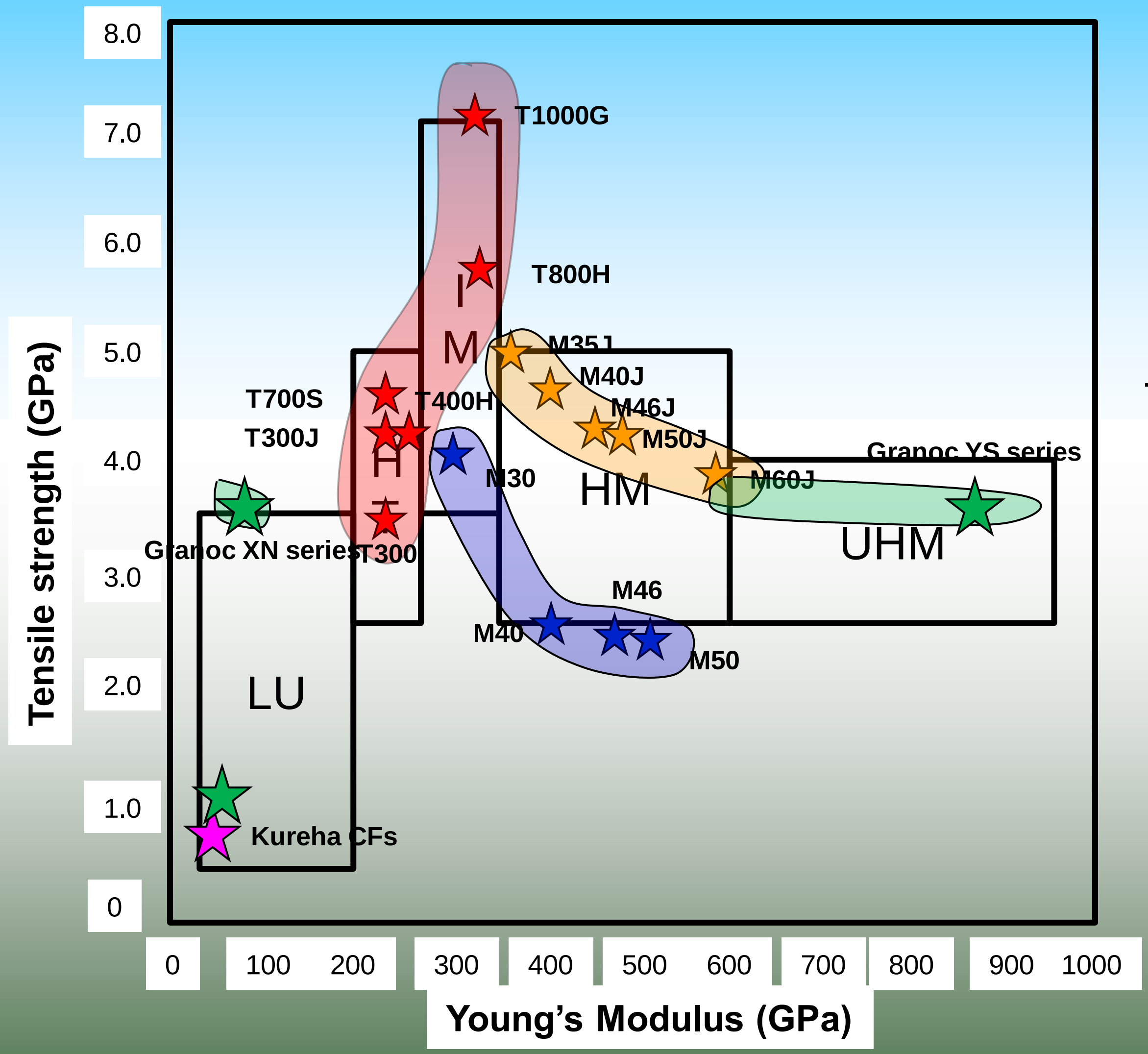
問題点：低圧縮強度　＞　複合材料使用制限

原因：ドメイン（プリット構造）の大きさ・均一さ



Pleat構造　＞　均一・縮小　＞　圧縮強度向

Classification of Carbon Fiber



・Ultra High Modulus Type（UHM）
Young's Modulus > 600GPa
Tensile Strength > 2500MPa

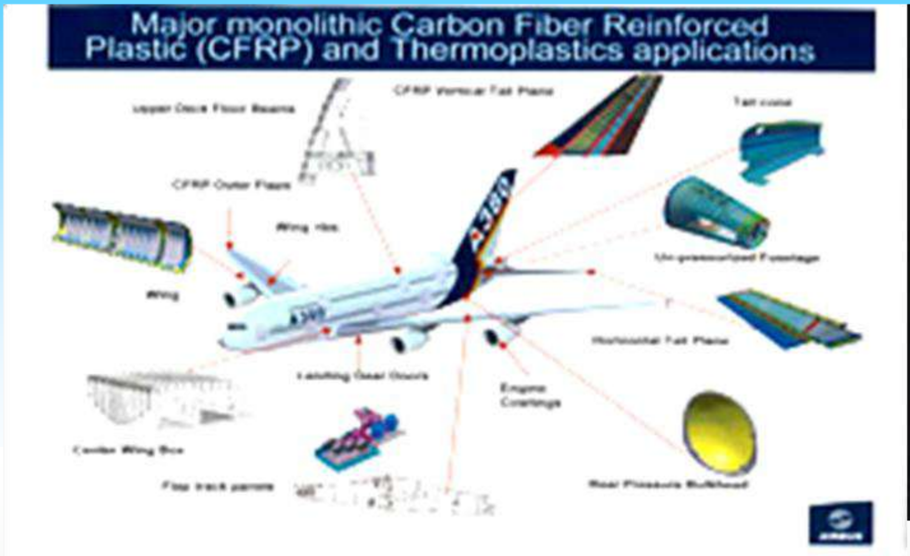
・High Modulus Type（HM）
Young's Modulus ：350～600GPa
Tensile Strength > 2500MPa

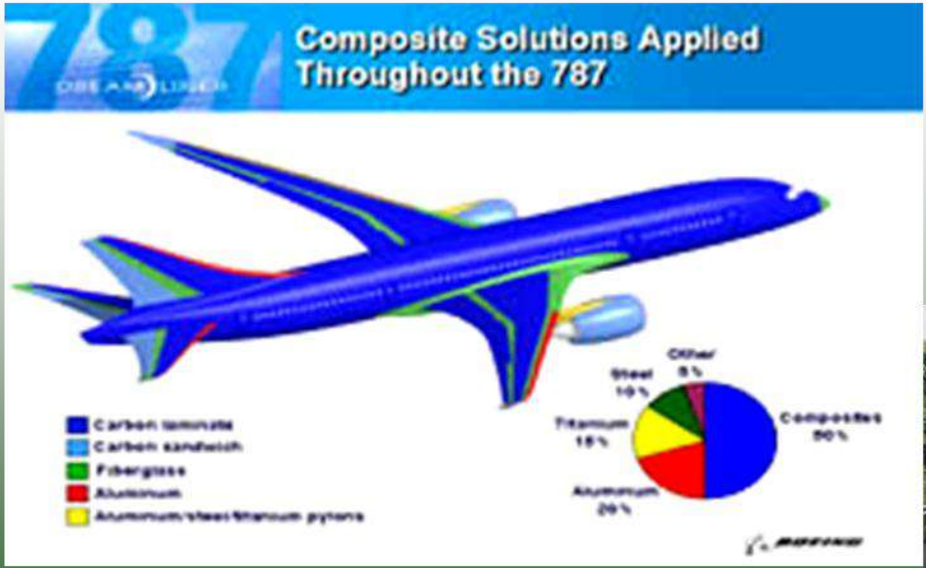
・Medium Modulus Type（IM）
Young's Modulus ：280～350GPa
Tensile Strength > 3500MPa

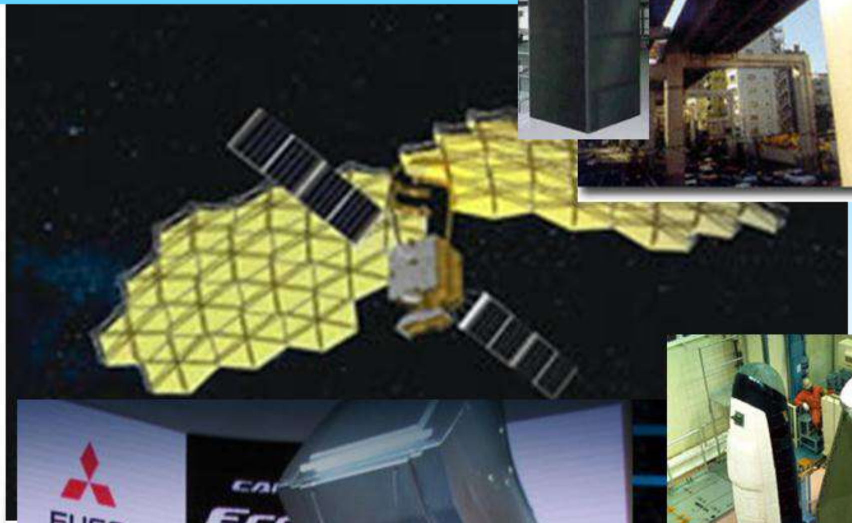
・Standard Modulus Type（HT）
Young's Modulus ：200～280GPa
Tensile Strength > 2500MPa

・Low Modulus Type（LM）
Young's Modulus < 200GPa
Tensile Strength < 3500MPa

Carbon Fiber





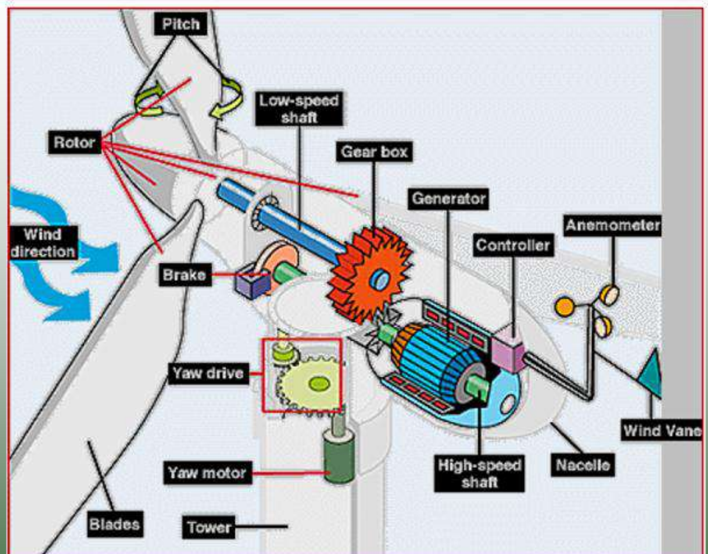


宇宙航空研究開発機構 提供

宇宙航空研究開発機構 提供

CFs for Construction

Windmill



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Wind power generation which has become popular recently is expected to require bigger and bigger blades to have higher and higher output capacity for each unit. In order to support big size blades, use of CFRP becomes vitally necessary. And **as the material for high speed rotating body for fly wheels which are attracting public attention as a technology to store energy effectively based on theory of top spinning, use of CFRP is becoming popular**.

Carbon is key element for Batteries !!

①Li-ion

[High capacity]

(+) : $LiCoO_2$
(-) : Carbon(Graphite)
Conductor : Carbon

②Dry Battery

[Cheap]
[Easy Available]

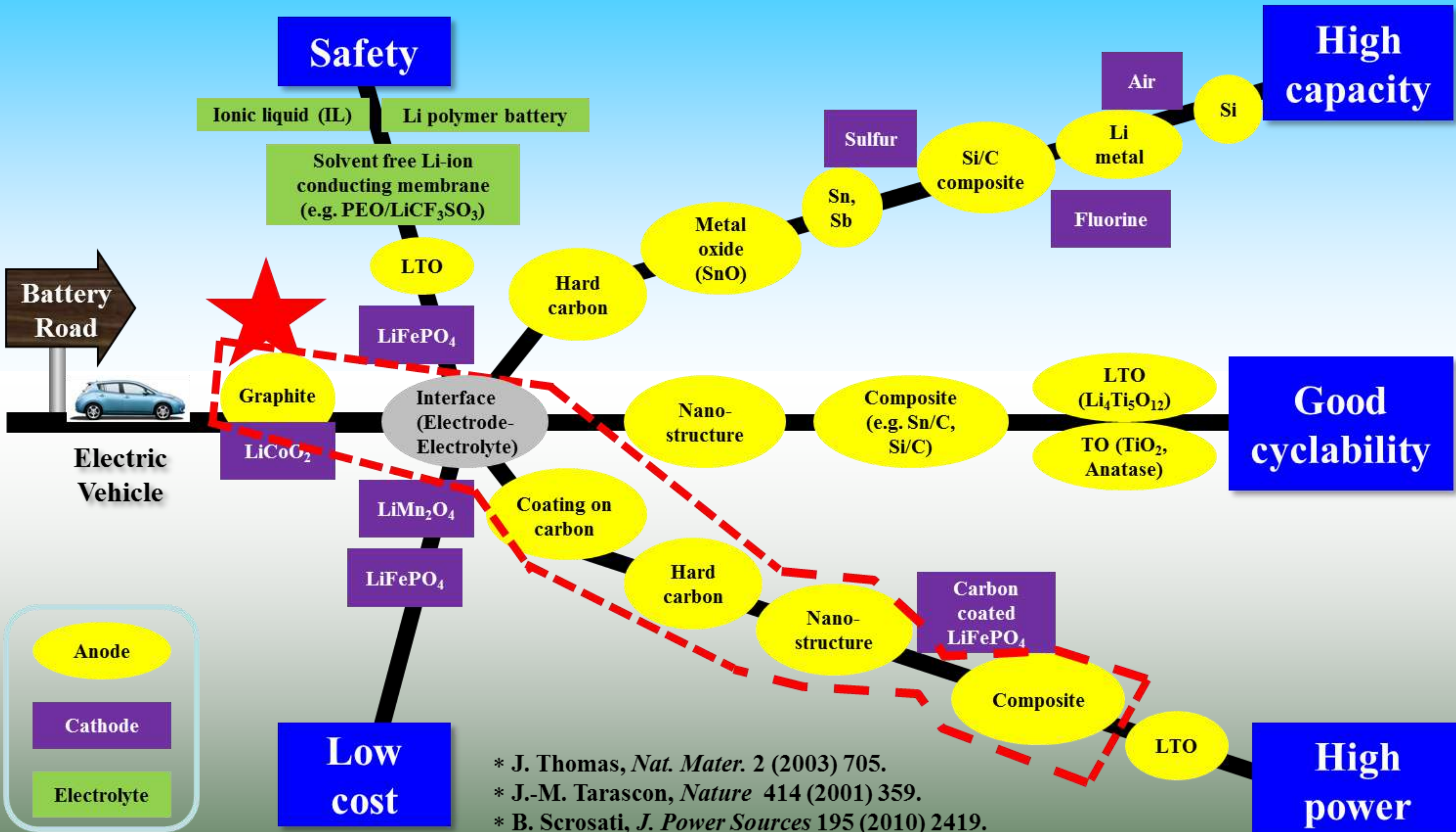
(+) : MnO_2
(-) : Zn
Conductor : Carbon

③Ni-MH

[High power]
[Total balance]

(+) : $\underline{(Ni\text{-}Co)(OH)_2}$
(-) : $\underline{Mm(Ni\text{-}Mn\text{-}Al\text{-}Co)_5}$
substrate: Nickel and Carbon

Research background : Battery Road



* J. Thomas, *Nat. Mater.* 2 (2003) 705.
* J.-M. Tarascon, *Nature* 414 (2001) 359.
* B. Scrosati, *J. Power Sources* 195 (2010) 2419.

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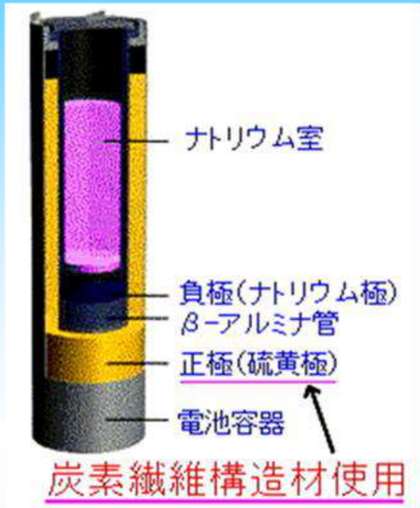
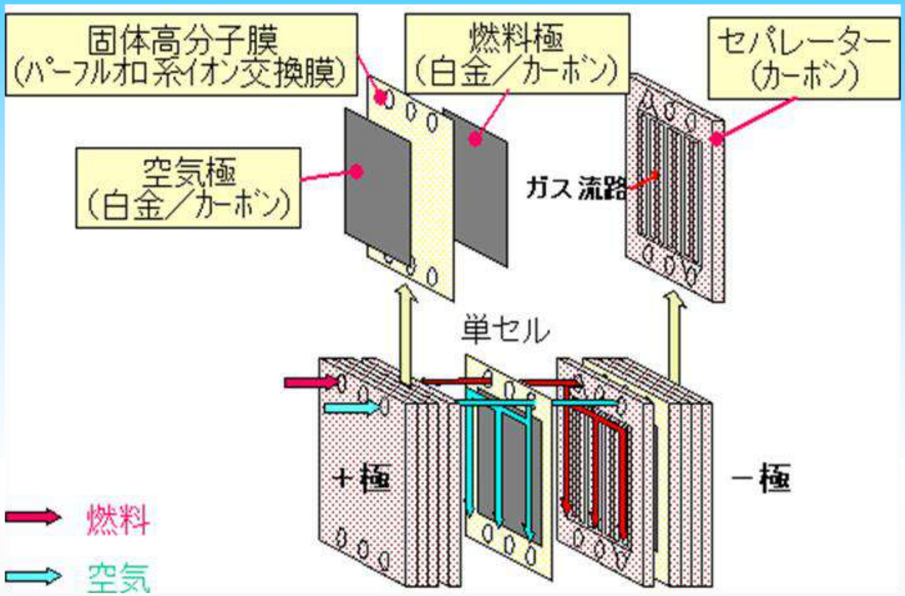
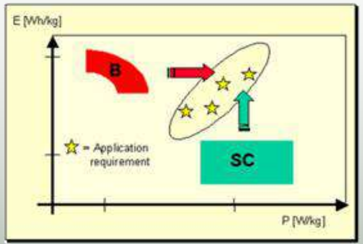
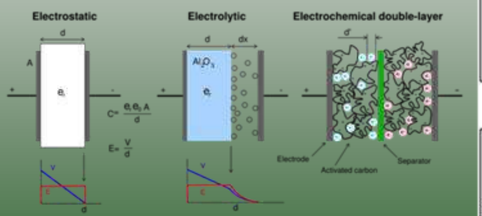
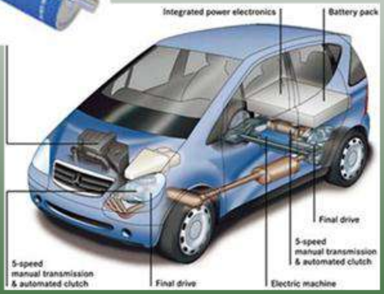
Carbons for Battery, Capacitor, Atomic and Coal Power Plants

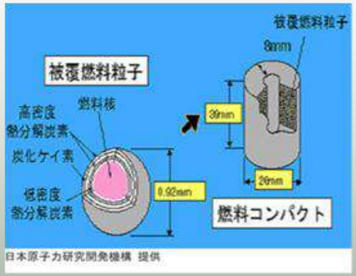


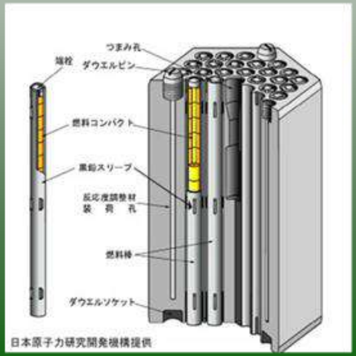








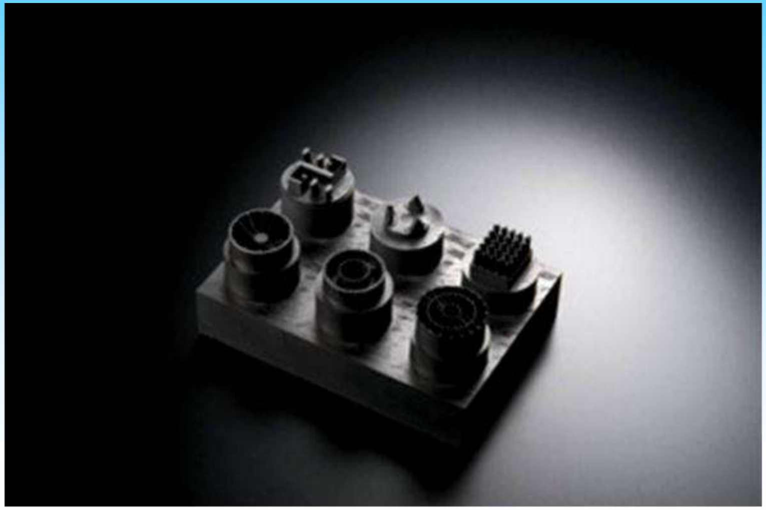




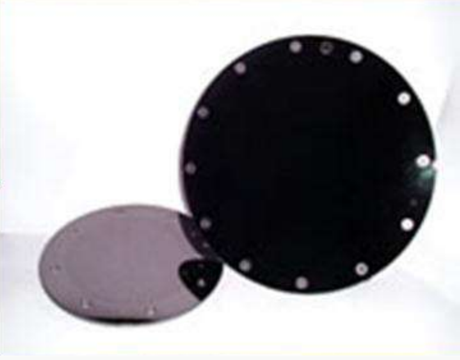

5トン/日バイオマス/廃棄物炭化ガス化実験設備

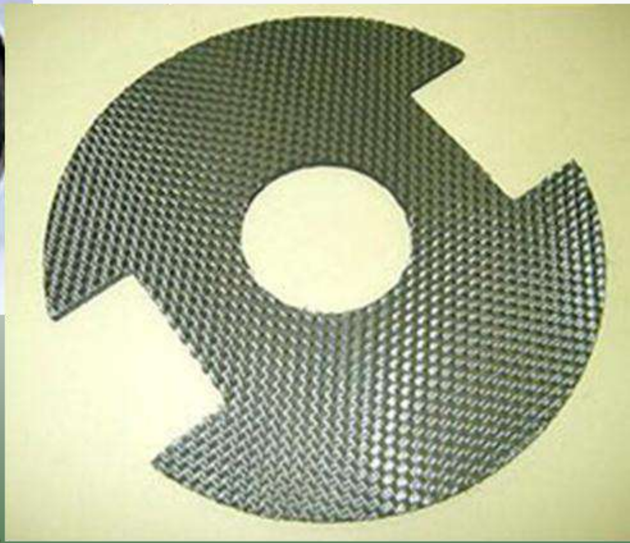
Small fuel cells

Semi-conductors





Carbon blacks

Activated Carbons

Carbons for Nuclear

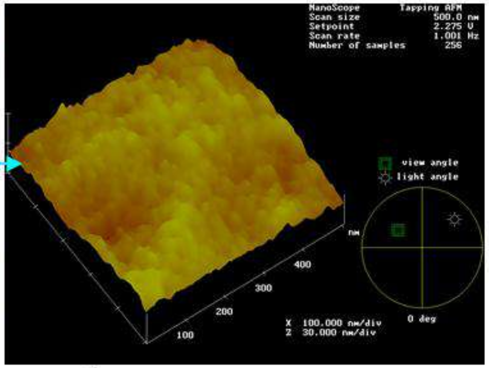
ガラス炭素(Glassy Carbon)

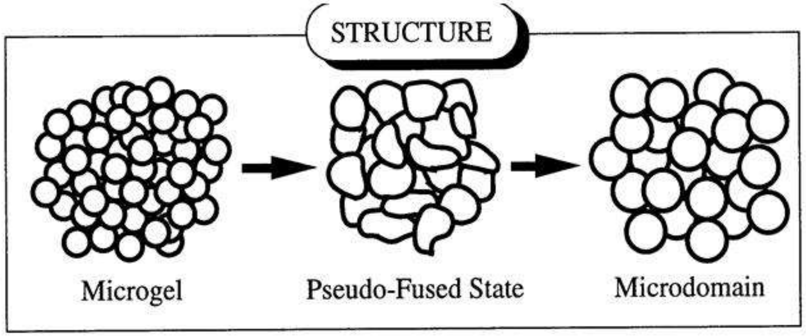
Resin → 硬化 → 熱処理 → 加工･後処理

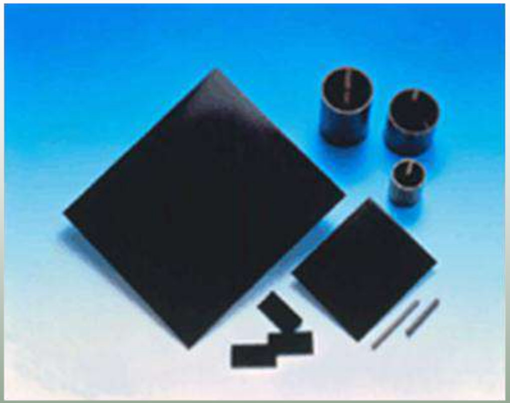
熱･電気伝導性、耐腐食性、高強度、ガス不浸透性

問題点例)放電加工用電極　>>半導体Wafer上の汚れ

原因:加熱放電時熱振動によるミクロドメイン粒子の落ち

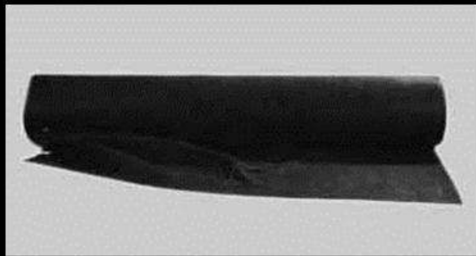


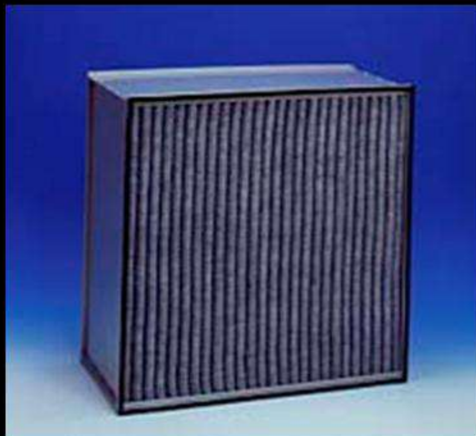


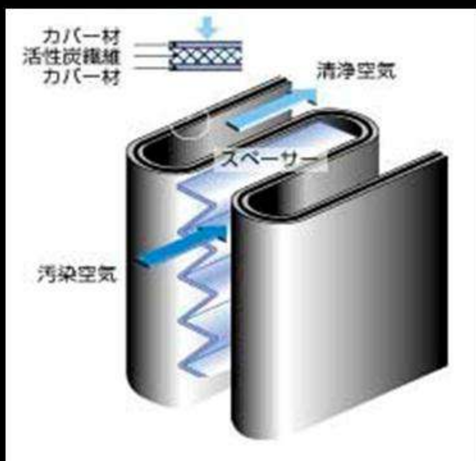


●高純度の炭素製品>金属系不純物元素に　よる汚染なし
●プラズマによる材料消耗を少なく、長寿命●フッ硝酸で、洗浄しても材料自体の消耗な　し

ピッチ系活性炭繊維





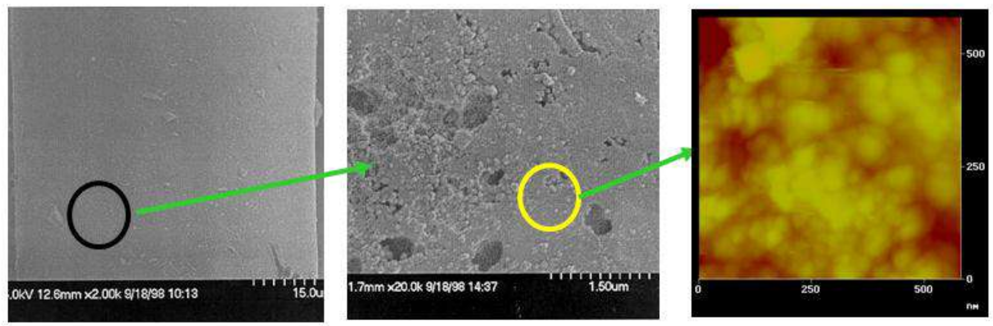


等方性ピッチ → 紡糸 → 不融化 → 活性化

高表面積、ミクロポア、繊維状、導電性

問題点:吸着量、連続吸着、選択性

原因:ポア構造、大きさ、表面特性

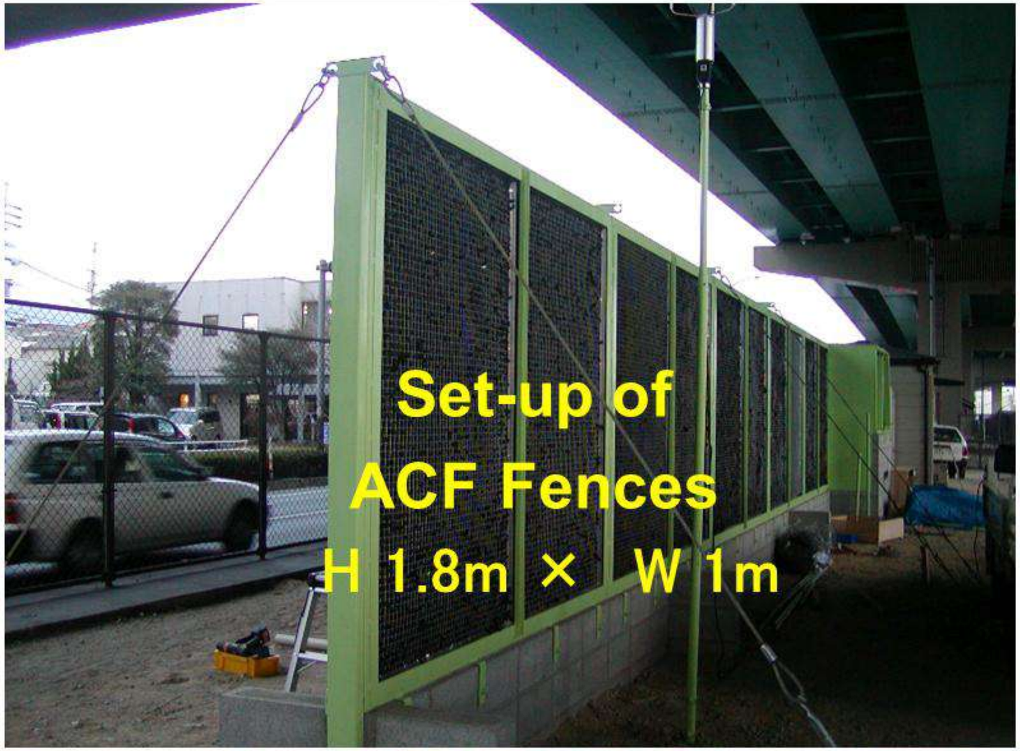


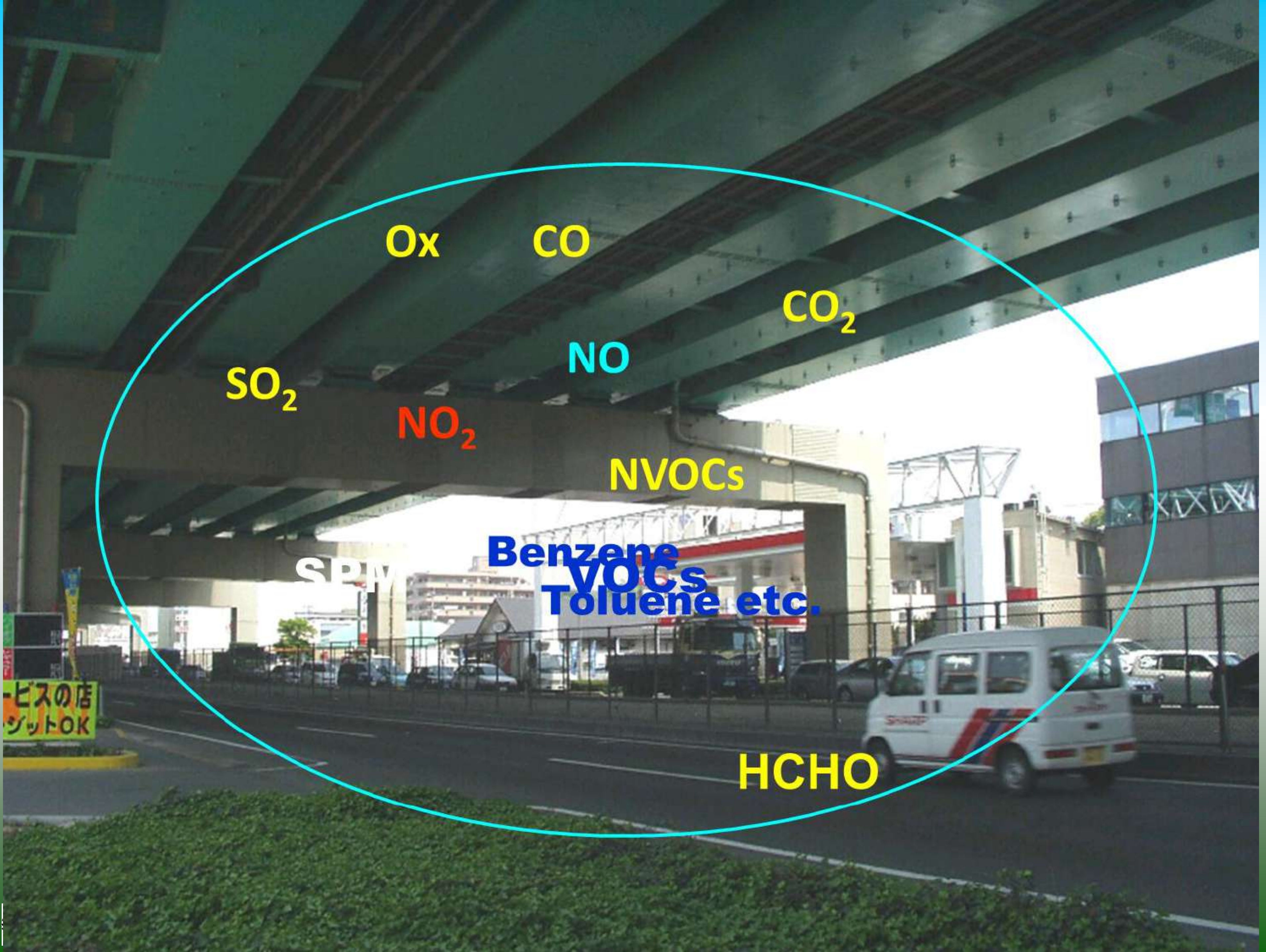
-KOH 賦活:Nanoporeサイズ制御:キャパシタ 物性画期的向上

-1050℃熱処理:表面性質制御:DeSOx性能画期的向上

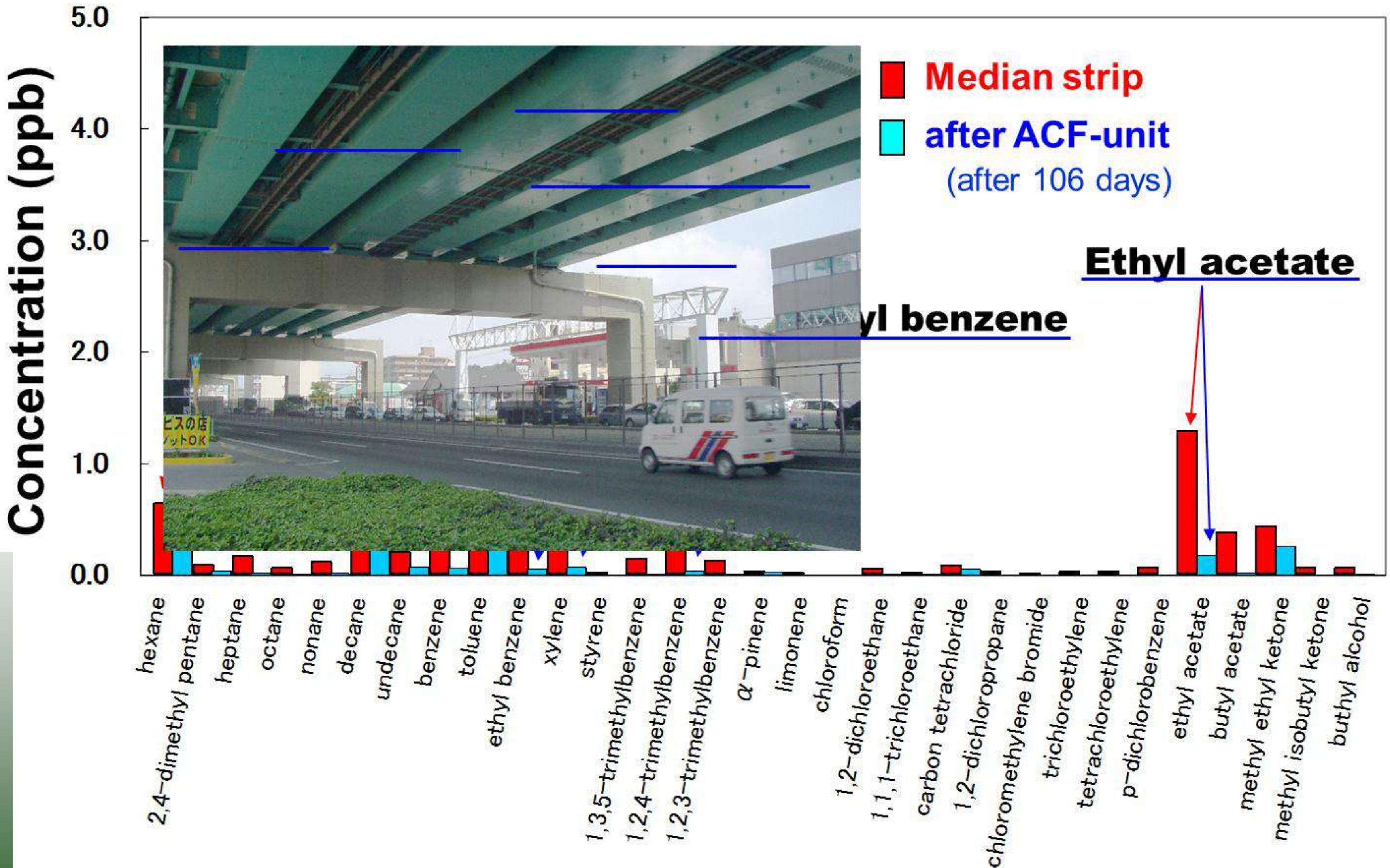
-硝酸処理:表面性質制御:Chloro-compounds除去能向上

Air Purification Using ACF (Remote Watching System)

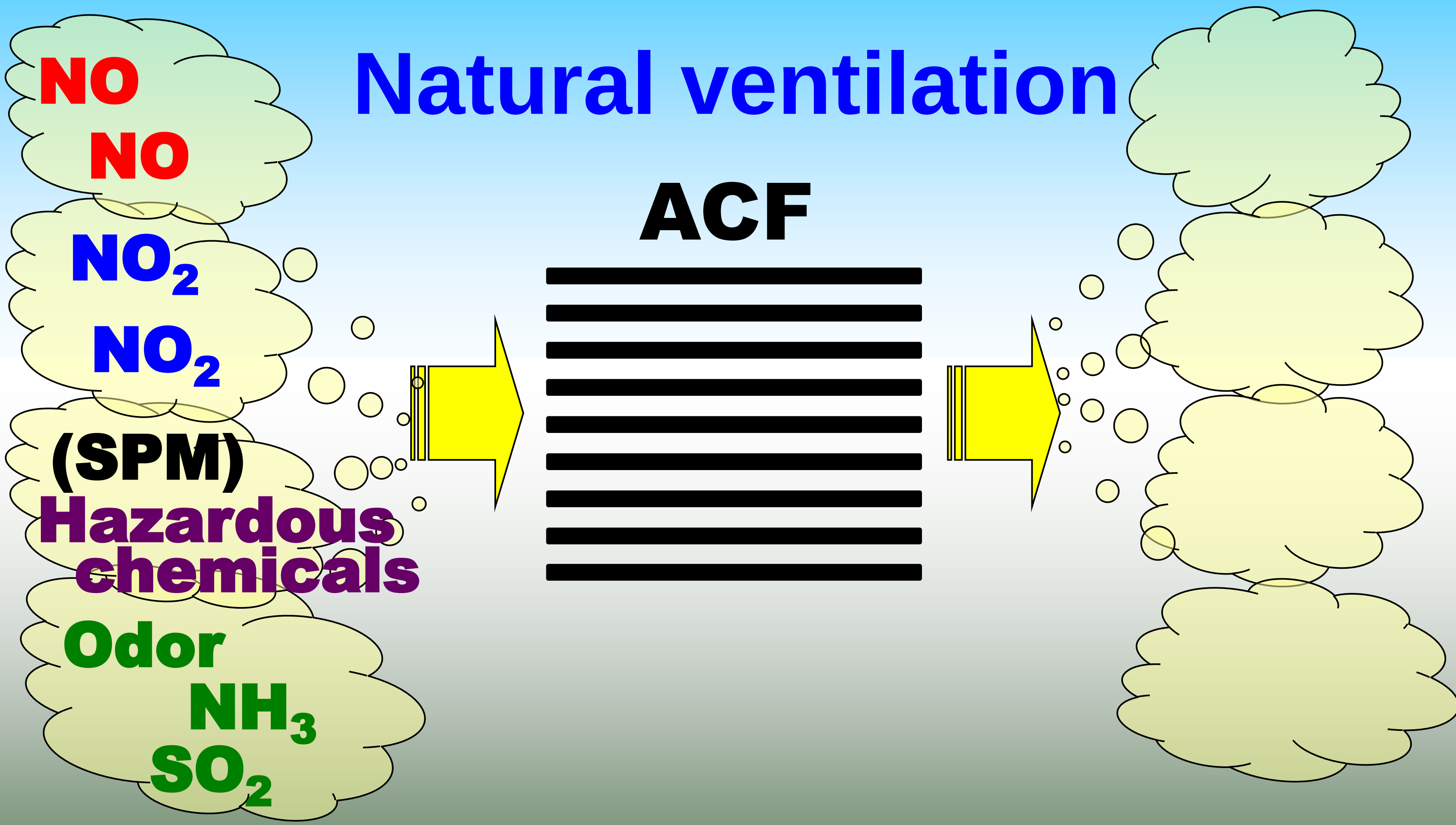



Ox
CO
CO_2
NO
SO_2
NO_2
NVOCs
SPM
Benzene
VOCs
Toluene etc.
HCHO

The VOC's concentrations on the road and scavenging effect of ACF-unit.

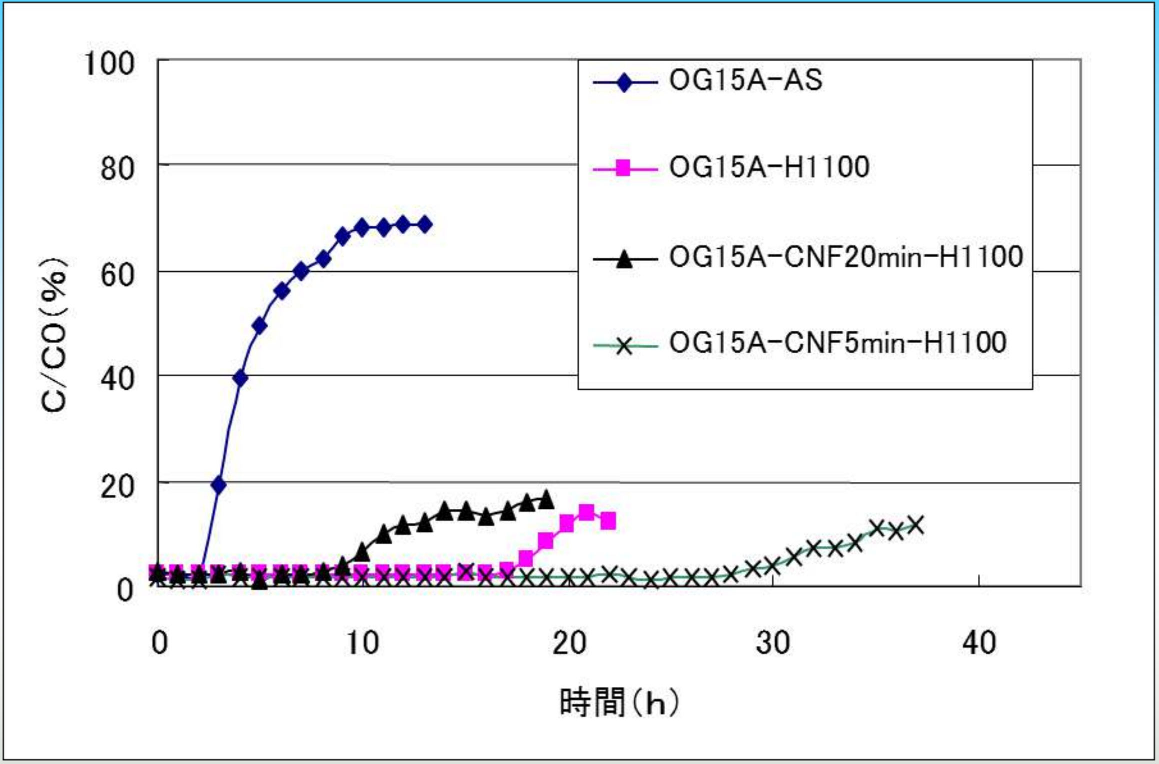


Characterization of ACF purification



Room temperature, ozonizer is no need, no light irradiation, compact design

Fig. 3 CNF-ACF複合体を利用したSO2連続除去プロファイル



OG15A-AS: Pitch based as-prepared ACF from Osaka Gas
OG15A-H1100: Heat treated OG15A-AS at 1100°C for 0h
OG15A-CNF5min-H1100: Heat treated CNF-OG15A-AS composites
(CNF生成時間:5分)

OG15A-CNF5min-H1100を利用し、OG15A-H1100よりさらに高い排煙脱硫性能を達成した。（完全脱硫:28時間以上、定常脱硫率:85%

OG15A-H1100を利用した硫酸回収型排煙脱硫装置は、パイロットテストを終え、2004年4月から実証Plant稼動（九大－三菱重工－大阪ガス）

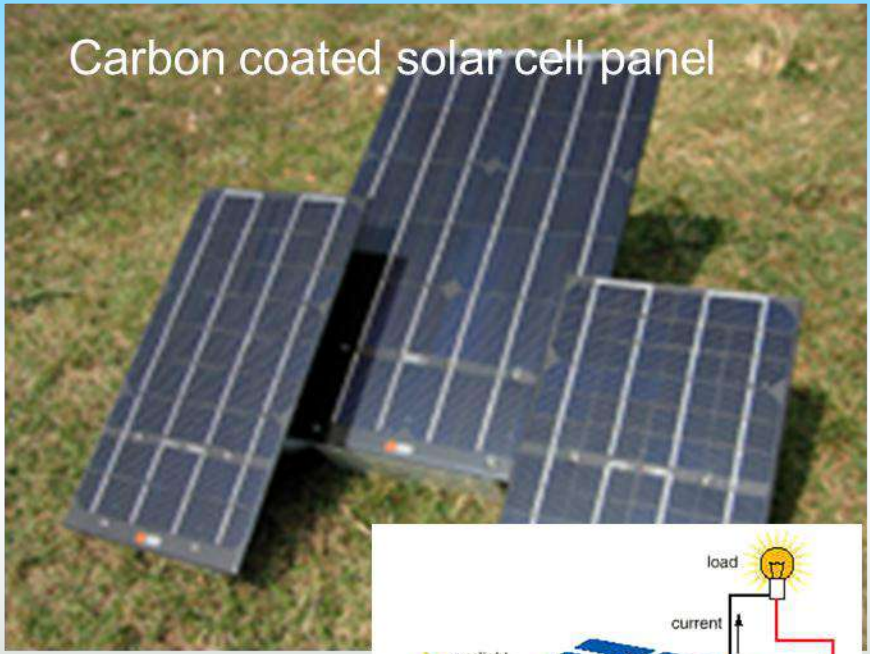
CNF-ACF 複合体（**OG15A-CNF5min-H1100**）の開発によってプラント容積を1/2まで縮小可能

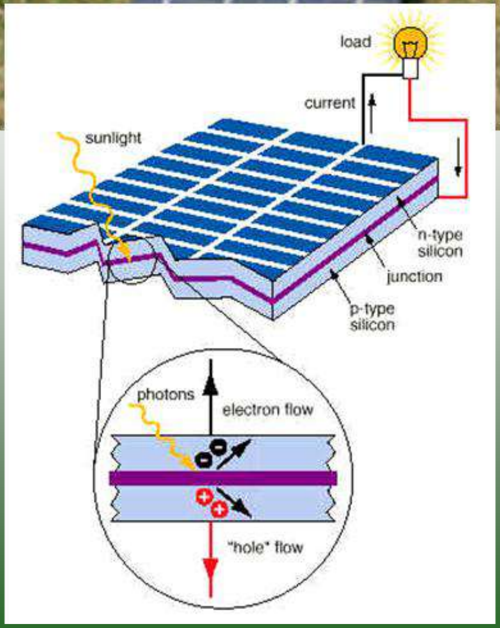
さらに高い脱硫率を目指している

Sun Light (Solar Cell)

Silica reduction agent

Silicone growing furnace





Reducing Agent Using Biomass Char and Tar

SiO_2 → Reduction Agent → Metallic Si

Silica reduction agent

Indonesian mangrove

→ Purification sizing → Carbonization (Char)

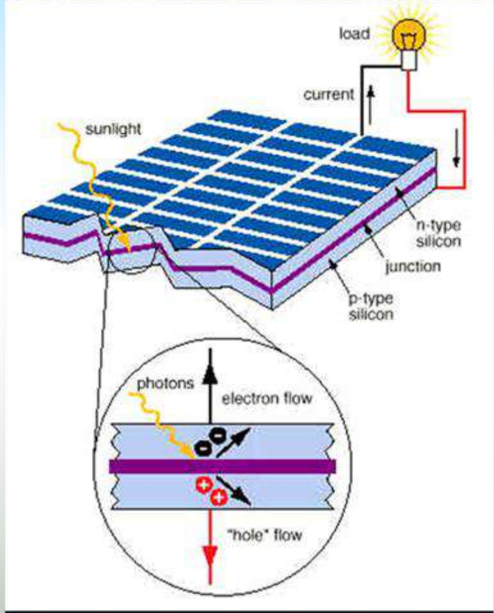
Char

↓ Wood tar

Coal tar or Hyper coal
With small ashes

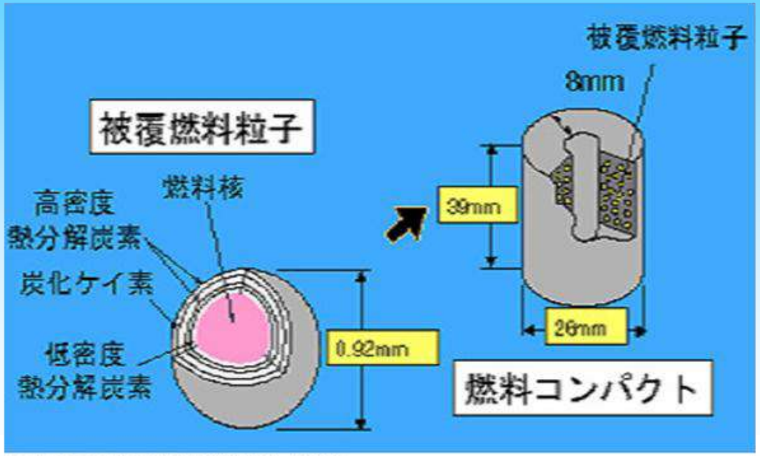
→ ↓ Cokes

↓ SiO_2 reducing agent

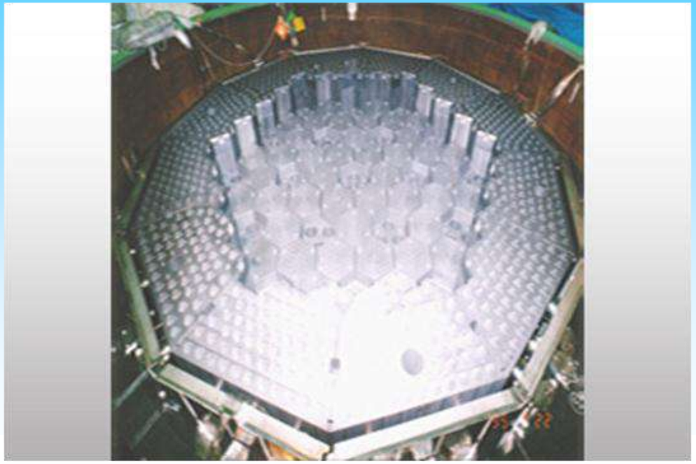


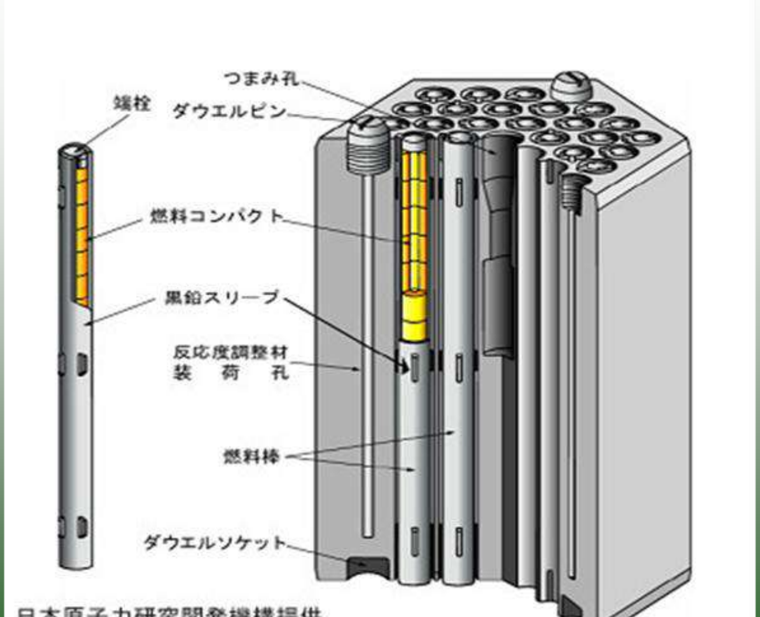
Silicone growing furnace

Atomic Reactor

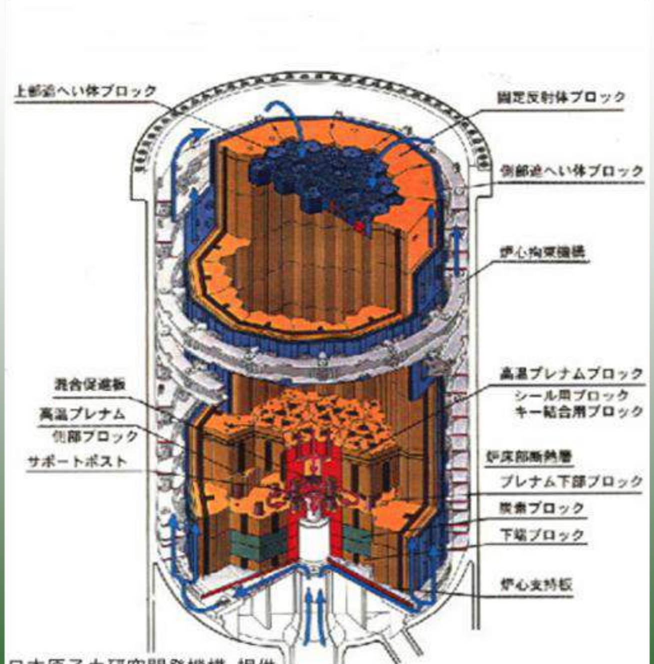


日本原子力研究開発機構 提供





日本原子力研究開発機構提供



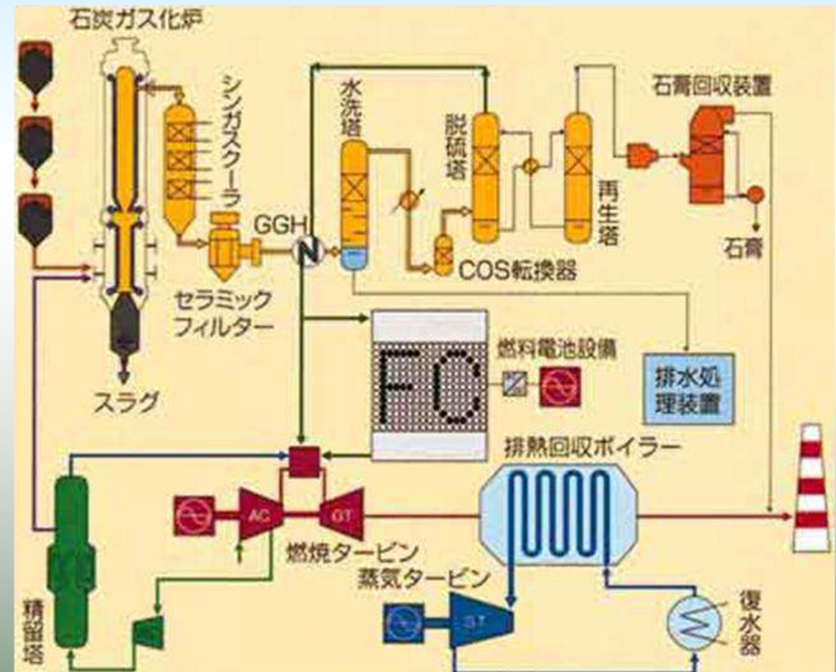
日本原子力研究開発機構 提供

IGCC & IGFC

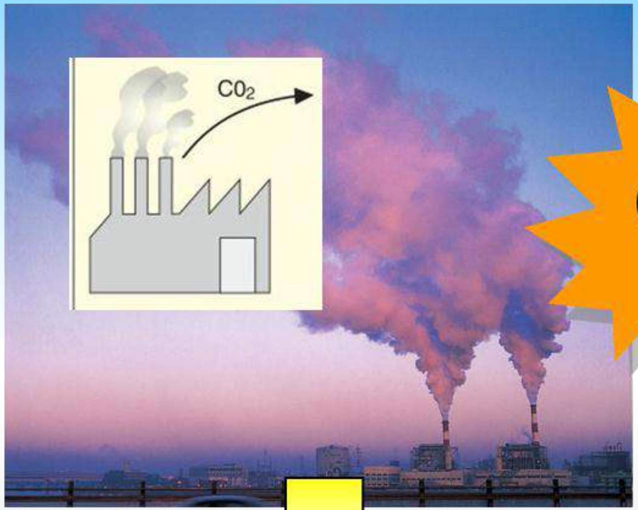
High Temperature Gasification Reactor & Fuel Cell

The Higher Temperature the operation, The higher Efficiency.
→ Carbon structural materials

５トン／日バイオマス／廃棄物炭化ガス化実験設備

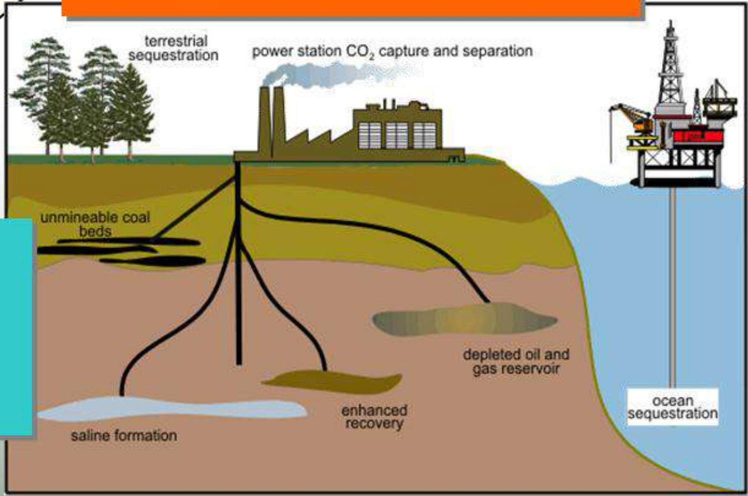


CCS - Carbon Dioxide Sequestration -



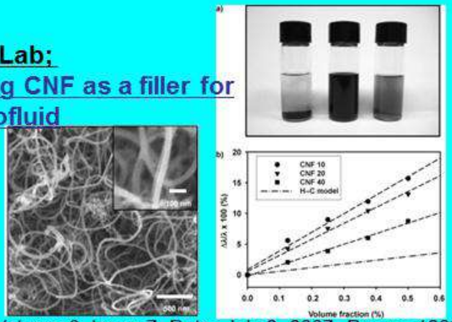
CO_2

Storage
Disposal / Re-use



Separation & Concentration (Over 98%)

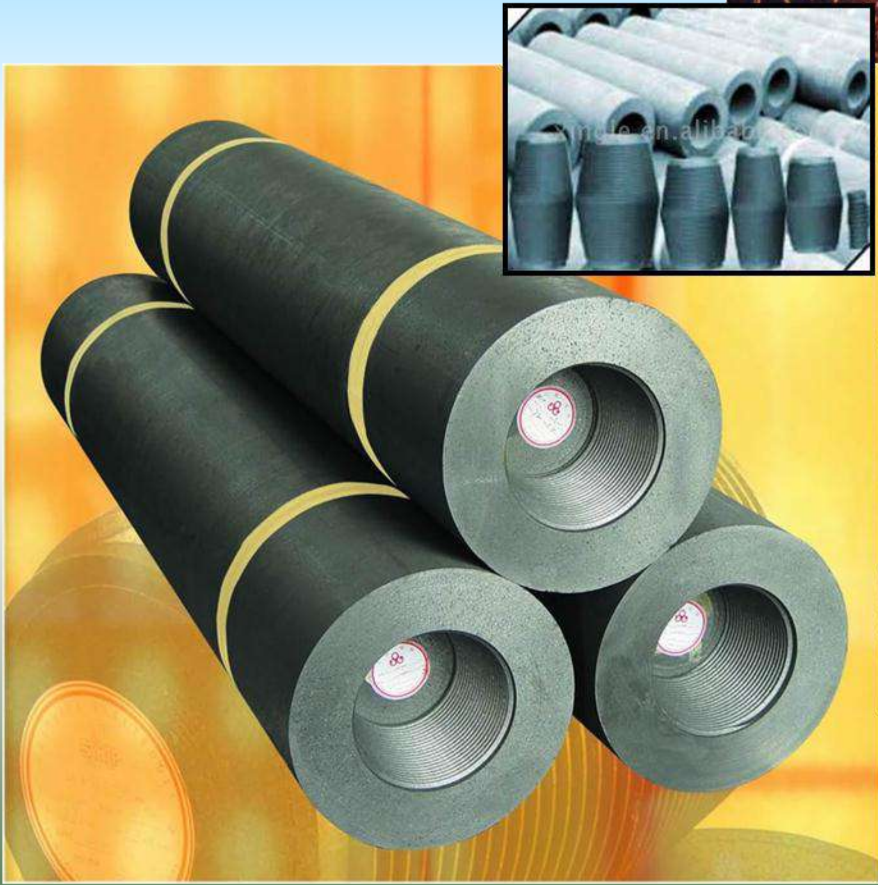
Our Lab;
Using CNF as a filler for nanofluid

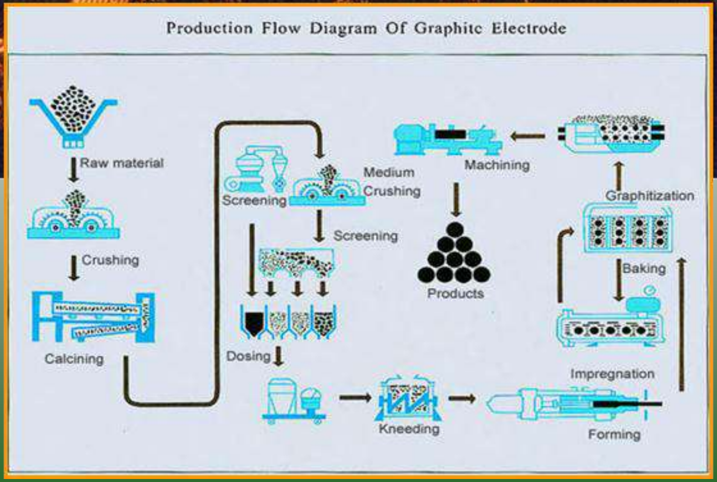


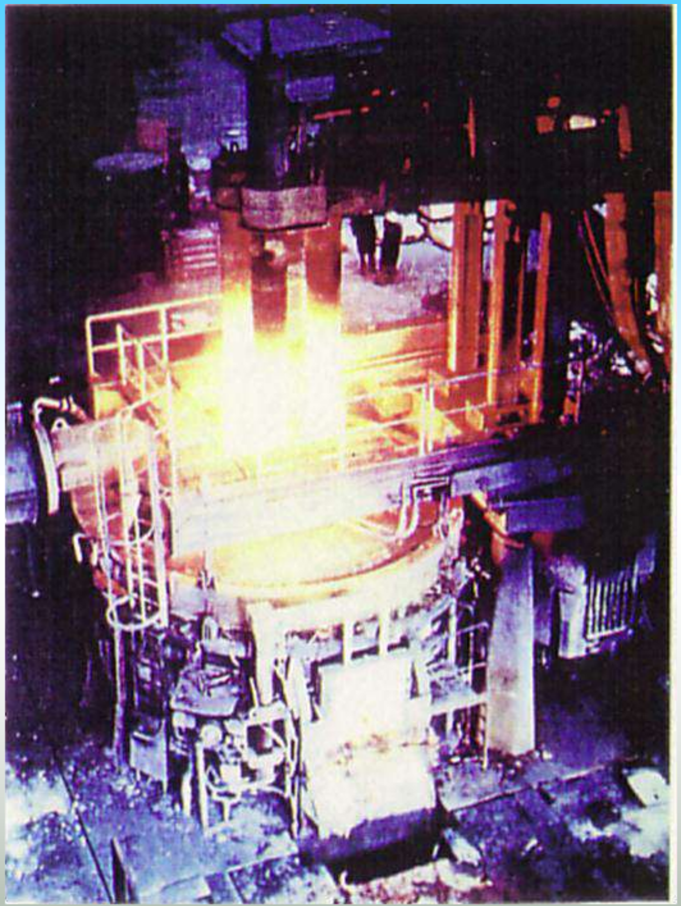
Small, Volume 3, Issue 7, Date: July 2, 2007, Pages: 1209-1213

PSA with Activated Carbon
Separation membrane with carbon ceramic filter
Absorption separation with organic amines

Graphite Electrode

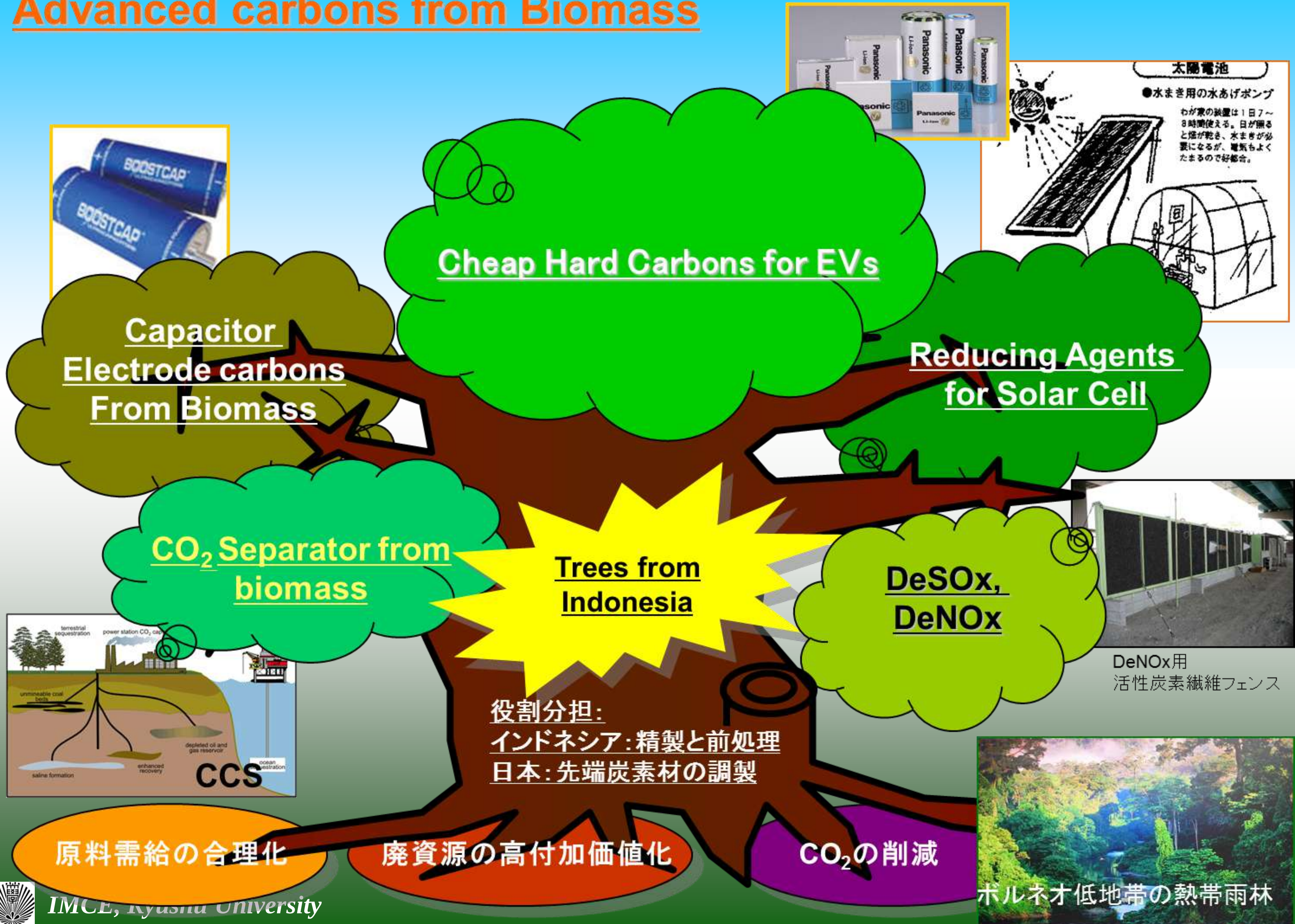




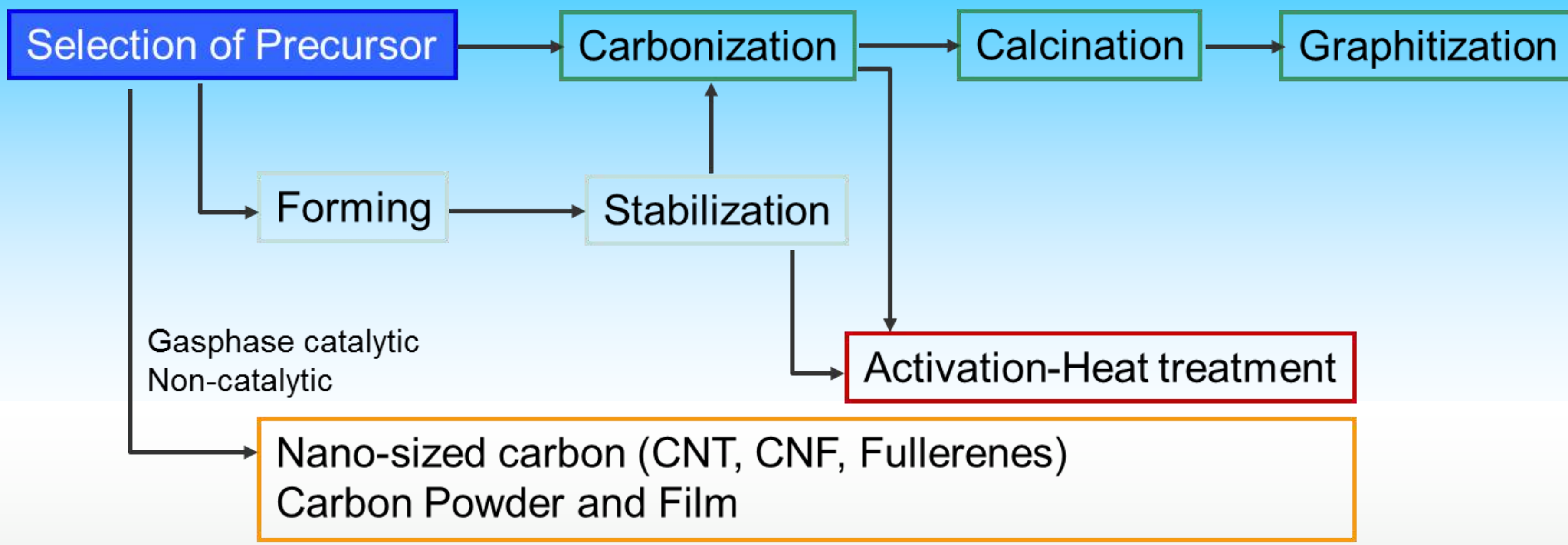


Iron Smelting in Electric Arc Furnace.
Needle Coke Electrode.

Advanced carbons from Biomass

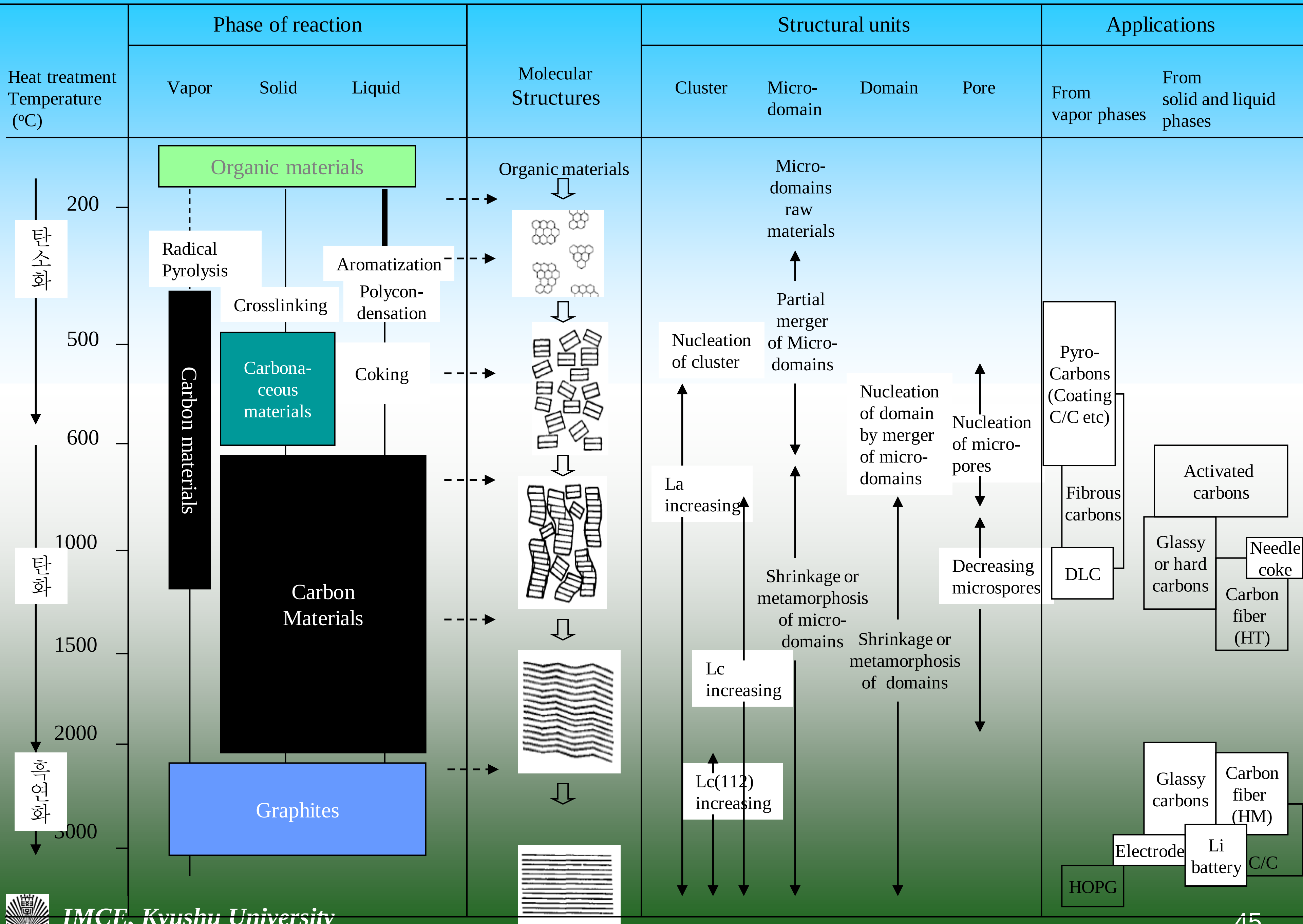


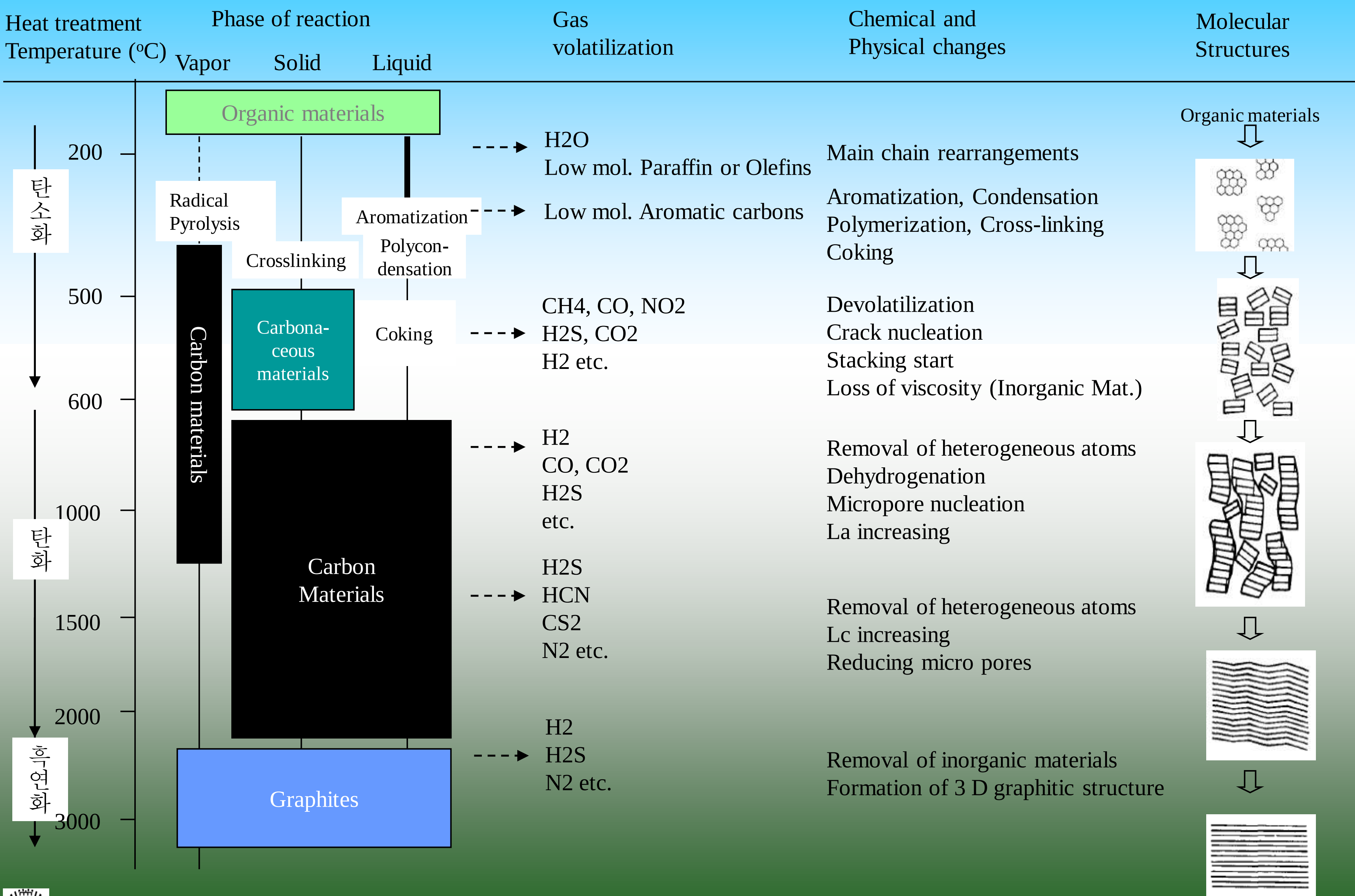
炭素材の製造



Preparation of Composite

Carbon Growth on the Substrate


Phase of reaction
Structural units
Applications
Heat treatment Temperature (ºC)
Vapor
Solid
Liquid
Molecular Structures
Cluster
Micro-domain
Domain
Pore
From vapor phases
From solid and liquid phases
200
500
600
1000
1500
2000
3000
탄소화
탄화
흑연화
Organic materials
Radical Pyrolysis
Crosslinking
Aromatization
Polycon-densation
Carbon materials
Carbona-ceous materials
Coking
Carbon Materials
Graphites
Organic materials
Micro-domains raw materials
Partial merger of Micro-domains
Nucleation of cluster
La increasing
Shrinkage or metamorphosis of micro-domains
Lc increasing
Lc(112) increasing
Nucleation of domain by merger of micro-domains
Shrinkage or metamorphosis of domains
Nucleation of micro-pores
Decreasing microspores
Pyro-Carbons (Coating C/C etc)
Fibrous carbons
DLC
Activated carbons
Glassy or hard carbons
Needle coke
Carbon fiber (HT)
Glassy carbons
Carbon fiber (HM)
Electrode
Li battery
C/C
HOPG


Heat treatment Temperature (°C)
Phase of reaction
Vapor
Solid
Liquid
Gas volatilization
Chemical and Physical changes
Molecular Structures
Organic materials
200
500
600
1000
1500
2000
3000
탄소화
탄화
흑연화
Radical Pyrolysis
Crosslinking
Aromatization
Polycon-densation
Coking
Carbon materials
Carbona-ceous materials
Carbon Materials
Graphites
H2O
Low mol. Paraffin or Olefins
Low mol. Aromatic carbons
CH4, CO, NO2
H2S, CO2
H2 etc.
H2
CO, CO2
H2S
etc.
H2S
HCN
CS2
N2 etc.
H2
H2S
N2 etc.
Main chain rearrangements
Aromatization, Condensation
Polymerization, Cross-linking
Coking
Devolatilization
Crack nucleation
Stacking start
Loss of viscosity (Inorganic Mat.)
Removal of heterogeneous atoms
Dehydrogenation
Micropore nucleation
La increasing
Removal of heterogeneous atoms
Lc increasing
Reducing micro pores
Removal of inorganic materials
Formation of 3 D graphitic structure
Organic materials

化石燃料から高機能性炭素材の製造と応用

Carbonaceous resources | **Side products** | **Advanced Carbon Materials for Energy Saving, Storing, And Environmental Protections and Improvements**

Effective conversion and utilization of fossil fuels and their residues

Carbonaceous resources:
- Petroleum → Heavy residues, C10+, Syngas
- Natural Gas → Syngas
- Coal → Coke, Syngas, COG, Tar
- Biomass → Char, Tar

Side products:
- Heavy residues
- $C10^+$
- Syngas
- Coke
- COG
- Tar
- Char

Energy Saving

Fuel Cell
- Catalyst
- Separator
- Bipolar Plate

Advanced Generation
- Structural Materials For IGCC, IGFC
- Structural Materials For Atomic Reactor

Light Weight
- Carbon Fibers
- Synthetic Carbon

Energy Storing

Battery
- Li-ion battery
- Na-S battery
- Air battery

Super capacitor
- EDLC for EV, FV

Hydrogen
- H-storing Bombe

Methane
- Methane storage

Environmental Protections

Water
- Purification
- Water conversion
- NO_3^-, PO_4^{-3} removal

Atmosphere
- AC, ACF for DeSOx, DeNOx, deVOCs
- AC, ACF for Sick-house gases
- CO_2 separation & Concentration

人造カーボンの構造の由来

Origin of Structural Units And Crystalline Defects

Organic materials → (Heat treatment) → Carbon

Basic structural units → Micro domain 4 ~ 6 nm

2 ~ 10 nm

Orientation
Rearrangement

Coagulation
Partial melt fusion

↓

Domain Modified Structures

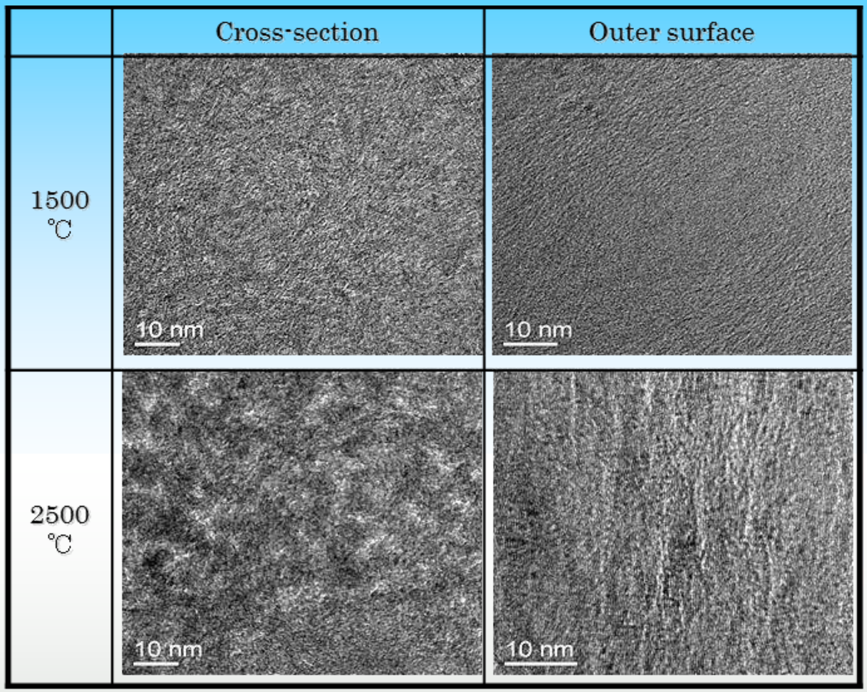
Gas
Liquid
} Carbon or carbonaceous materials

Solid → Varieties of structural unit

↓

Heat treatment

PAN系炭素繊維の構造



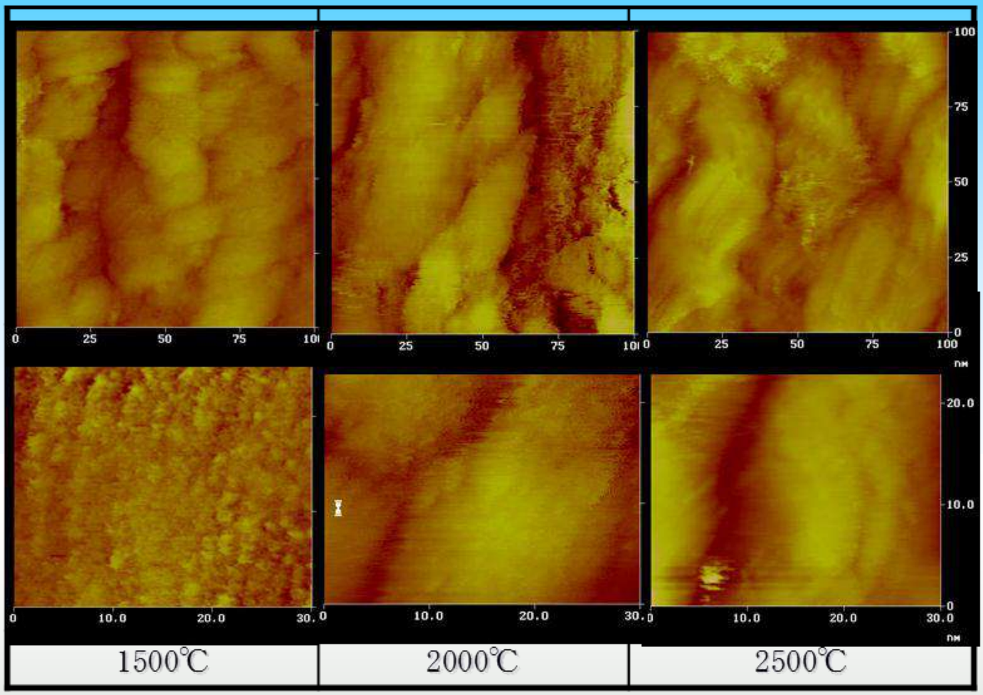
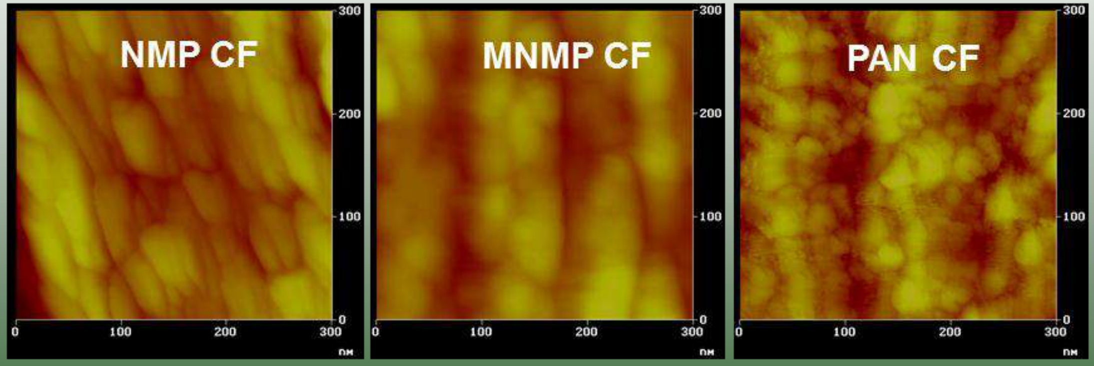
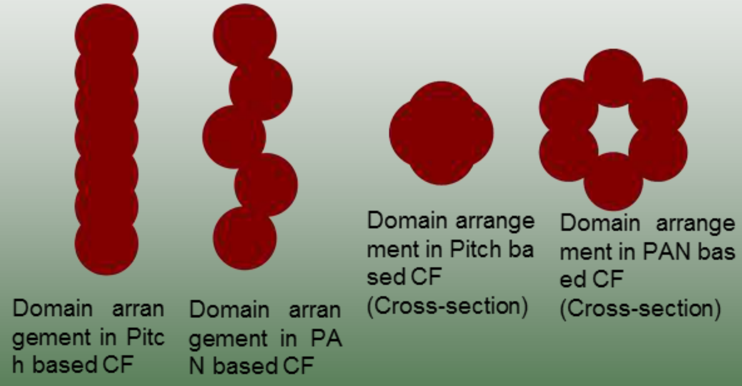


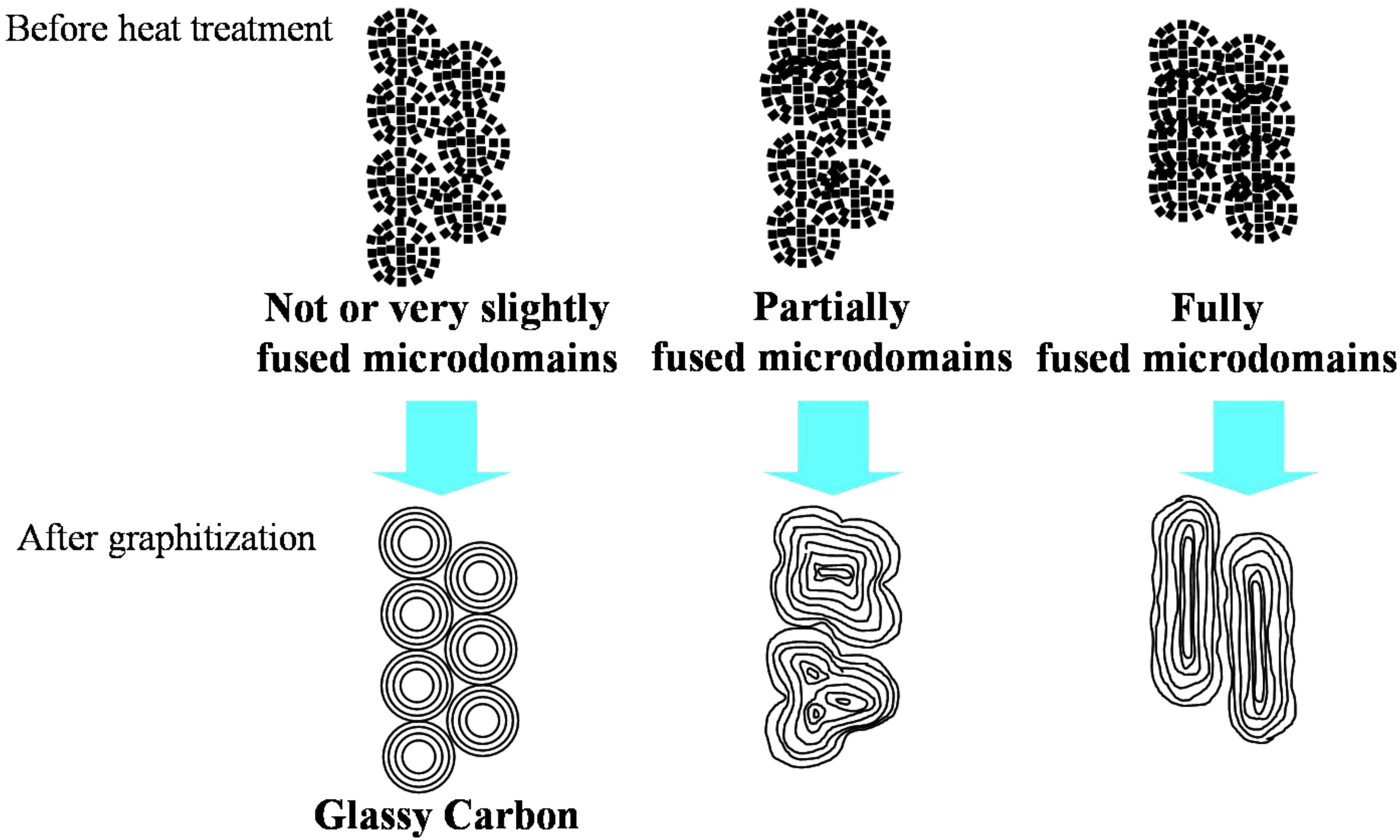
Figure SEM & STM images of heat treated PAN based CFs at 1500、2000、2500℃





"Structural comparison of mesophase and PAN based carbon fibers"
S.H. Hong, S. H. Yoon, I. Mochida *Carbon2006*、 (2006、7) England

単位構造と構造の制御



 "Axial nano-scale microstructure in the graphitized fiber inherited from liquid crystal mesophase pitch"
Carbon, 34, 83-88 (1996) S. H. Yoon, Y. Korai, K.Yokogawa, S. Fukuyama, M. Yoshimura, I. Mochida

構造概念からの炭素材

Nano

Structures
- Structural units
- Nano-phased units

Spaces
- Pore size and homogeneity
- Pore amounts

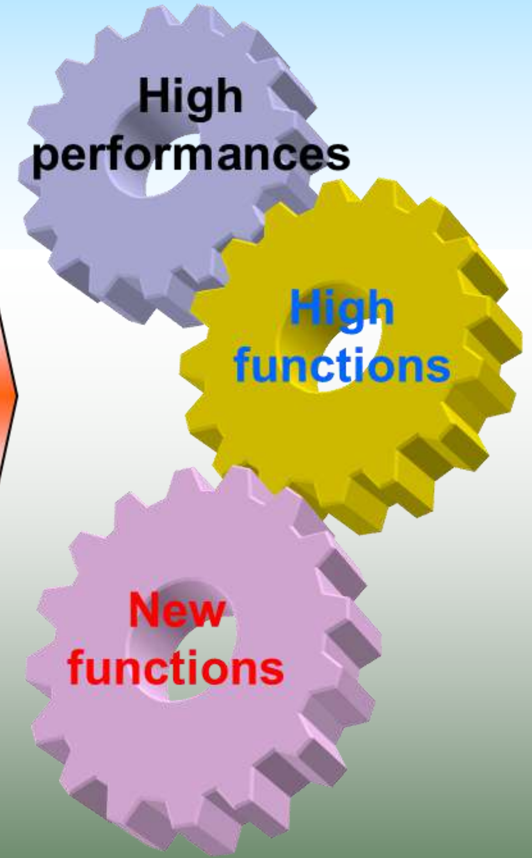
\+

Surfaces
- Edges (Kinds and amounts)
- Basals (Perfectness and Orientation)

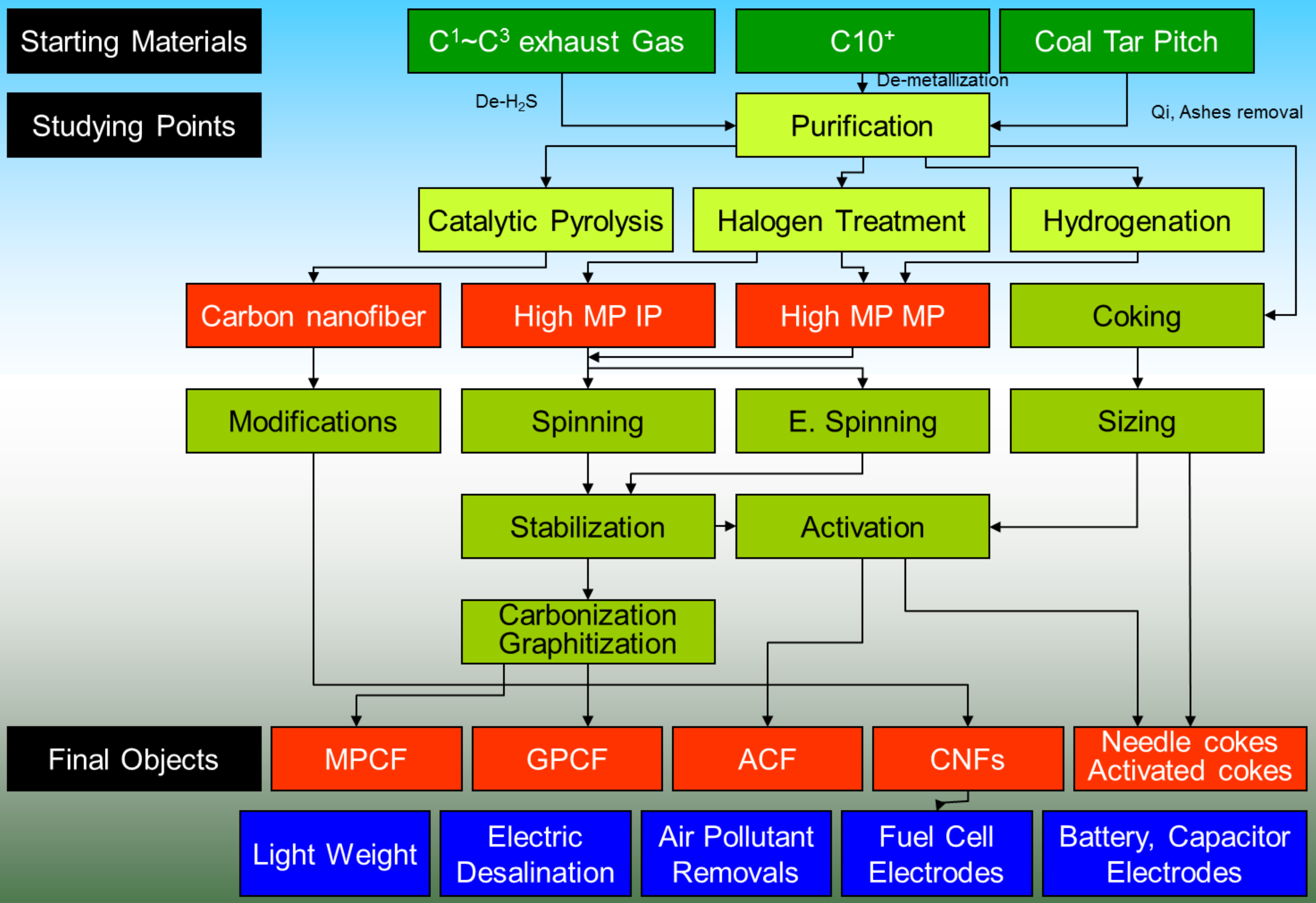
Productions

Hybridization
→
Improving Performances and Functions
→
Creating New Functions

Applications



構造の制御はどこから?



Starting Materials
Studying Points
C1~C3 exhaust Gas
C10+
Coal Tar Pitch
De-H2S
De-metallization
Qi, Ashes removal
Purification
Catalytic Pyrolysis
Halogen Treatment
Hydrogenation
Carbon nanofiber
High MP IP
High MP MP
Coking
Modifications
Spinning
E. Spinning
Sizing
Stabilization
Activation
Carbonization Graphitization
Final Objects
MPCF
GPCF
ACF
CNFs
Needle cokes Activated cokes
Light Weight
Electric Desalination
Air Pollutant Removals
Fuel Cell Electrodes
Battery, Capacitor Electrodes

Purities of Advanced Materials

- High performance pitch based carbon fibers: less than 50 ppm
- Capacitor : less than 500 ppm
- High performance needle coke : 500 ppm
- Carbon medicines: less than 300 ppm?
- Carbon anode for LIB: less than 100 ppm
- …

Mesophase Pitch

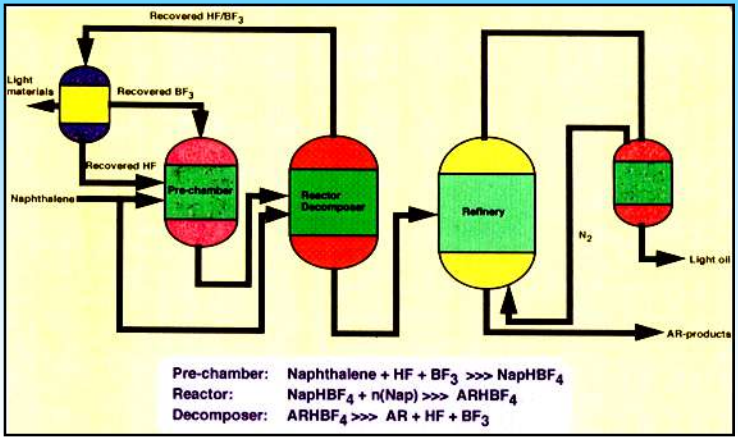
Kyushu University and Mitsubishi Gas Chemical Co.

Catalytic Condensation of Aromatic Compounds into Oligomers

Non-hydrogenation Condensation: Naphthalene Rings

Inheritance of Stacking Structures

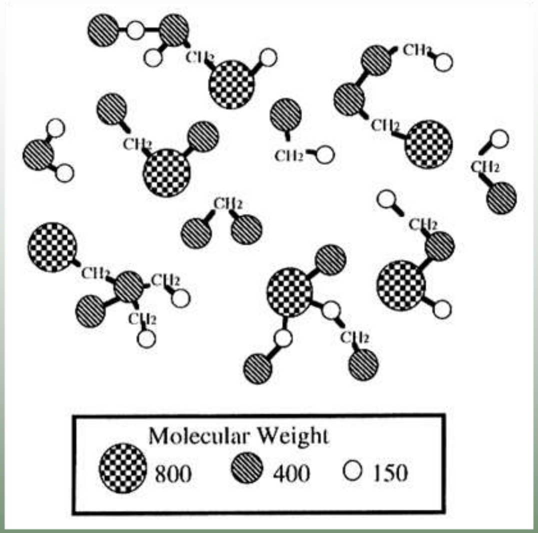
Aromatic Rings
Hetero-atomic Constituents in the Reaction Substituents



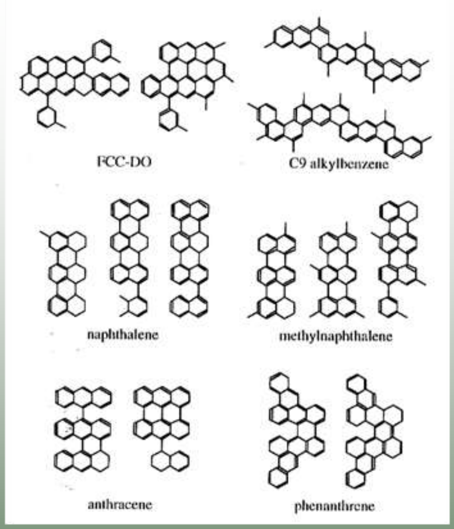
⇨ Aromatic Resin (AR)
Mesophase Pitch

⇨ Large Variety of
Mesogen Molecules

- Removal, Recovery, and Repeated Use of HF/BF_3 Catalyst



Models of mesophase constituent molecules

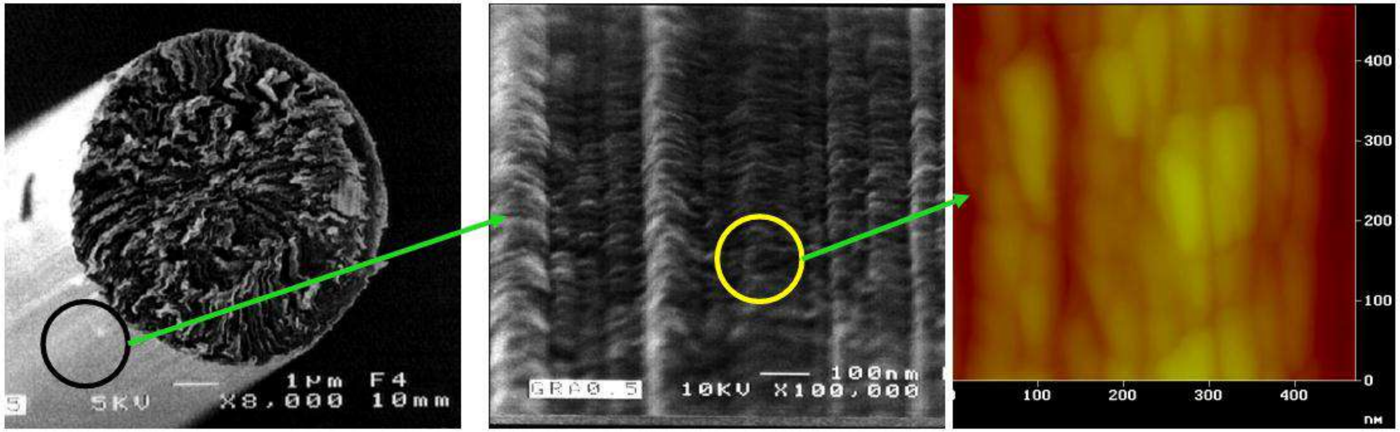


Typical mesogen units in various mesophase pitches
(Mochida et al. Carbon 1990, 28, 311)

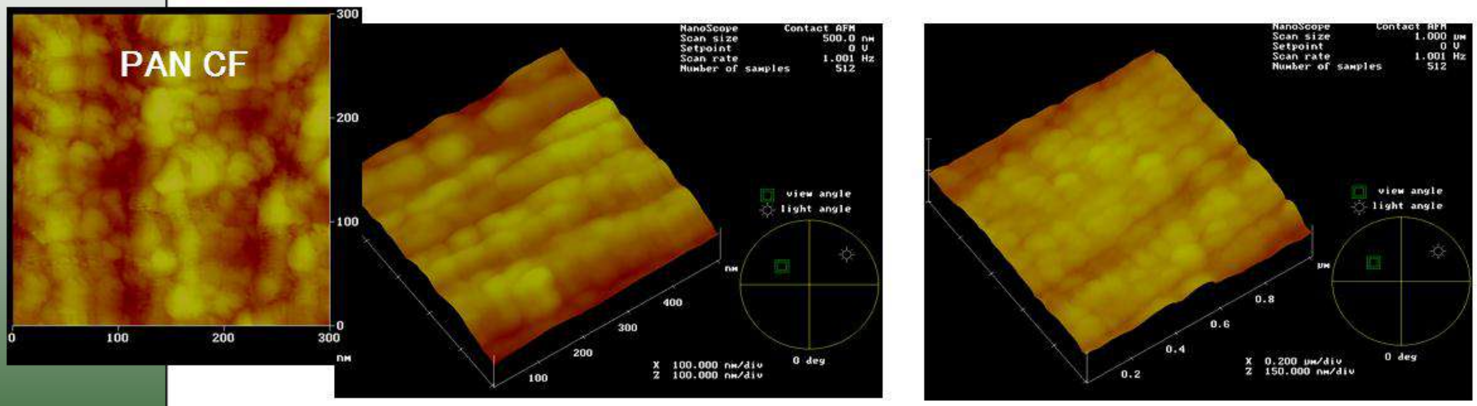
Relationship between the structures and mechanical properties in carbon fibers

Problem : Low Compressive Strength > Restriction of CFRP Application

Factor: Size and Distribution of Micro-domain

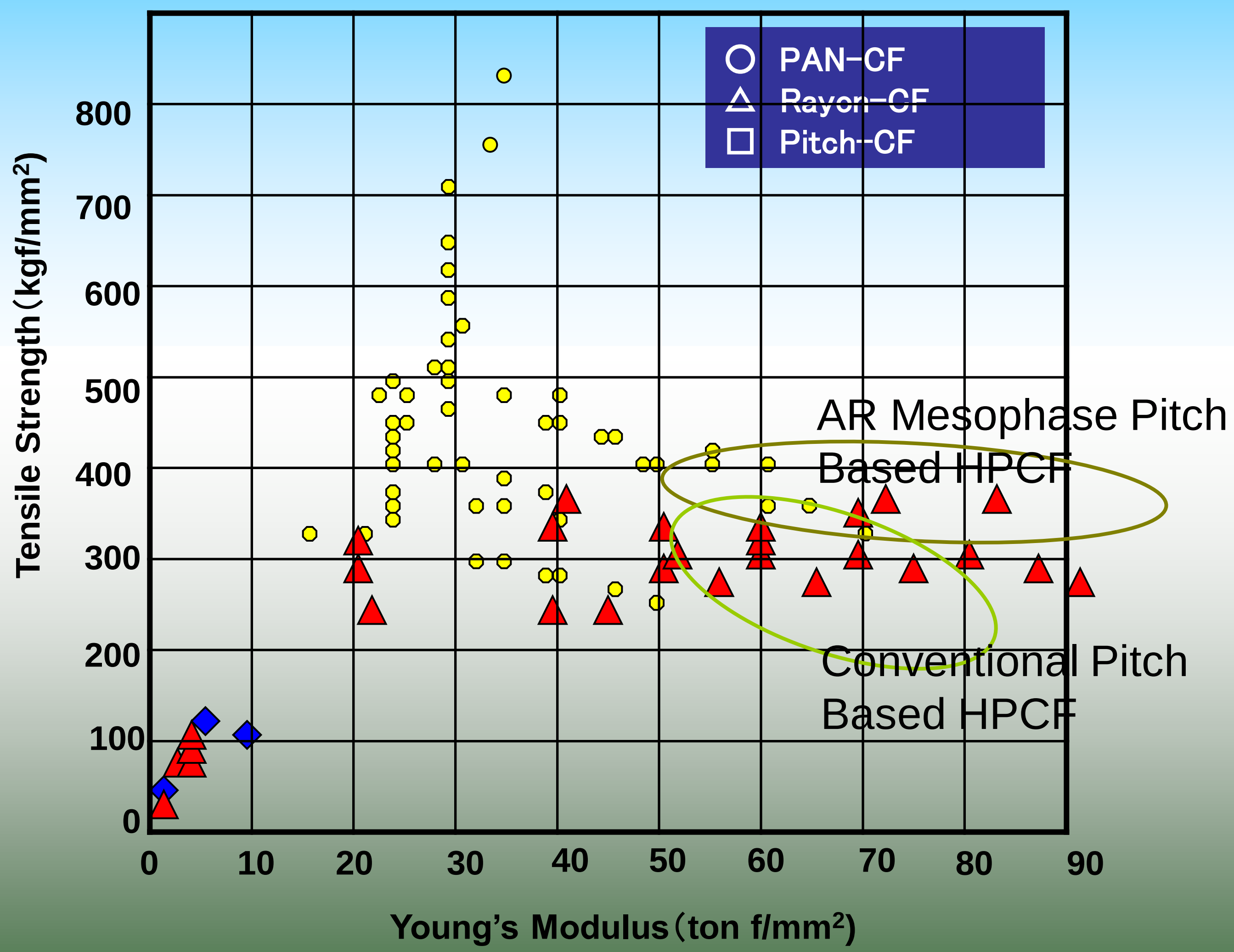


Pleat Structure > Homogeneous / Small > Increasing Compressive Strength

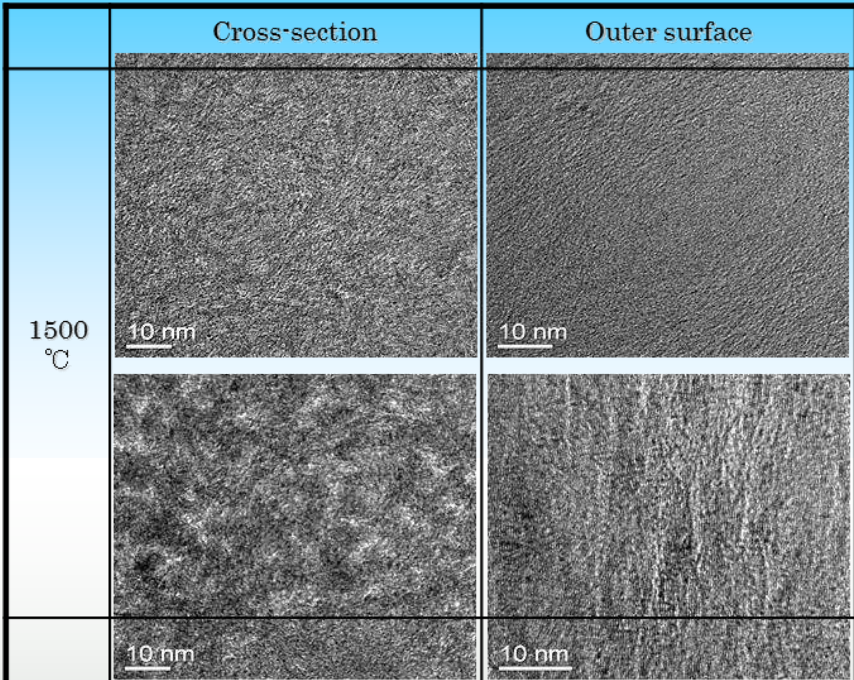


"Pleat structure of mesophase pitch based carbon fiber"
S. H. Yoon, Y. Korai, I. Mochida *Carbon*, 32, 1182-1186 (1994)

Mechanical Properties of Carbon Fibers



Nanoscopic Structure of PAN Based CF



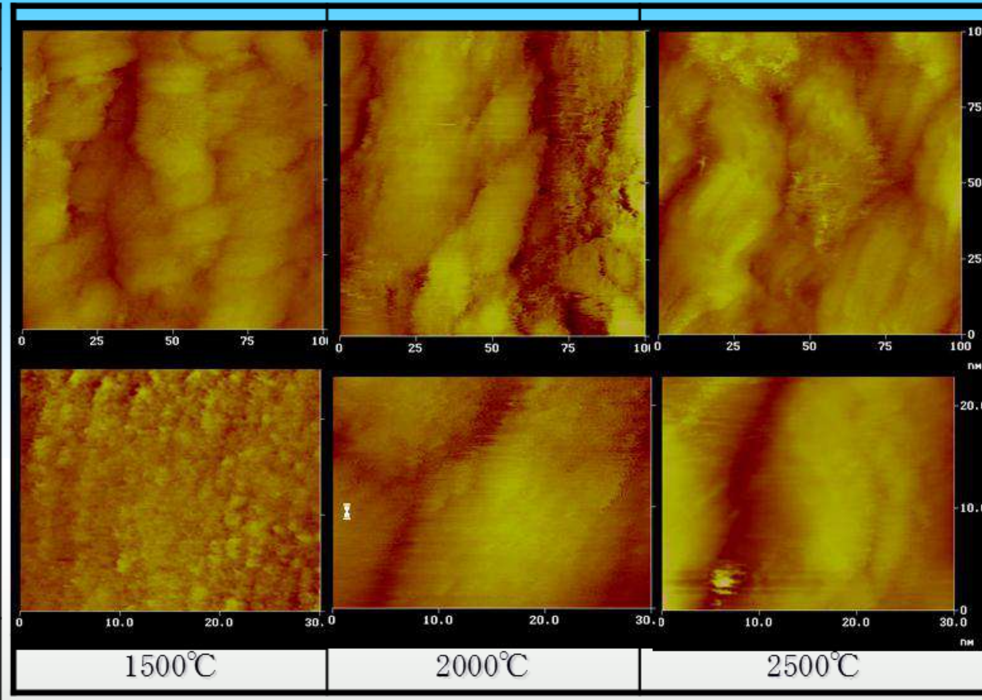
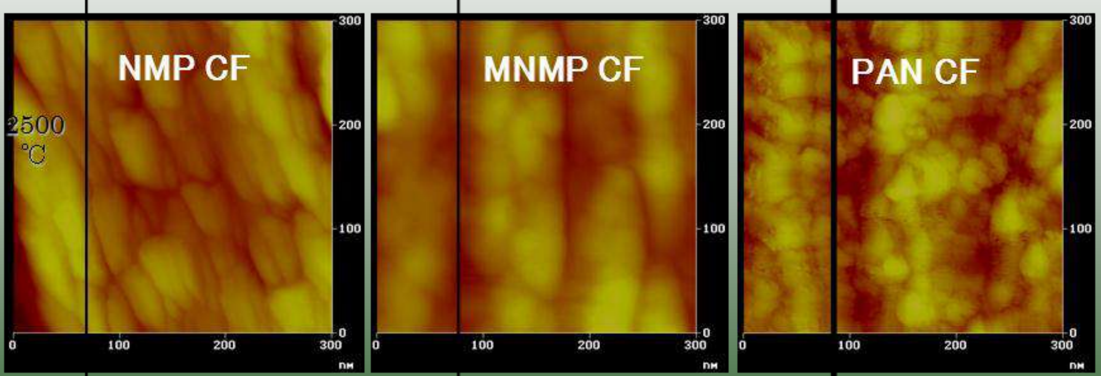
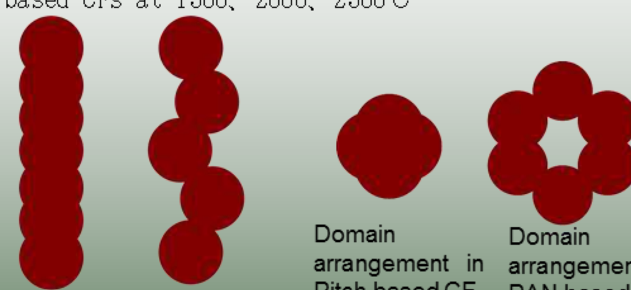


Figure SEM & STM images of heat treated PAN based CFs at 1500、2000、2500℃





"Structural comparison of mesophase and PAN based carbon fibers"
S.H. Hong, S. H. Yoon, I. Mochida *Carbon2006*、(2006、7) England

Nano-carbons

Fullerene	Zero dimension Basal surface Nano-size	High price, very limited application Mass-production (Solved) (Frontier Carbon)
CNT	One dimension Basal surface Nano-size	Relatively high price (Under study) Patent problems (?) Mass-production Limited application
CNF	Various surfaces and structures Nano-size	Relatively low price Patent problems (Solved) Mass-production (Solved) Various applications Large diameter (Solved)
Graphene	Dimension-less Particular surfaces	Relatively low price Patent problems (Solved) Mass-production (Solved) Various applications

Selective Preparation of CNFs and Relatives

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

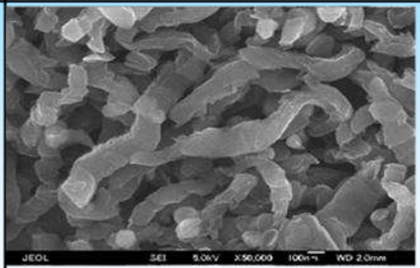
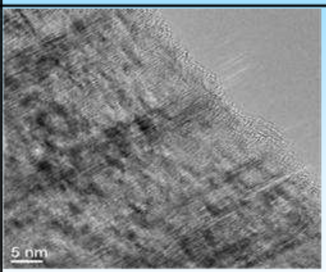
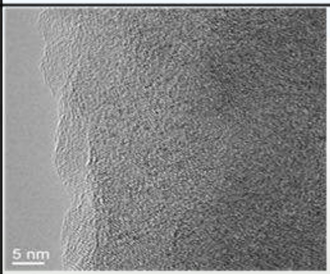
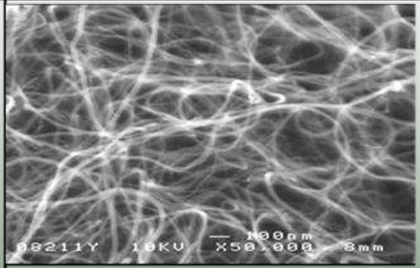
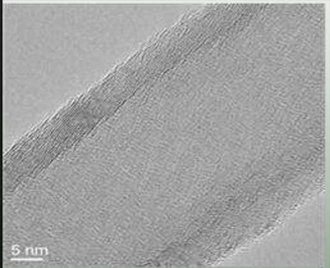
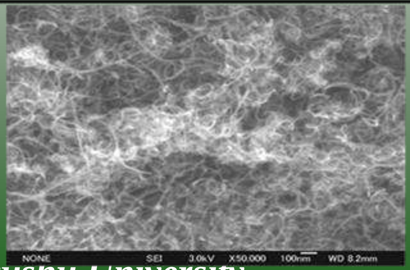
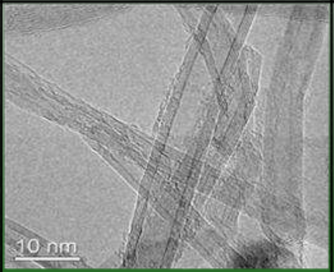
Activation

Electric oxidation

Electro-spun CNF

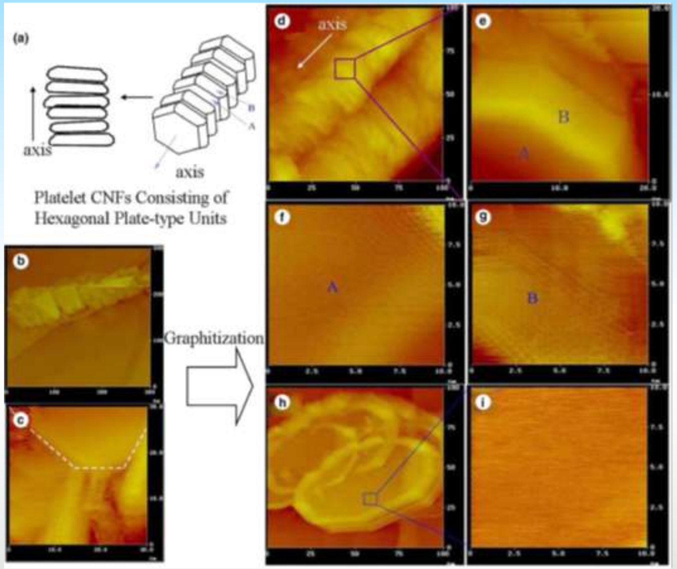
Indoor pollutions
Dilute NOx
De-metal, De-particulates¥

Standard CNFs

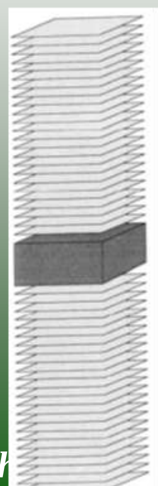
Sample #	SEM	TEM	Properties	Applications	Etc.
KNF-SPR **Platelet** **Nano-rod**			Platelet high grapht. deg. 80 ~ 400 nm, SA 90 m^2/g d_{002} 3.36Å, Lc(002) 30 nm	電池材料, 触媒担体, 触媒担体 例)　高活性水素化触媒Ru/PCNF	70 g/日
KNF-SH **Herring-bone**			Herringbone high surface area 70 ~ 500 nm, SA 150 m^2/g d_{002} 3.45Å,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

Preparation of uniform graphene disc

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

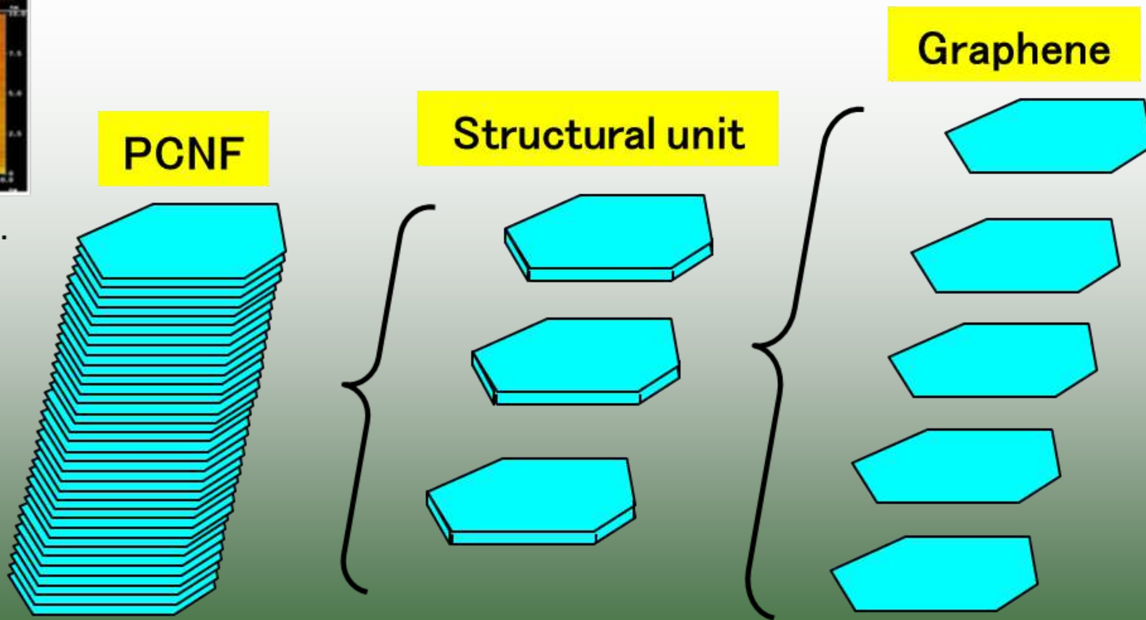


Yoon SH et al. *Carbon* **43**, 1828 (2005).



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.

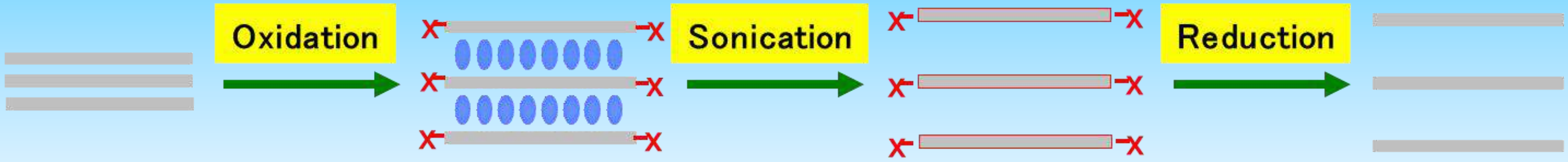


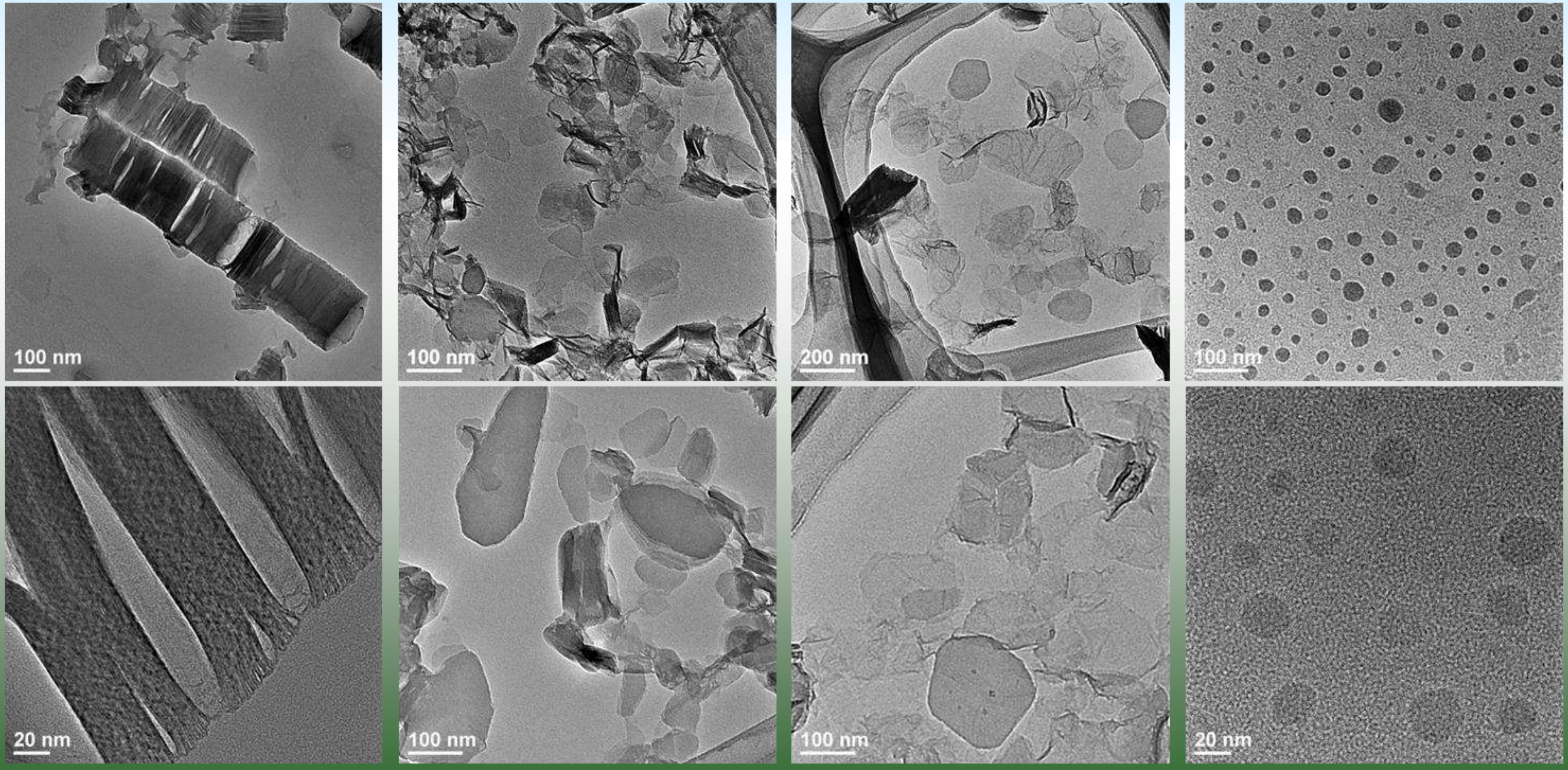
Cutting to structural unit, and then graphene

1. Preparation of graphene discs

Chemical reduction of GPCNF oxide

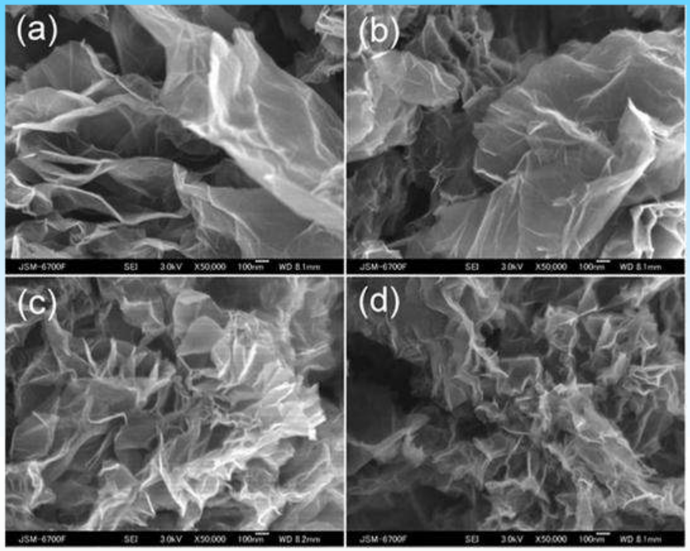
Hydrothermal reduction using $NaBH_4$ at 130°C for 5 h

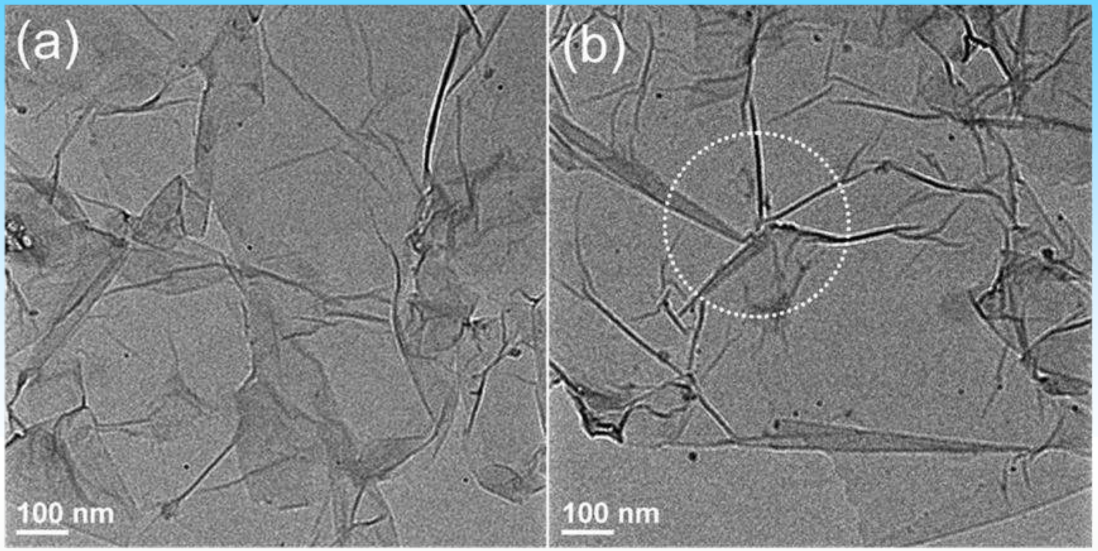


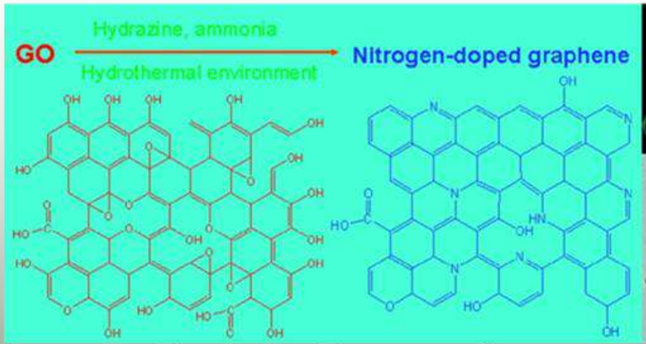


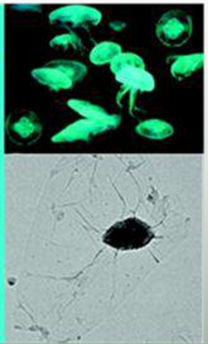
K/GP = 1 K/GP = 3 K/GP = 5 K/GP = 6

Nitrogen-Doped Graphenes by a Combined Chemical and Hydrothermal Reduction *Langmuir*, **2010**, *26* (20), pp 16096–16102

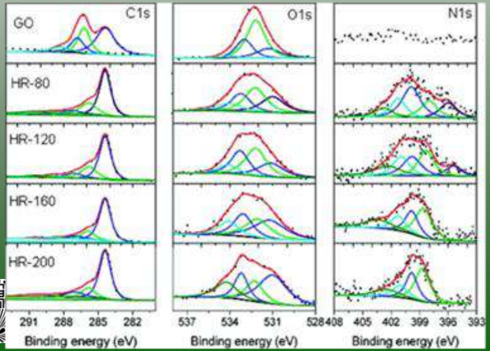








samples	C (wt %)	H (wt %)	N (wt %)	O[a] (wt %)	N/C (at./at.)	O/C (at./at.)
GO	49.59	2.28	0.03	48.05	0.0018	0.72
HR-80	80.43	1.23	5.21	13.13	0.074	0.12
HR-120	80.76	1.15	4.57	13.52	0.064	0.12
HR-160	84.15	1.15	4.09	10.61	0.055	0.091
HR-200	86.12	1.23	4.01	8.64	0.051	0.077



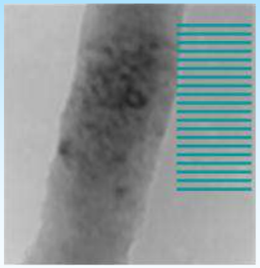
			N distribution (at. %)				
samples	N/C (at./at.)	O/C (at./at.)	395.7 ± 0.3 eV	398.7 ± 0.3 eV	400.3 ± 0.3 eV	401.4 ± 0.3 eV	402–405 eV
GO	0	0.45					
HR-80	0.11	0.16	16	18	37	18	11
HR-120	0.095	0.13	11	27	24	21	17
HR-160	0.071	0.13	0	39	25	17	19
HR-200	0.052	0.098	0	42	28	16	14

2. Preparation of mesoporous CNFs

Preparation of mesoporous HCNF and TCNF

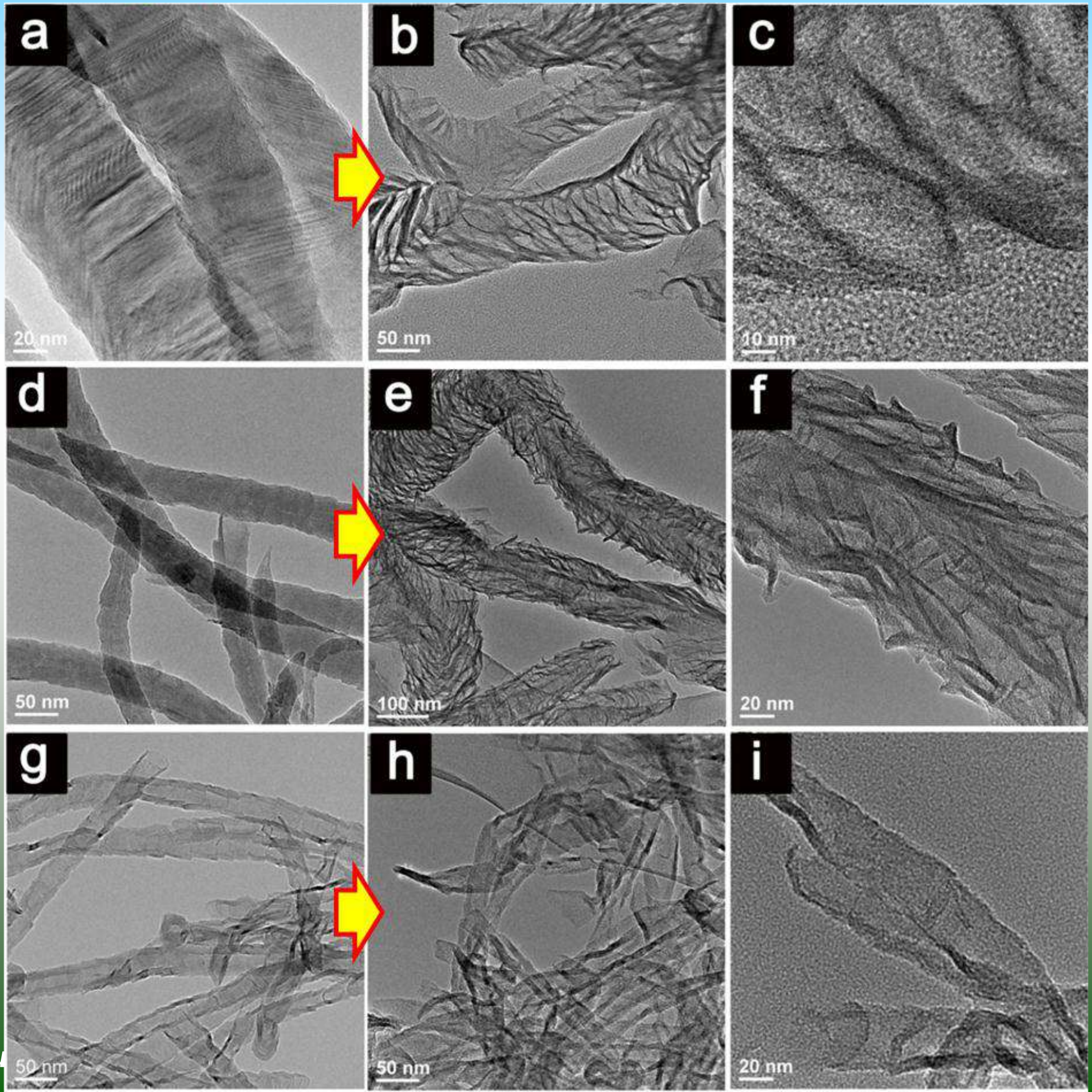
From **graphitized** HCNF and TCNF (GHCNF and GTCNF)

GPCNF



GHCNF

GTCNF

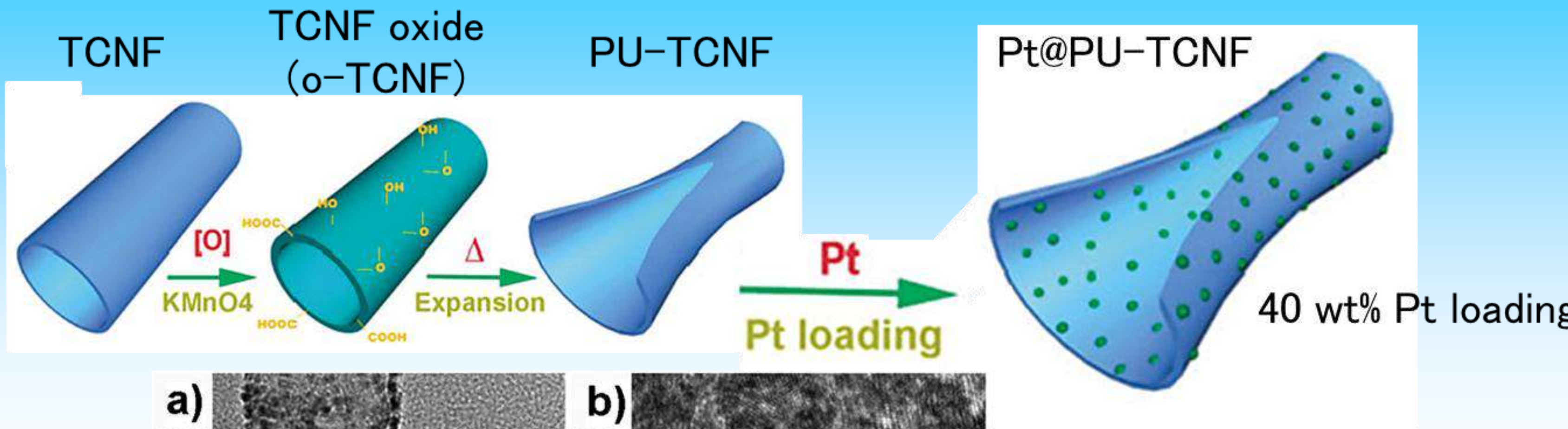


S_{BET} = 307 m^2/g

S_{BET} = 215 m^2/g

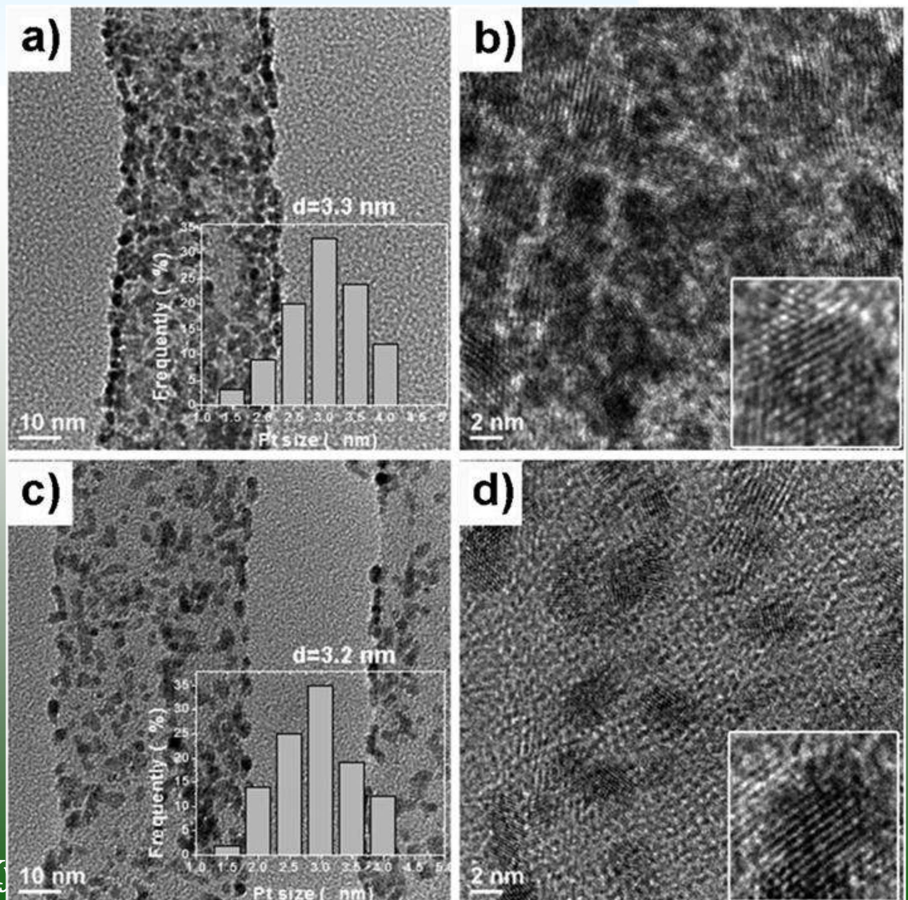
S_{BET} = 168 m^2/g

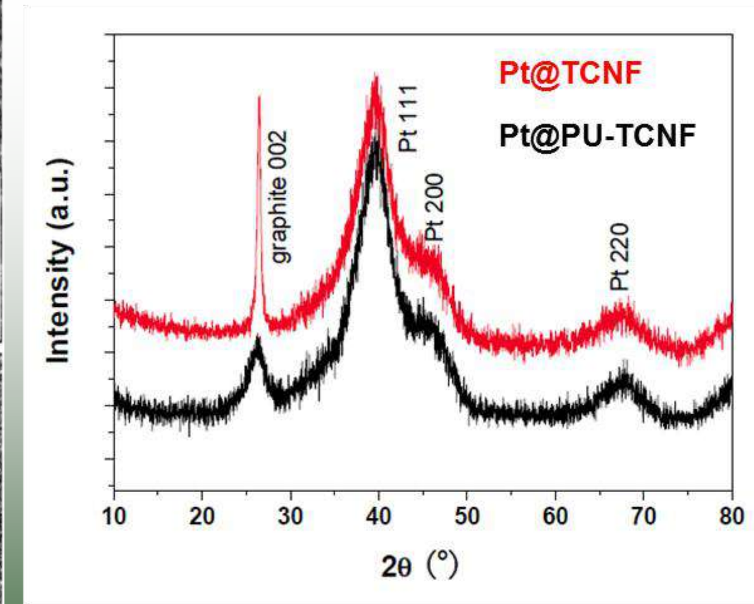
4. Electrochemical applications



Pt@
TCNF

Pt@
PU-TCNF





XRD patterns

⇨ d(avg.) = 3.2 nm

What is a functional Nano-material

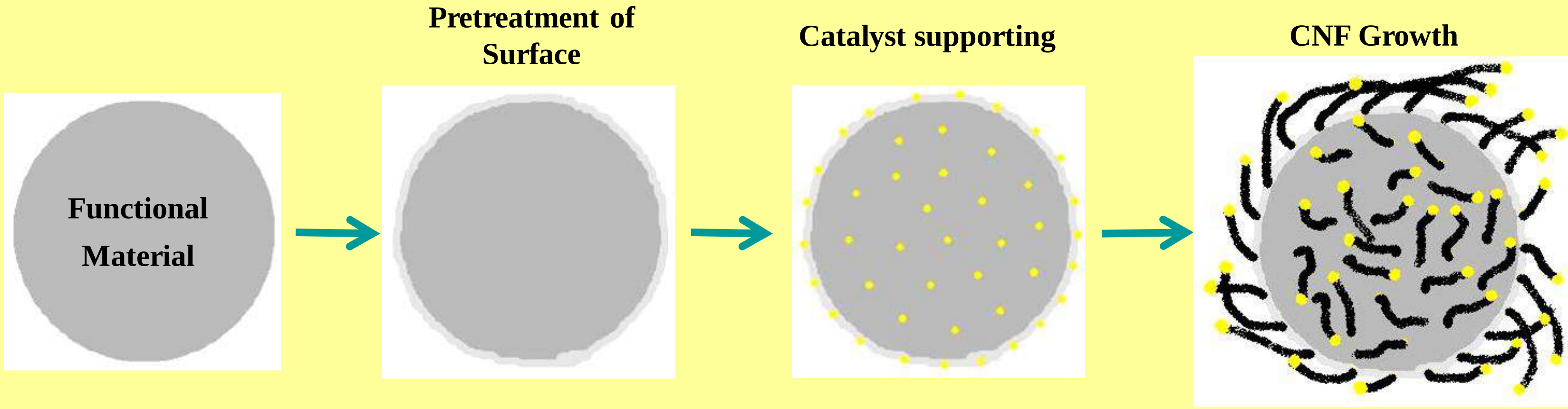
Functional Material

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

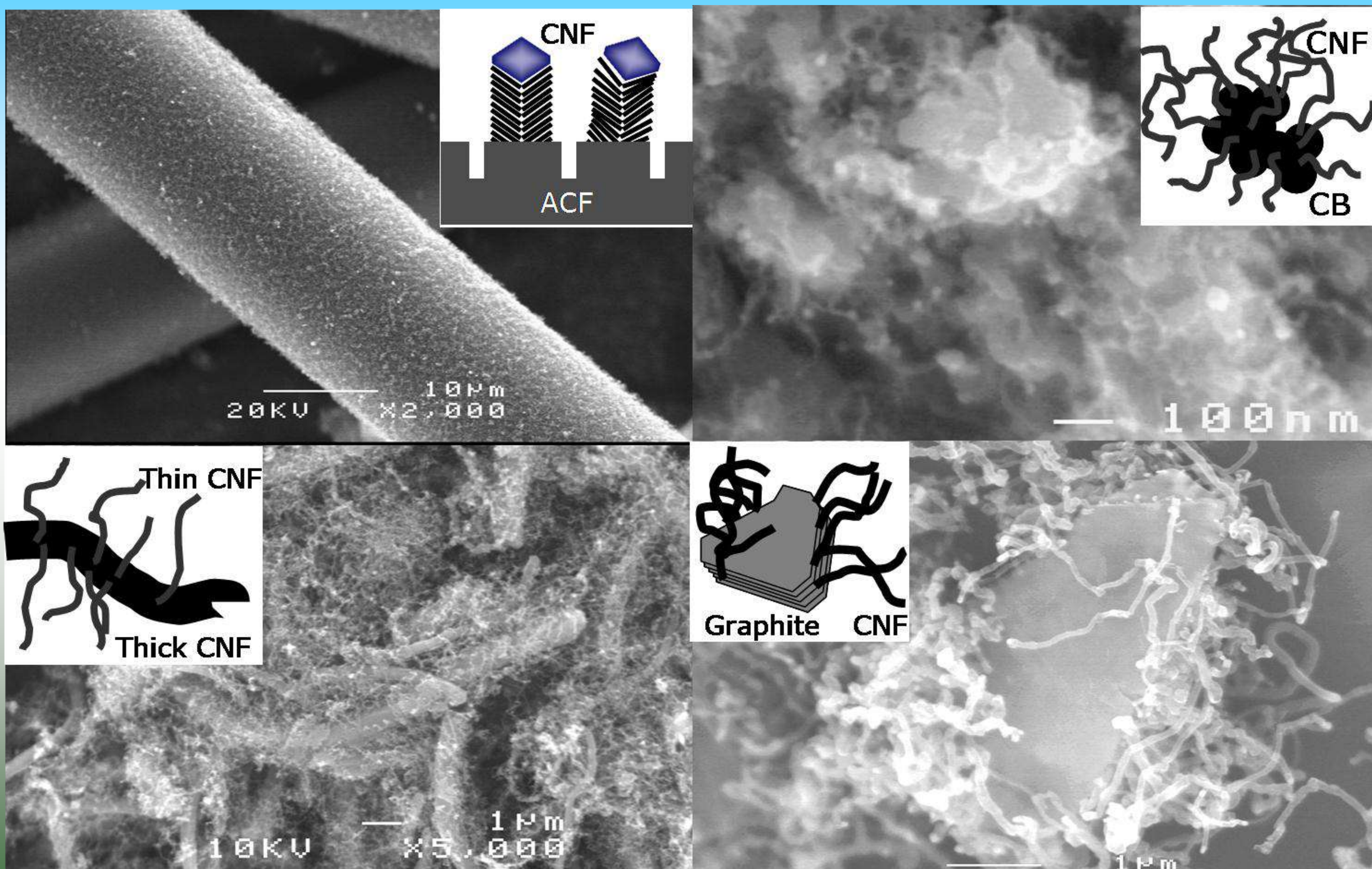
Improvement of Functions by Growing CNFs

CNF 複合化 →

Function improvement
Function Hybridization
Novel Function Creation

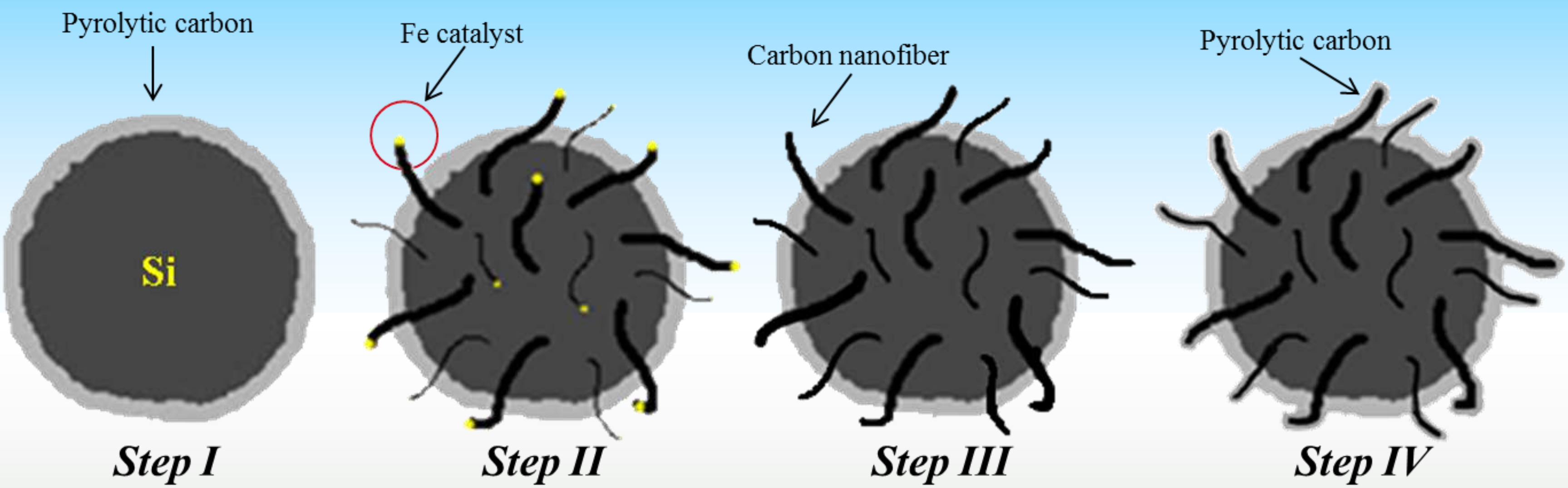


Various CNF Composites



“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

Pyrolytic carbon coated Si-CNF composite



- P/C provides the catalyst to be impregnated easily and strongly on Si surface

- Strong bond bet. Si and CNF
- Effective to relieve volume expansion (**Good cycle life**)

- Re-coated p/c improved **initial efficiency** by the decreased surface area, and showed **good cycle life**

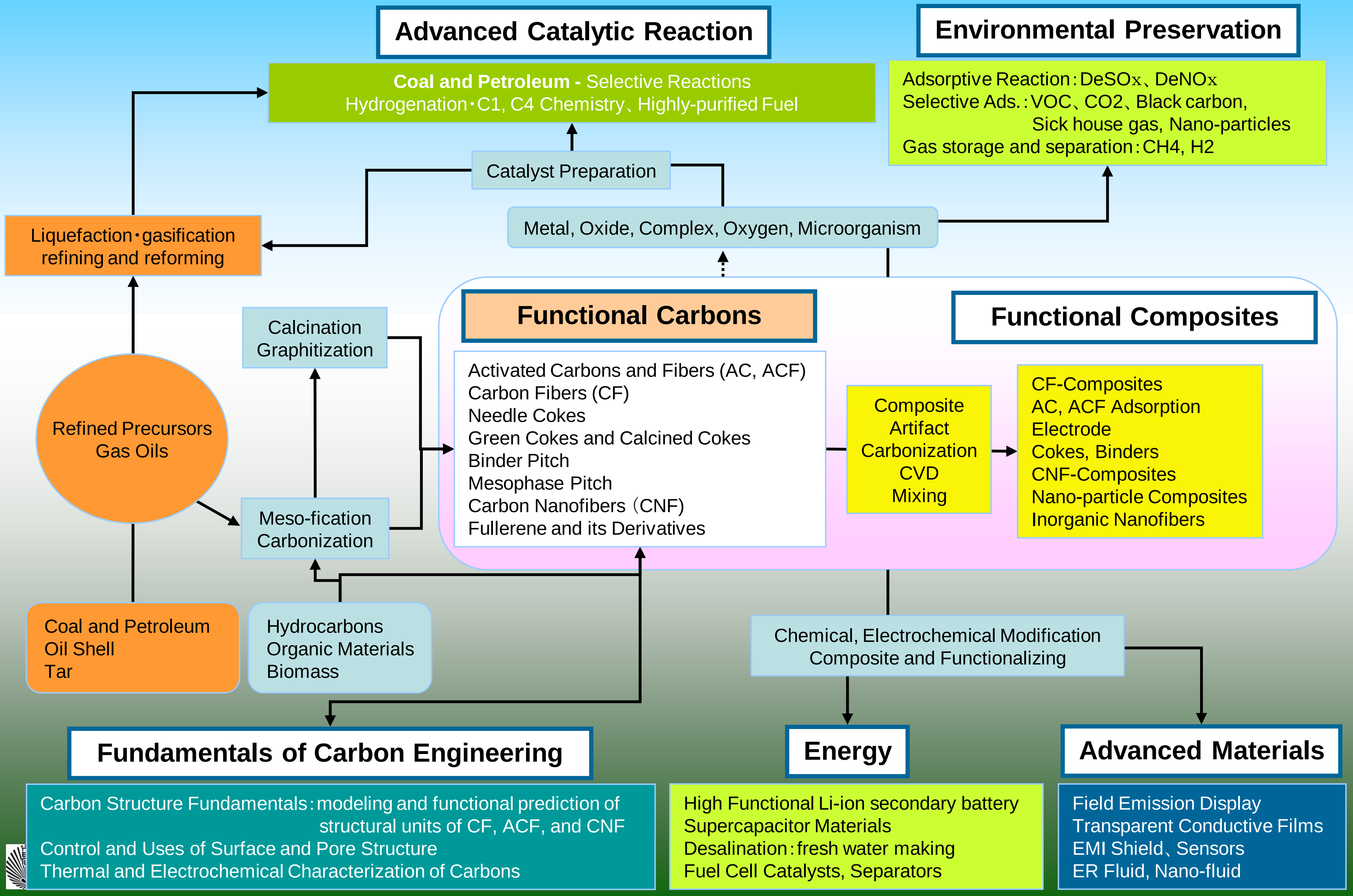
- After removal catalyst, the composite is changed to unstable (**bad cycle life**)

All of the p/c coated Si-CNF composite showed the improved reversible capacity and cycle lifes

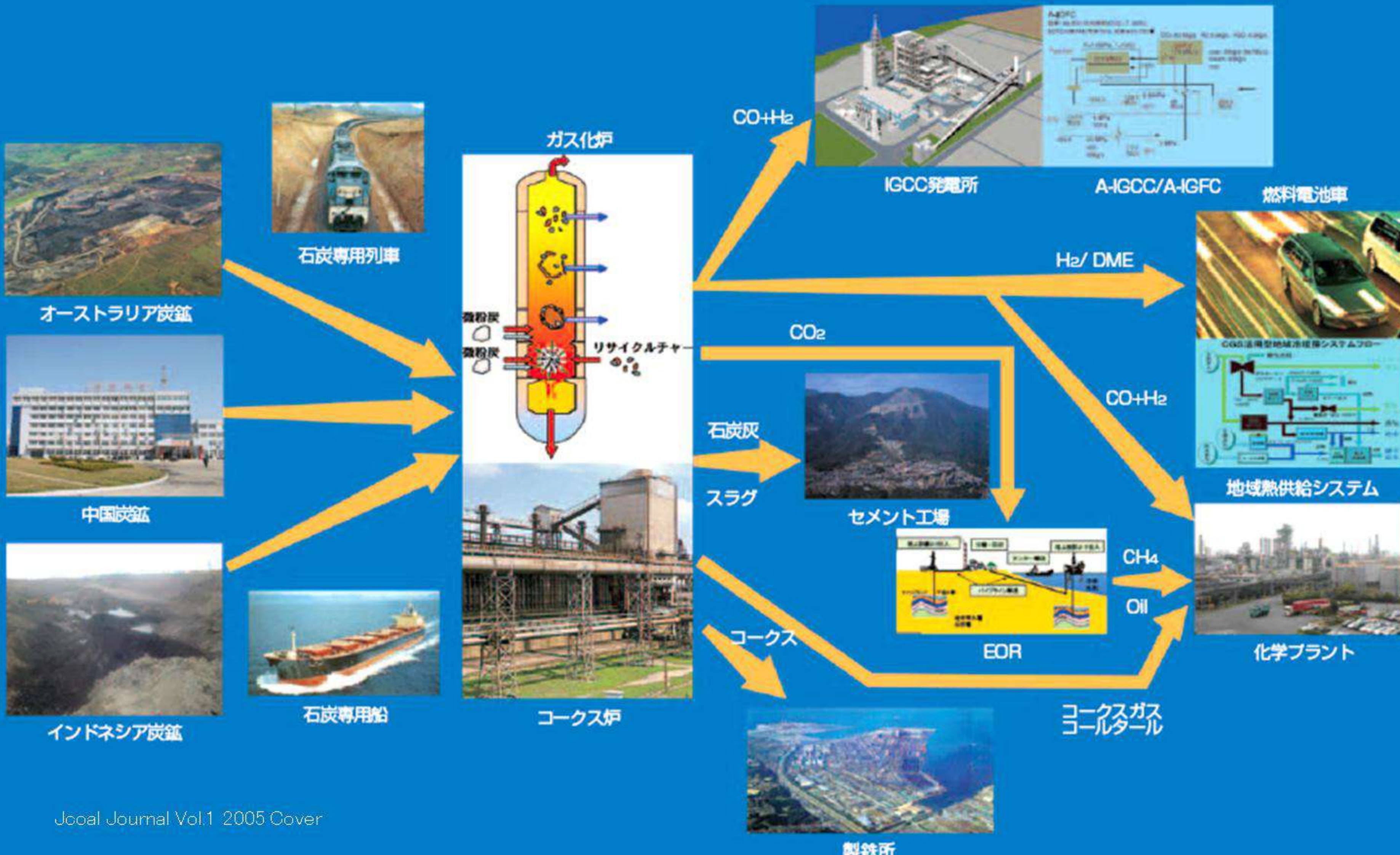
Research scope of Yoon's Lab

- Outline and Interrelation of Research Topics

- Synthesis and applications of functional materials
- Energy and environmental engineering

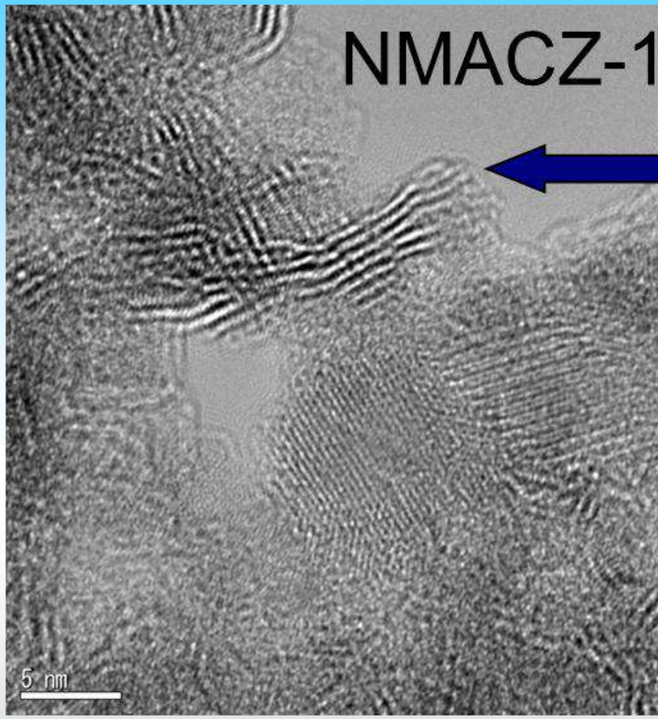


Effective Utilization of Coals and Biomass

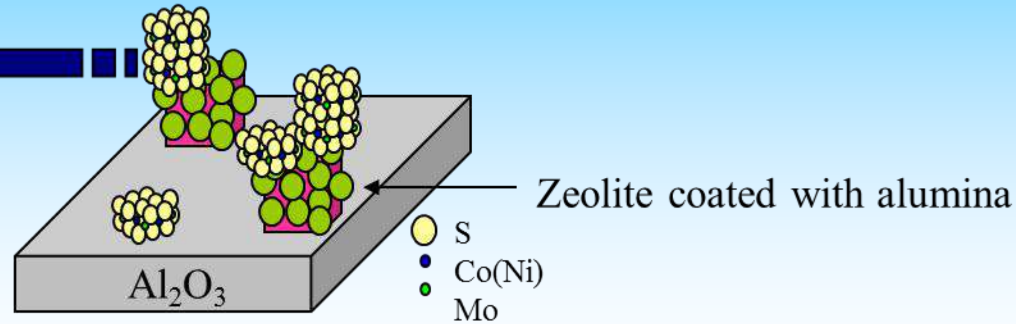


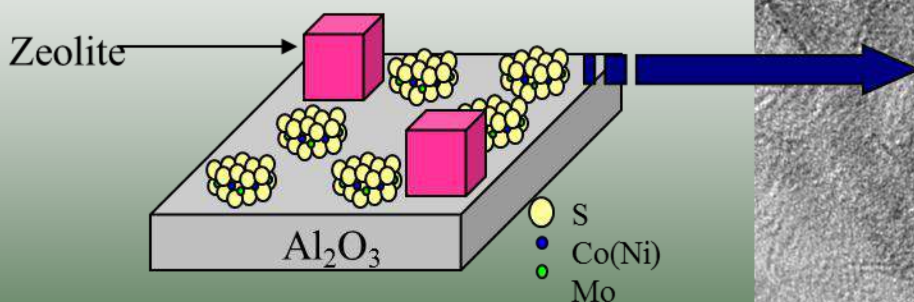
Jcoal Journal Vol.1 2005 Cover

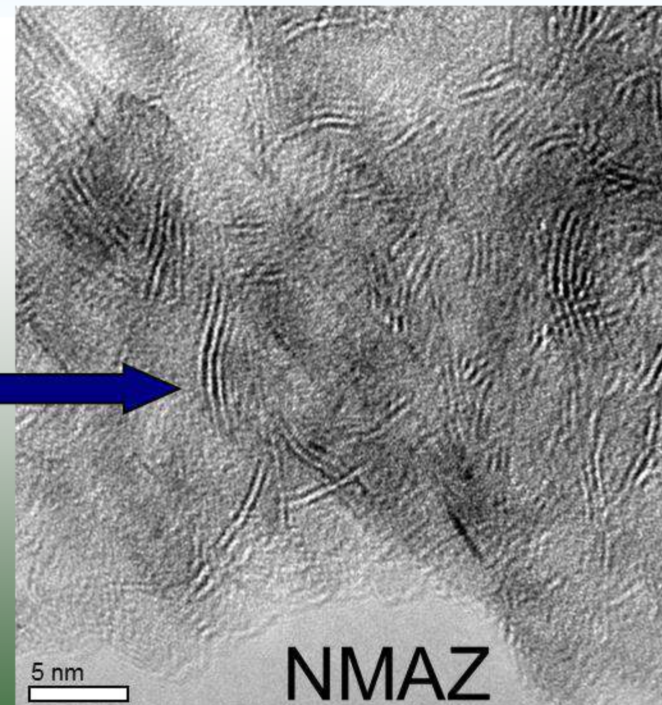
Stacked Structure of Catalyst for Petroleum



MoS_2 Average Stacking Layers ; 4-6







MoS2 Average Stacking Layers ; 2-4

Carbons from now

Era of **nano-carbons** are almost finished. Only special applications are promising!

Era of **GOOD Raw material to GOOD Product** are almost finished. China and other developing countries will take over whole markets!

Era of **BAD Raw material to GOOD Product** are coming. Developed countries only have chances on such materials

Novel carbon, if it can be found, still has a chance to change the paradigm.
But what is that?

Nano-carbons
(Concept, methodology)

Fusion

Conventional carbons
(Waste Materials)

New carbon materials, New processes for manufacturing, New markets for carbon applications

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**

Conclusion

- Carbon is Key Materials for Energy and Environmental Devices.
- High Utilization of Fossil Fuels and Their Bi-products is most urgent task to solve.
- New Structural Concept and Producing Method Can Increase the Industry Realization.
- Best Structure Must Be Selected For Each Objective and Prepared.
  - Preparation step (Selective and Controlled Synthesis)
  - Modifications

⇒

- **It is time to re-innovate!**

Report

1. 炭素材が省エネルギー・環境保全デバイスのKeyマテリアルになる理由を分子構造、物性の側面から記述せよ。（半ページ程度）
2. 比表面積を増やすにはどうすればよいか？
   炭素材に細孔を導入する手法としてガス賦活（物理賦活）と薬品賦活（化学賦活）がある。それぞれを説明せよ。

- 提出期限：次の授業時間まで
- Word Processorを使わずに作成すること。
- A4　1枚で作成すること。
- 授業日時と講義者（Yoon教授）を明記すること。