不活性気体のナノ細孔性カーボンへの吸着

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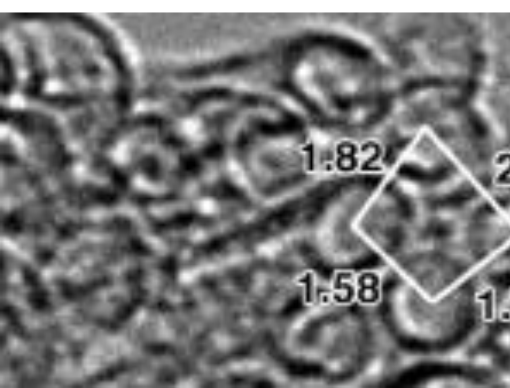
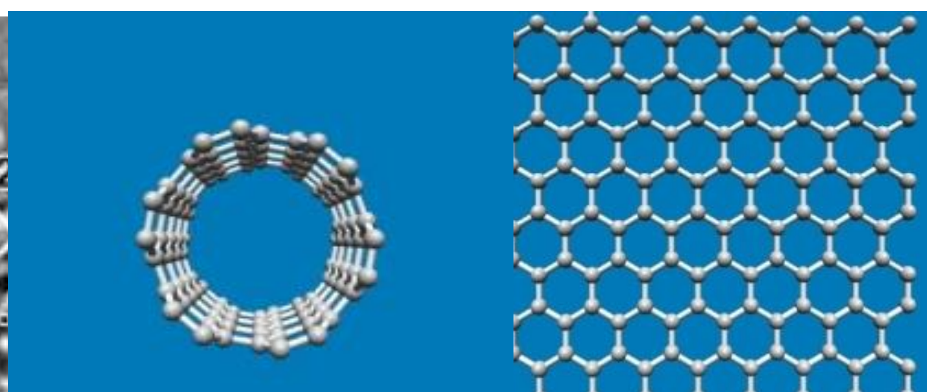
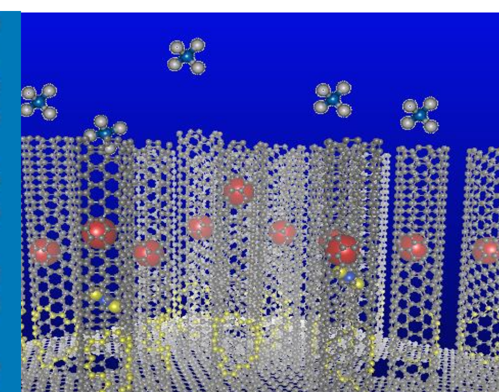
第1回地下素核研究　研究会

2014年8月23,24日

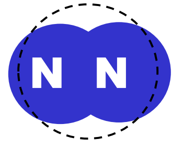
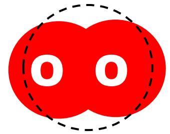
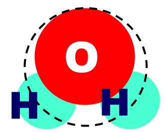
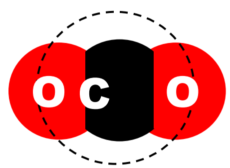
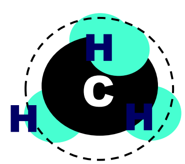
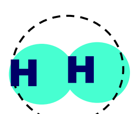
大阪大学　豊中キャンパス:シグマホール



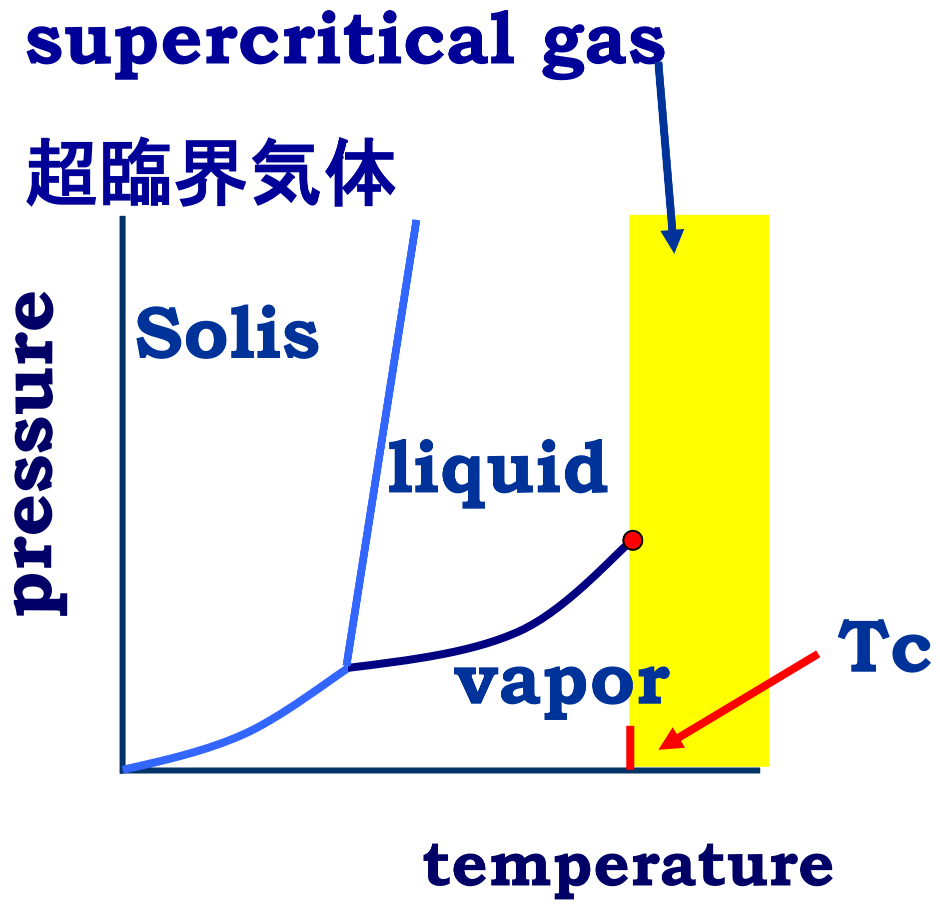




Molecules in Atmosphere *“Treasure of Human”*

	content/vol. %	structure	size
N_2	78		0.36 nm
O_2	21		0.34 nm
H_2O	< 4		0.32 nm
Ar	0.9		0.33 nm
CO_2	0.0036		0.38 nm
CH_4	0.00017		0.37 nm
H_2	0.00005		0.29 nm

Supercritical Gases and Vapors



No saturated vapor pressure P_0 for supercritical gases

Critical temp.

H_2 33 K

CH_4 196 K

Inert Gases

	LJ σ/nm	LJ ε/K	T_b/K	T_c /K	Quantum
He	0.257	10.8	4.4	5.195	◎
Ne	0.275	35.8	27.3	44.40	△
Ar	0.34	122	87.4	150.7	x
Kr	0.359	183	121.5	209.4	x
Xe	0.396	217	161.7	289.7	x
Rn	0.436	283	202.2	377	x

J.G. Hirshfelder et al. Molecular Theory of Gases and Molecules, John Wiley& Sons,1954

Critical Temperature of Representative Gases

gas	T_b /K	T_c / K	P_c /Pa	σ_{ff} /nm	ε_{ff} /k_B	multipole moment	magnetism
H_2	20.3	33.0	1.29	0.292	38.0	*qu* $+2.1 \times 10^{-40}$	*dia*
O_2	90.2	154.6	5.04	0.338	126.3	*qu* -1.33×10^{-40}	*para*
N_2	77.3	126.2	3.39	0.363	104.2	*qu* -4.90×10^{-40}	*dia*
NO	121.4	180	6.48	0.347	119	*di* 0.158×10^{-30}	*para*
CO	81.6	132.9	3.50	0.359	110	*di* 0.112×10^{-30}	*dia*
CO_2	194.7	304.2	7.48	0.376	245.3	*qu* -14.9×10^{-40}	*dia*
CH_4	111.6	190.5	4.60	0.372	161.3	*oc*	*dia*

Four categories of gas-solid interaction

Storage-related concepts

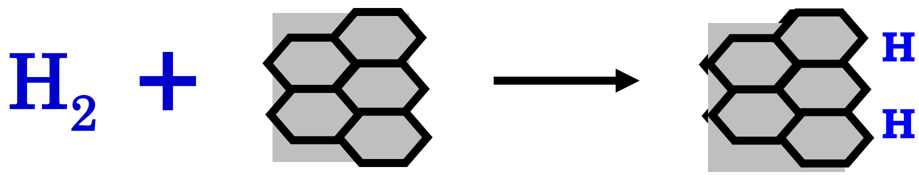
	molecule	solid (not surface)
Physical adsorption	none	none
Chemisorption	change	none
Absorption	none	change
Occlusion*	change	change

*(narrow concept of storage)

- Kaneko's classification

Chemisorption, Occlusion, Absorption

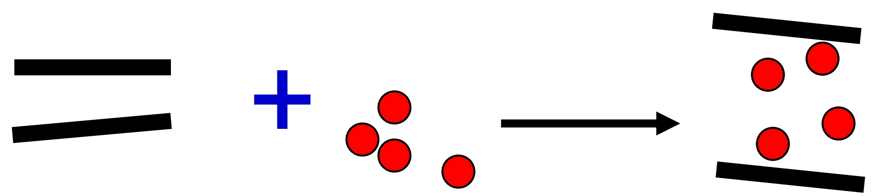
Chemisorption



Occlusion

$$Pd + H_2 \rightarrow Pd_xH_y$$

Absorption



Physical Adsorption and Chemisorption

	Phys. adsorption	Chemisorption
Attractive interaction	Dispersion nonspecific	Chem. bonding specific
Adsorption rate	Large	Small
Adsorption capacity	Large	< monolayer cap.
Reversibility	Reversible	Irreversible
Temp. dependence	Lower temp. vapors	Higher temp. supercritical gases + vapors

Interaction of an Inert Gas with Solid

Only physical adsorption is available

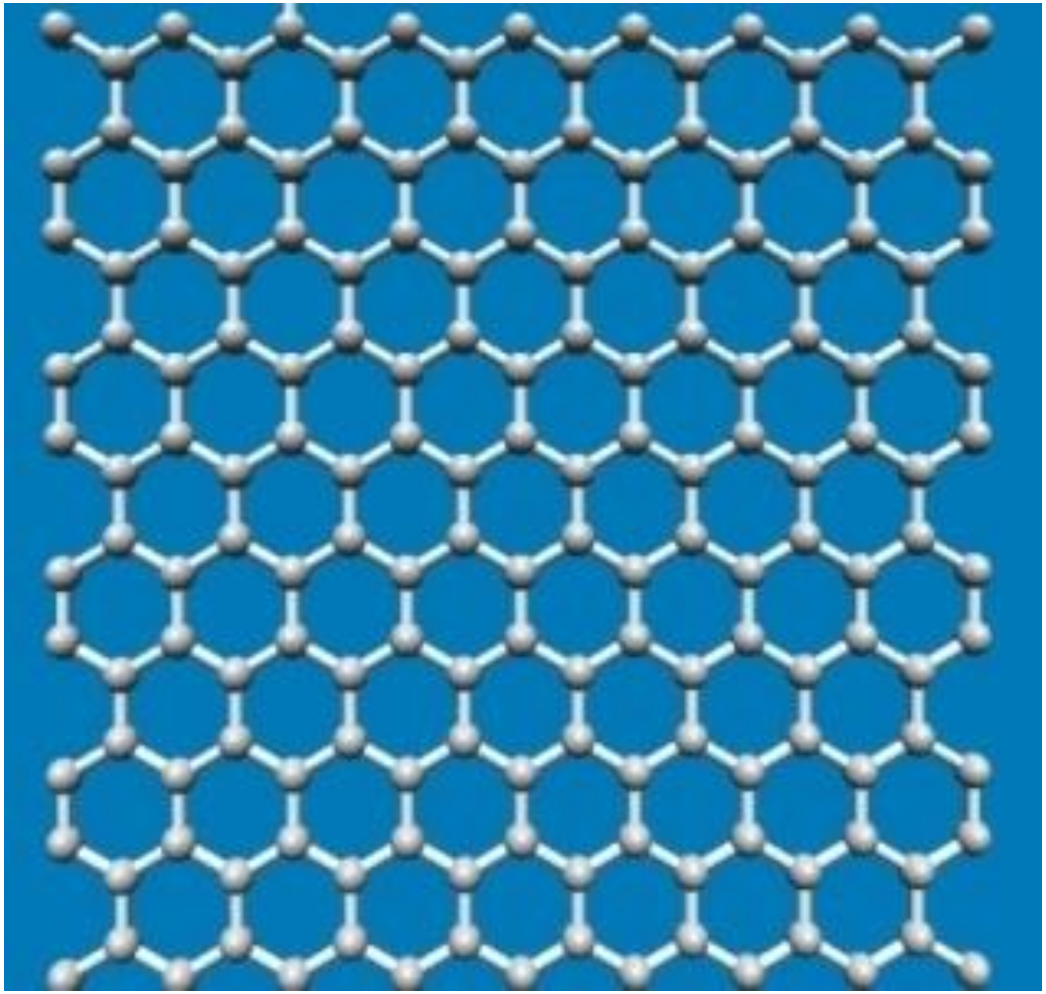
Removal of low concentrated inert gases

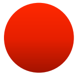
Pores whose width is **less than 1 nm**

A deep interaction potential well

Cylindrical pores > Slit pores
(less accessible) (more accessible)

Adsorption of a Molecule on Graphite



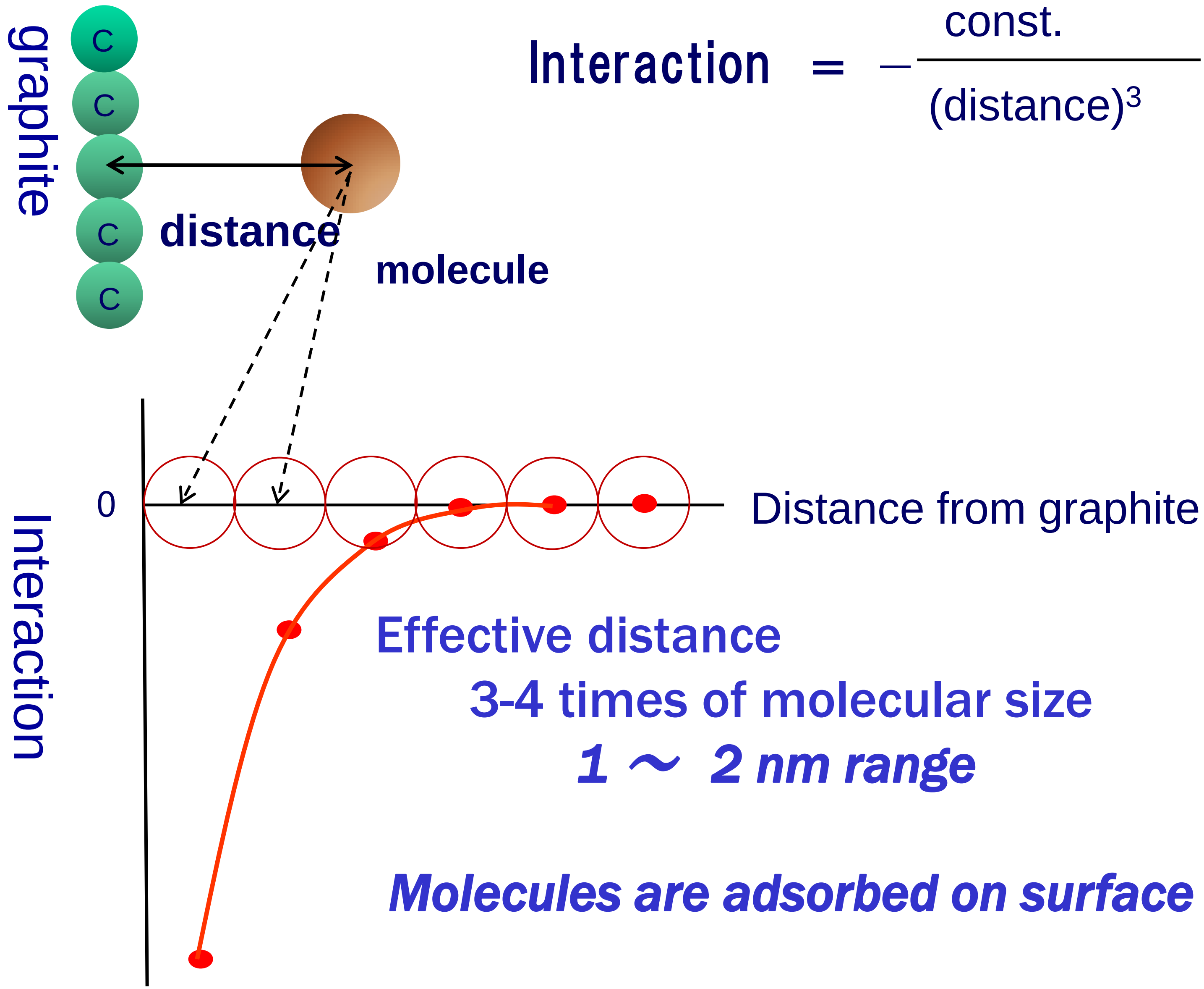


Why is a molecule adsorbed on solid surface ?

van der Waals force attracts the molecules (dispersion interaction)

Short-range force: van der Waal interaction

$$\text{Interaction} = -\frac{\text{const.}}{(\text{distance})^3}$$



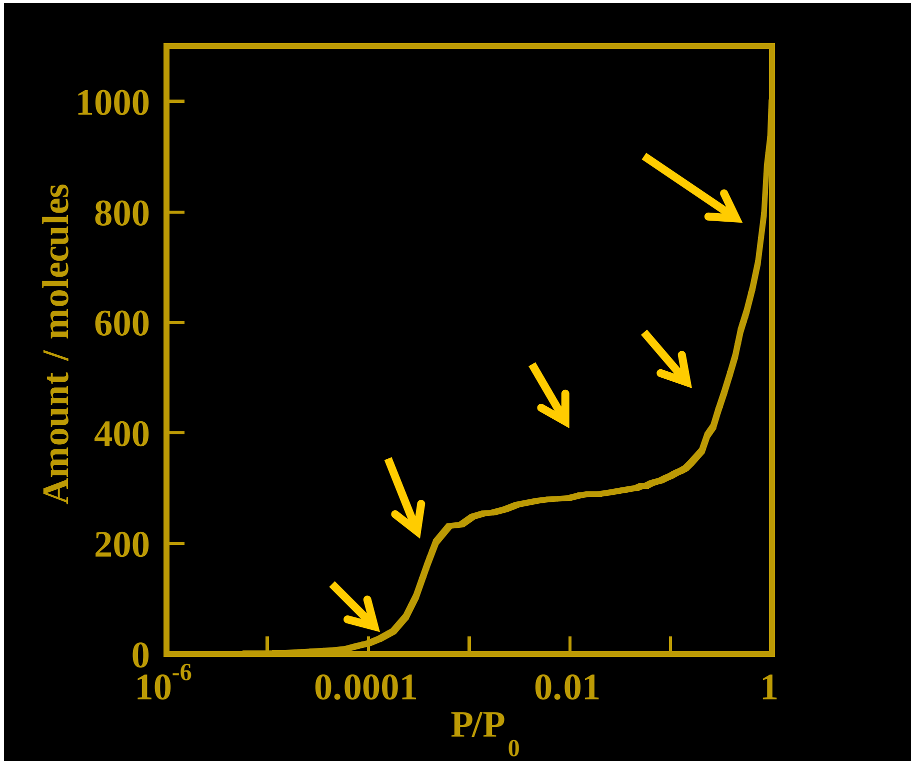
Effective distance

3-4 times of molecular size

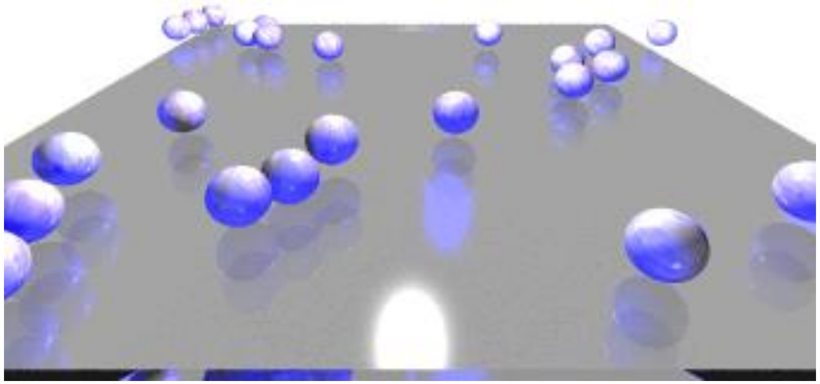
1 ～ 2 nm range

Molecules are adsorbed on surface

Adsorption on Graphite Surface



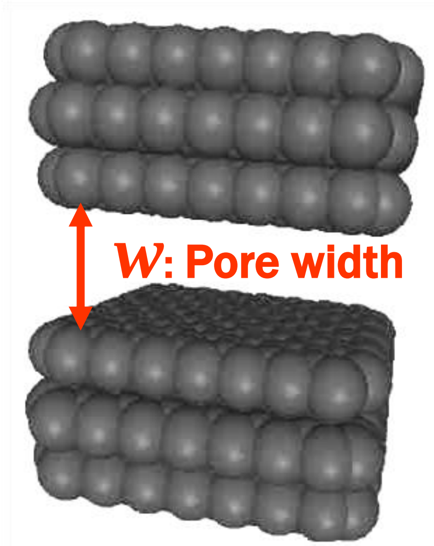
Adsorption isotherm



Layer-by-layer adsorption

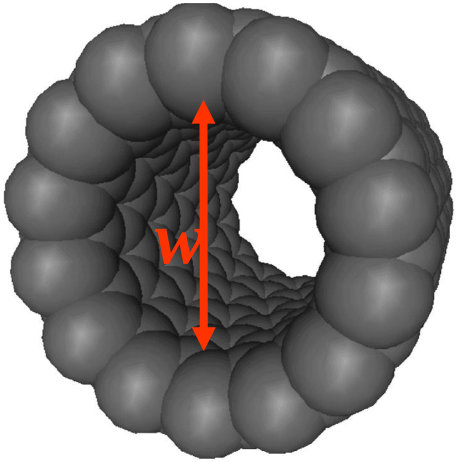
Nanopores

Micropores   *w*<2nm



Slit-shaped pores

Activated carbon

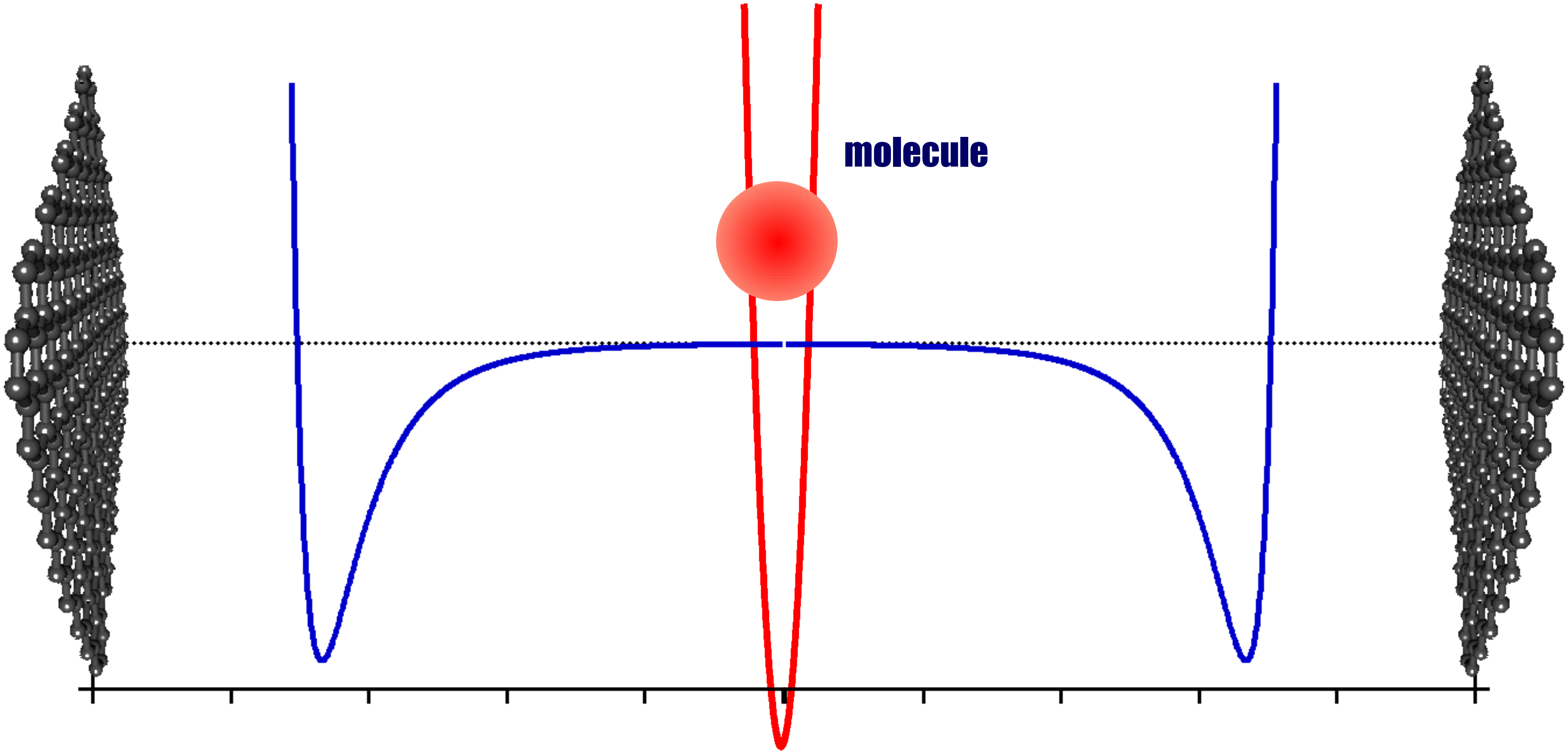


Cylindrical pores

Single wall carbon nanotube

(SWCNT)

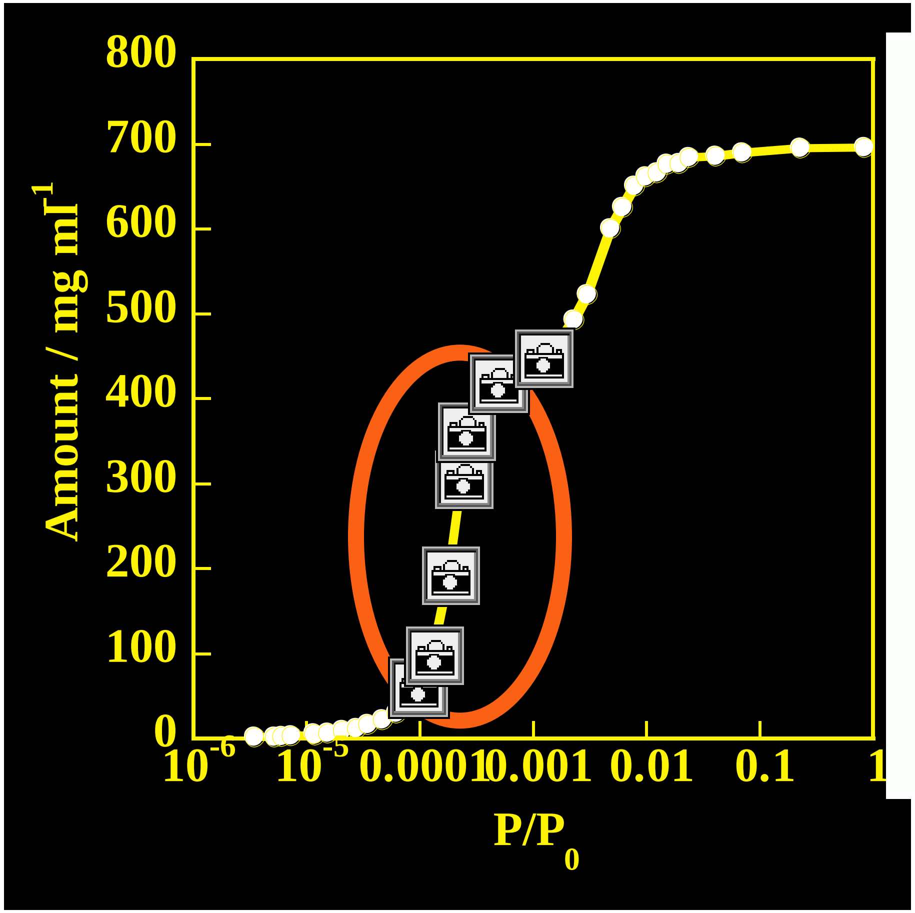
Stabilization Change of a Molecule in Graphene Pore



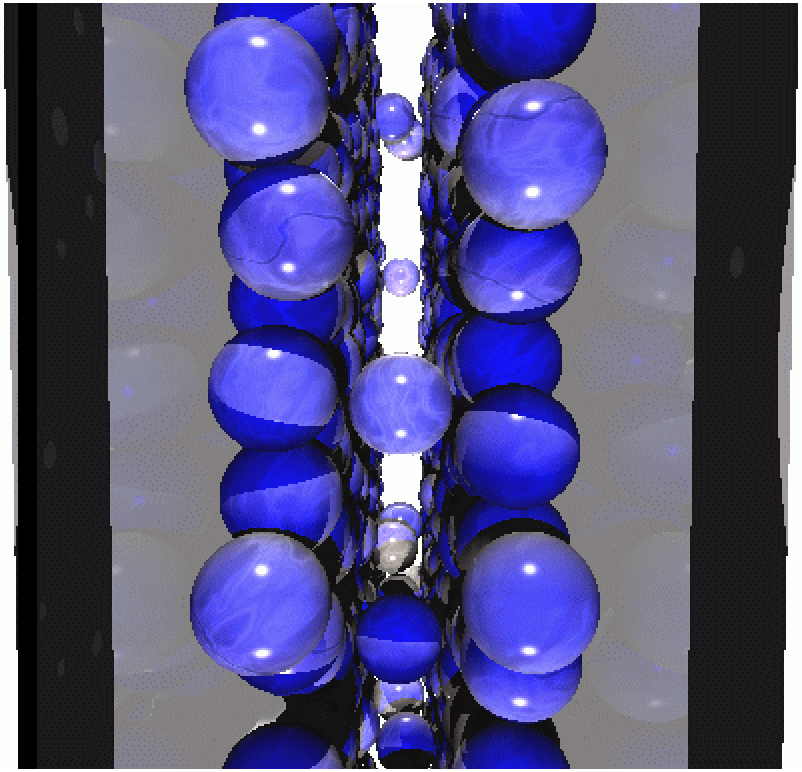
1 nm order pores: Remarkably high density phase in pores

Adsorption of N_2 in 1.2 nm- Slit Pore

Theoretical isotherm

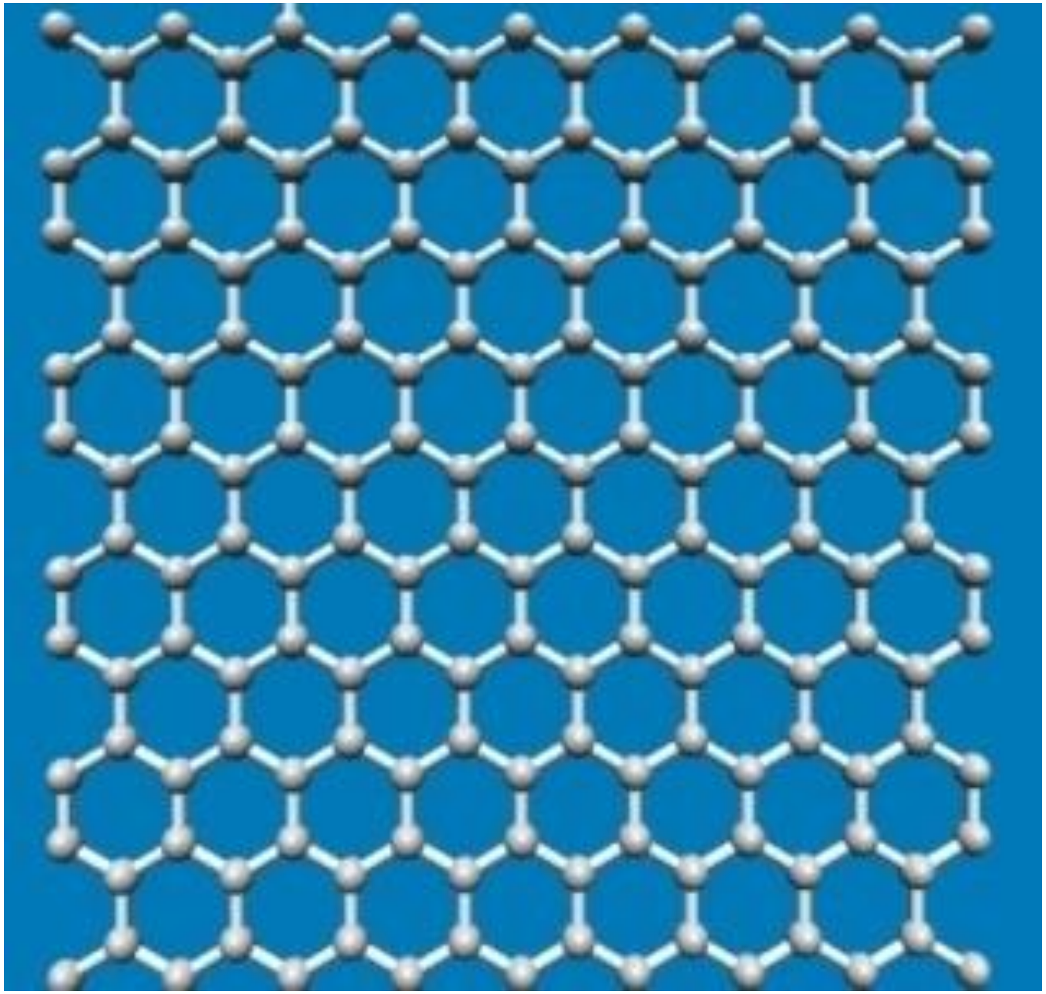


Images



Model of pores of activated carbon

Basal Plane of Graphite

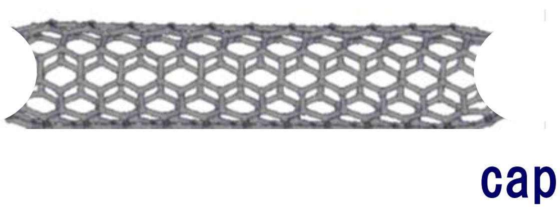


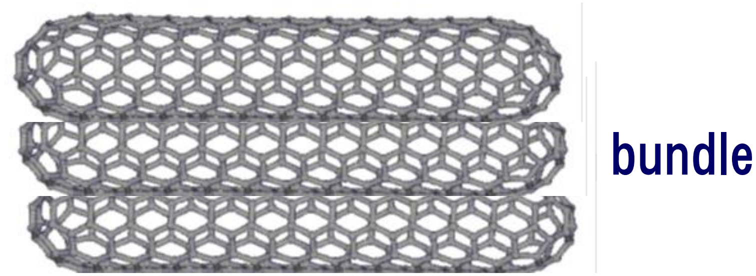
Carbon hexagon network structure

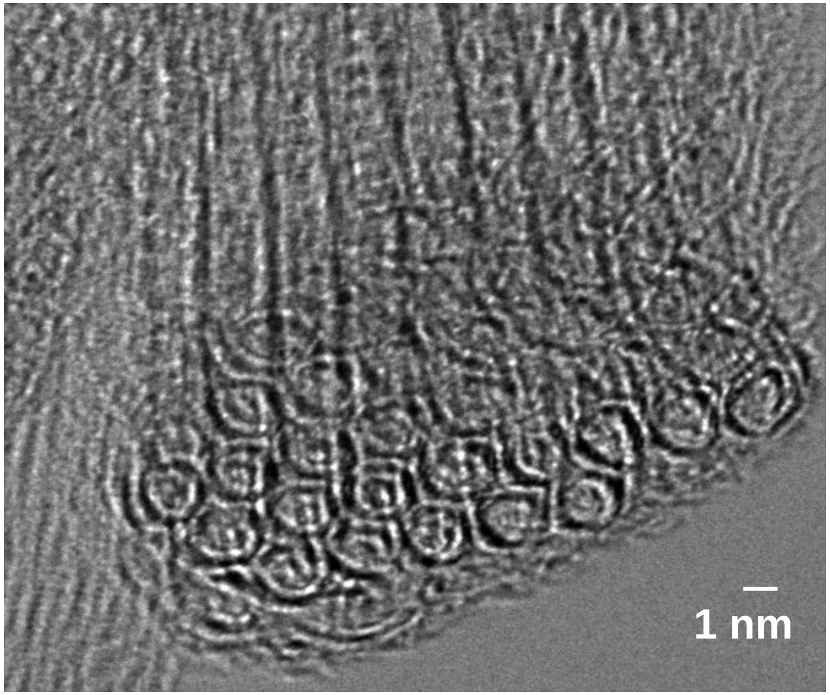
High atomic density

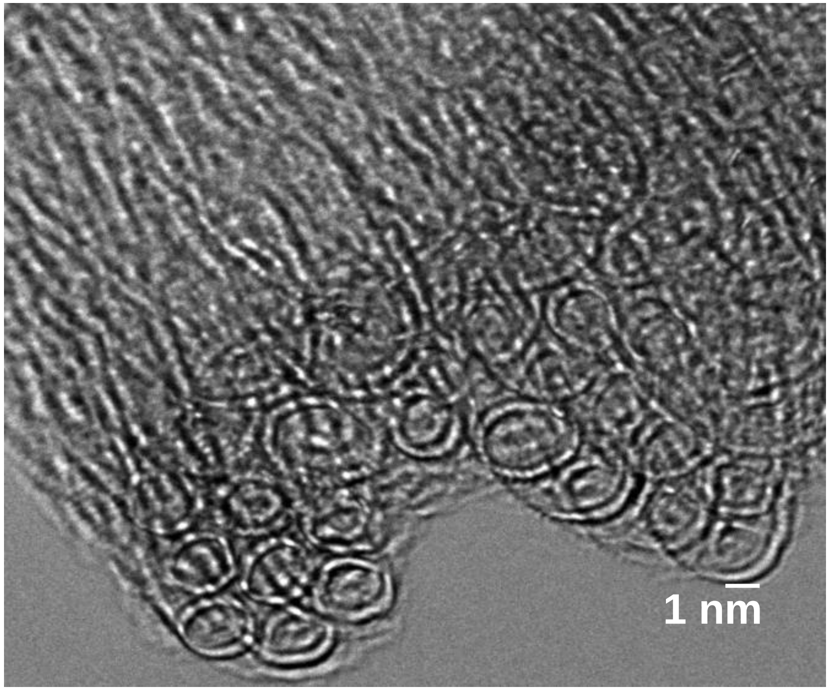
The strongest interaction potential per unit weight

Single Wall Carbon Nanotube



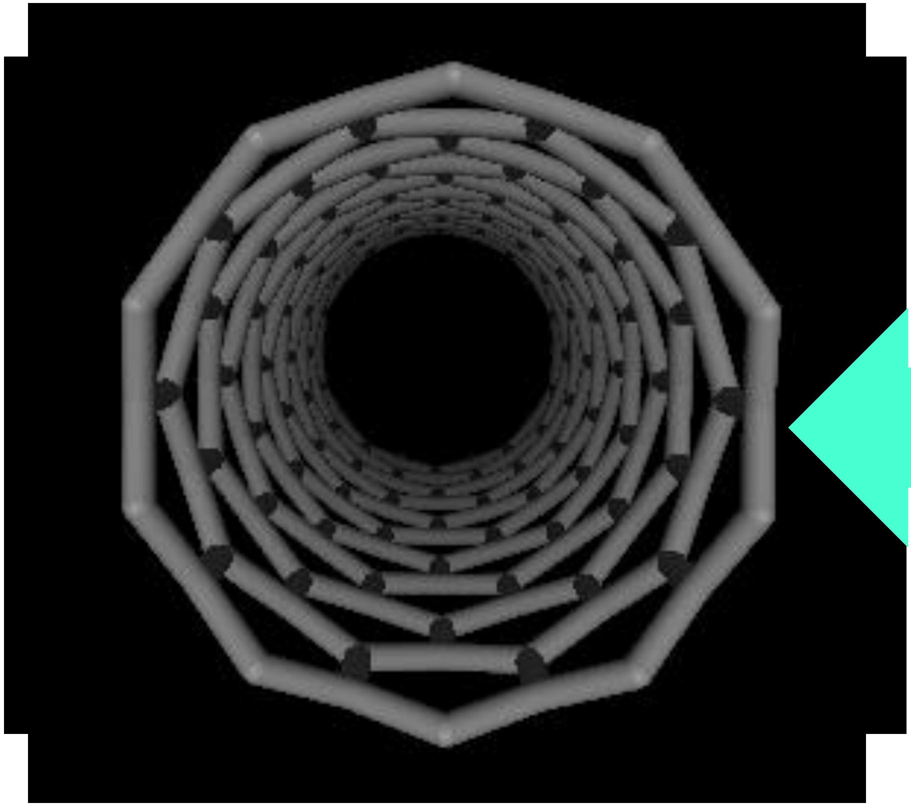


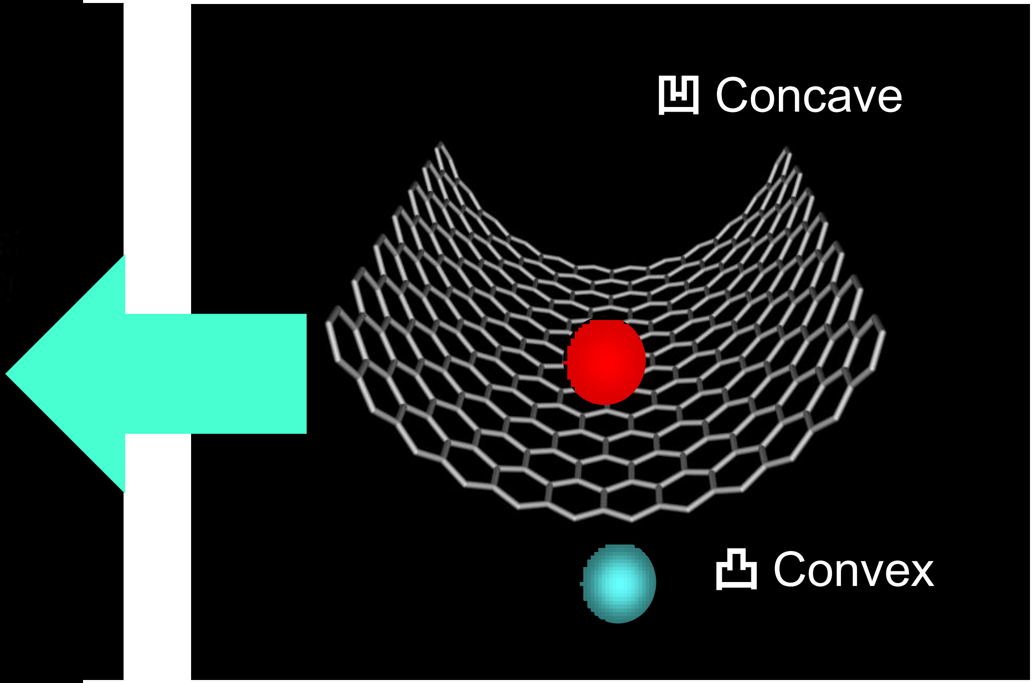




Ideal Surface Solids

All carbon atoms facing internal and external phases





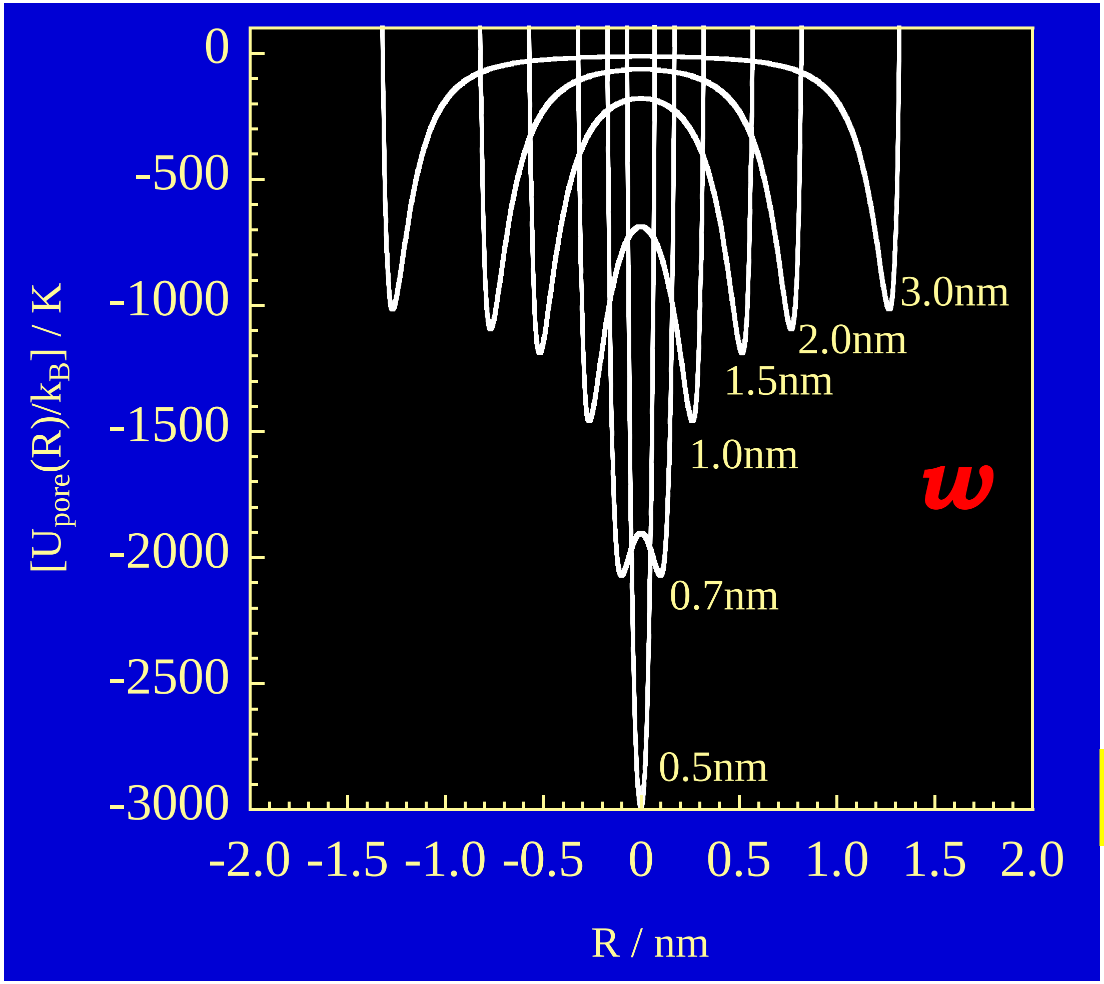
Super surface area 2630 m^2/g

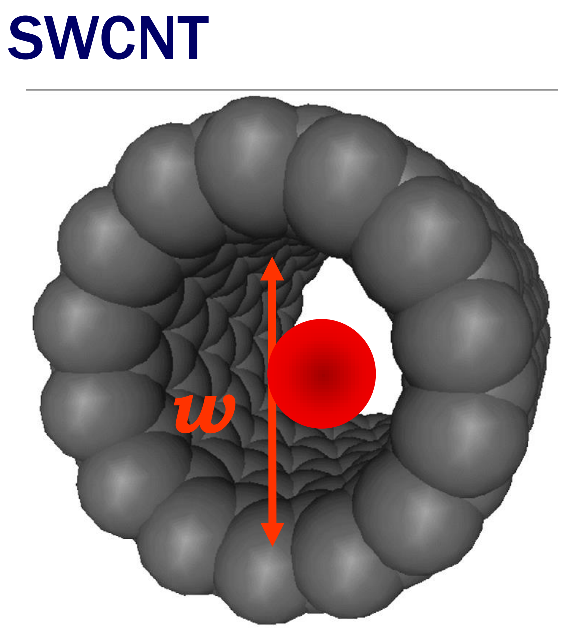
Bi-surfaces: Surface Solids

Nanoenvironment Sensitive Nature of Single Wall Carbons

Carbon Nanotube Spaces Show an Intensive Confinement Effect

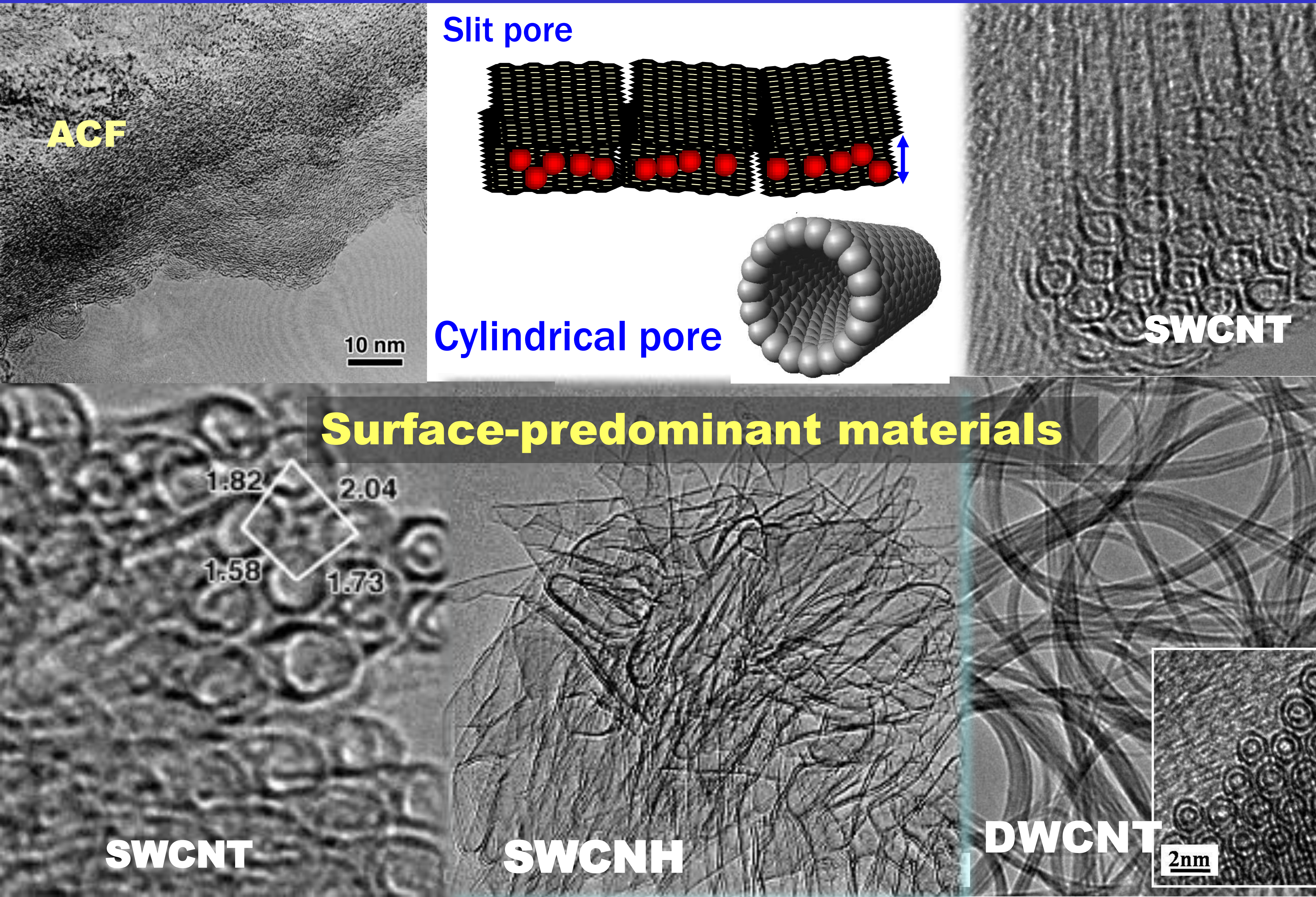
Deep Interaction Potential Wells: N_2-SWCNT





In-pore high pressure effect

Carbons of High Surface Area



Nanoporous Carbon Has Several Merits

	zeolite	carbon	PCP	silica
Electrical conductivity	×	○	×	×
Thermal conductivity	×	○	×	×
Thermal stability	○	○	△	○
Anti-oxidation property	○	×	×	○
Hydrophobicity	○	○	×	×
Ion exchangeability	○	×	×	×
Pore structure	Micro pore	Micro- and mesopore	micropore	mesopore
Uniform porosity	○	△	○	○
Tunability of pore size	○	△	○	○
high surface area (>1000 m^2 g^{-1})	×	○	○	○

Intensive Confinement Effect

Superhigh pressure

compression effect

1D S-metal

High Pressure Compression Effect

In Slit-shaped Nanospaces

High pressure (>20 MPa) gas phase reaction occurs below 0.1 MPa

K. Kaneko et al. *J. Chem. Phys.*, 87, 776 (1987). NO dimers

K.Kaneko et al, *J. Phys. Chem*. **95**,9955 (1991) $3(NO)_2 = 2N_2O + (NO_2)_2$

20MPa

K. Hashimoto, A.Fujishima et al, *J.Electrochem. Soc*. **147**, 3393 (2000). Exp. Study

Electrochemical reduction of CO_2 to CO under 10MPa

Theoretical studies

K.E.Gubbins et al, *J.Chem.Phys*. **125**, 084711(2006).

Phys. Chem. Chem. Phys.13 (2011) 17163.
Micro. Meso. Mater. 154 (2012)19.

Metallic Sulfur Is formed under > 90 GPa in Bulk

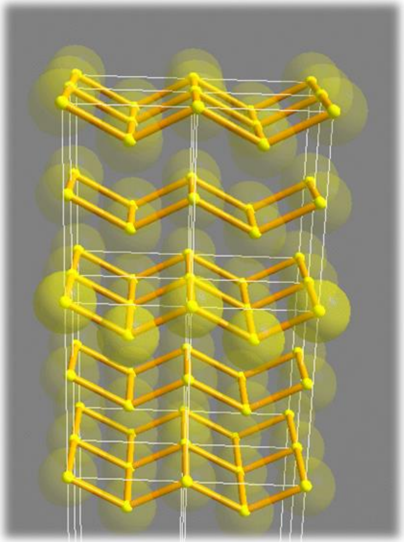
Insulator

@ambient pressure

90 GPa

Metallic phase of sulfur

R. Steudel Ed., "Elemental Sulfur and Sulfur-Rich Compounds I" (Springer, 2003).

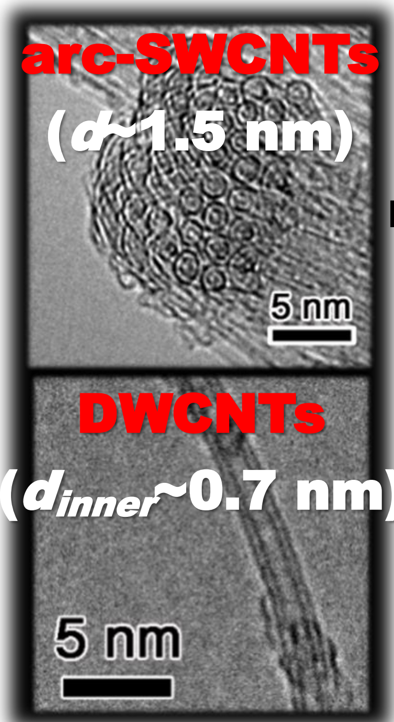


zigzag chain

Highly conductive 1D Sulfur chain inside CNT

T. Fujimori et al, Nature Comm. (2013)

Doping of Sulfur in Tube Spaces



Sulfur (99.9999%)

① ***Encapsulation***

Heating@773 K for 48 h

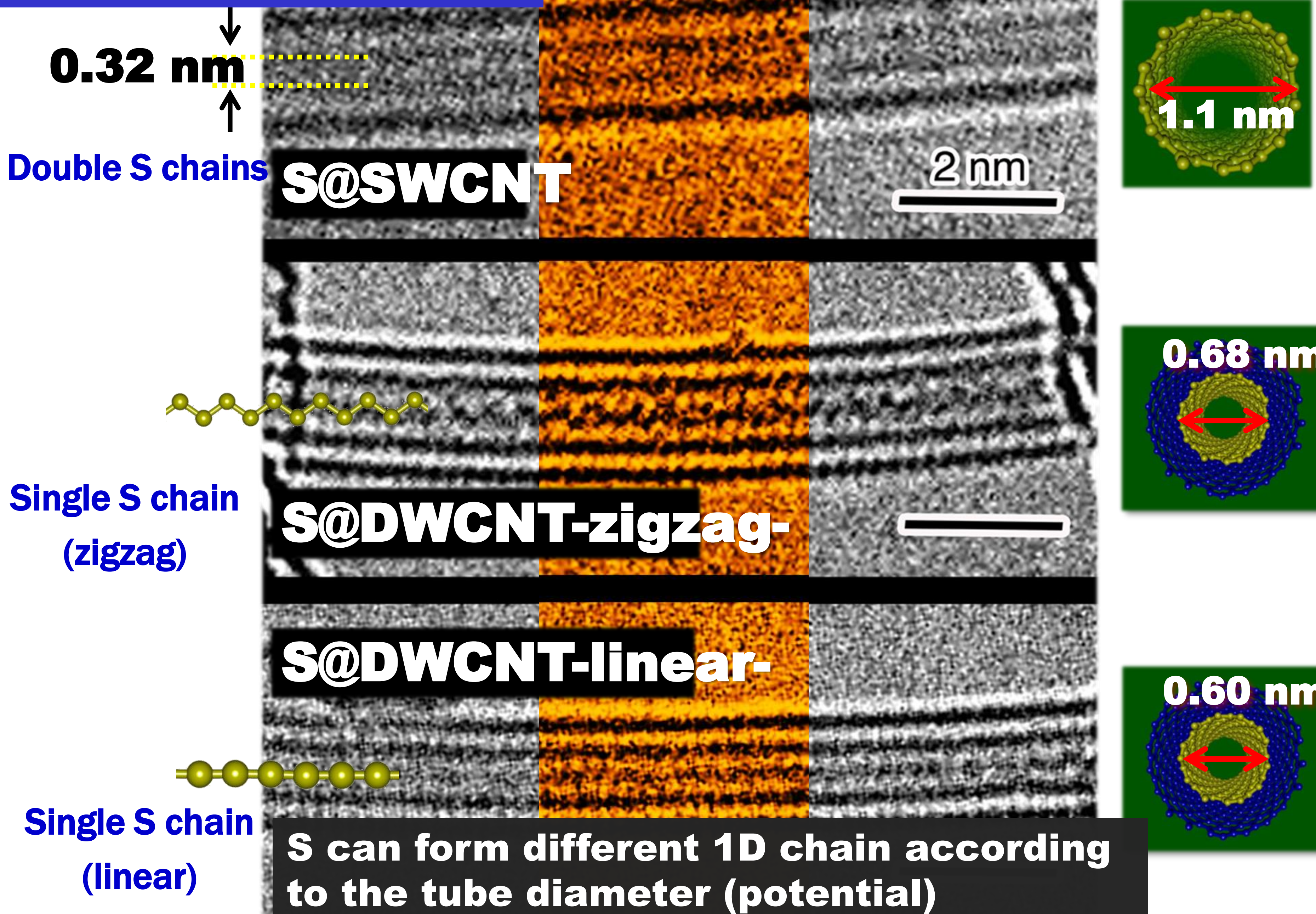
Below 0.1MPa

② ***Removal of extra sulfur with CS_2***

③ ***Evaporation of CS_2***

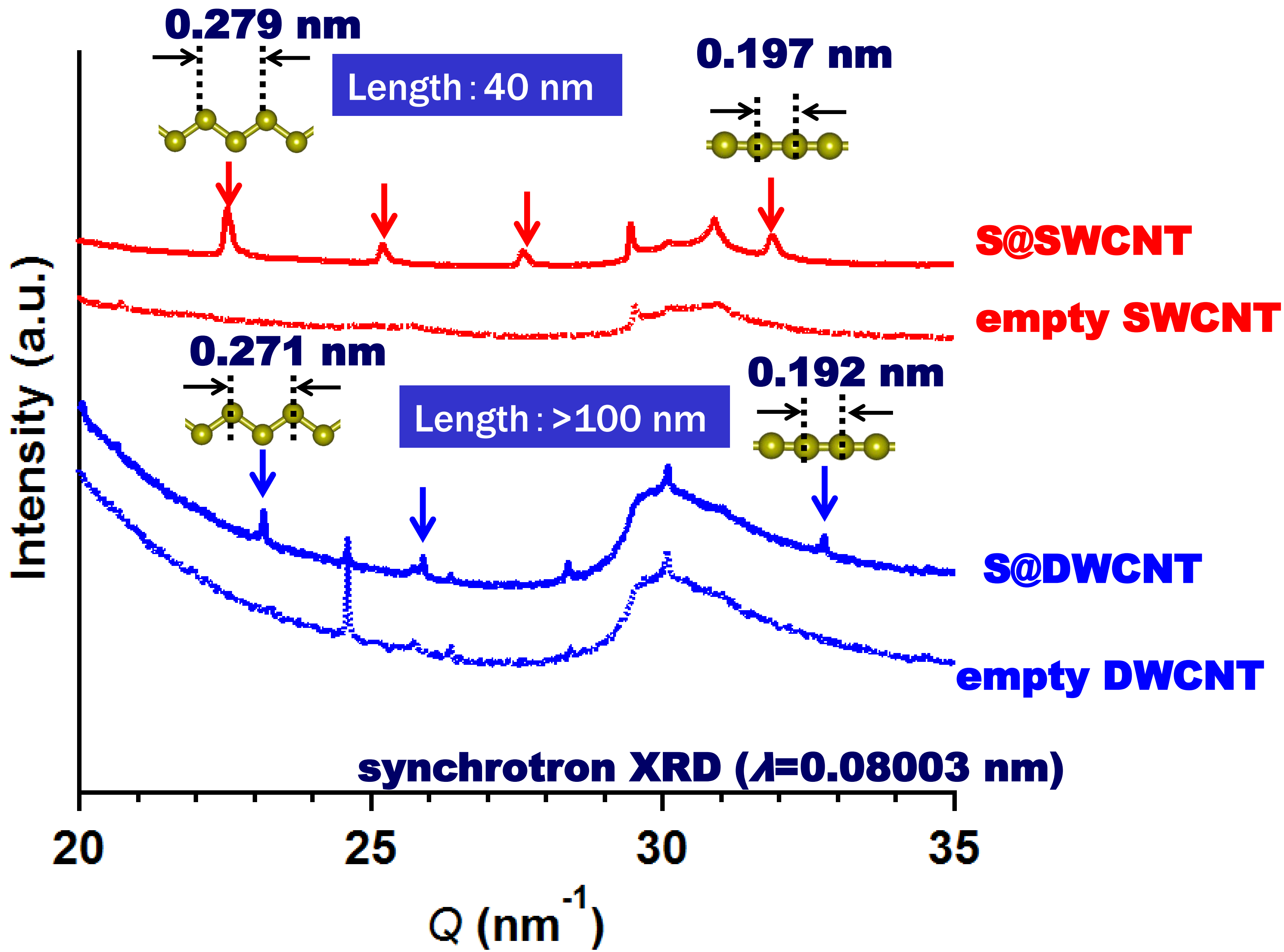
S@SWCNT
S@DWCNT

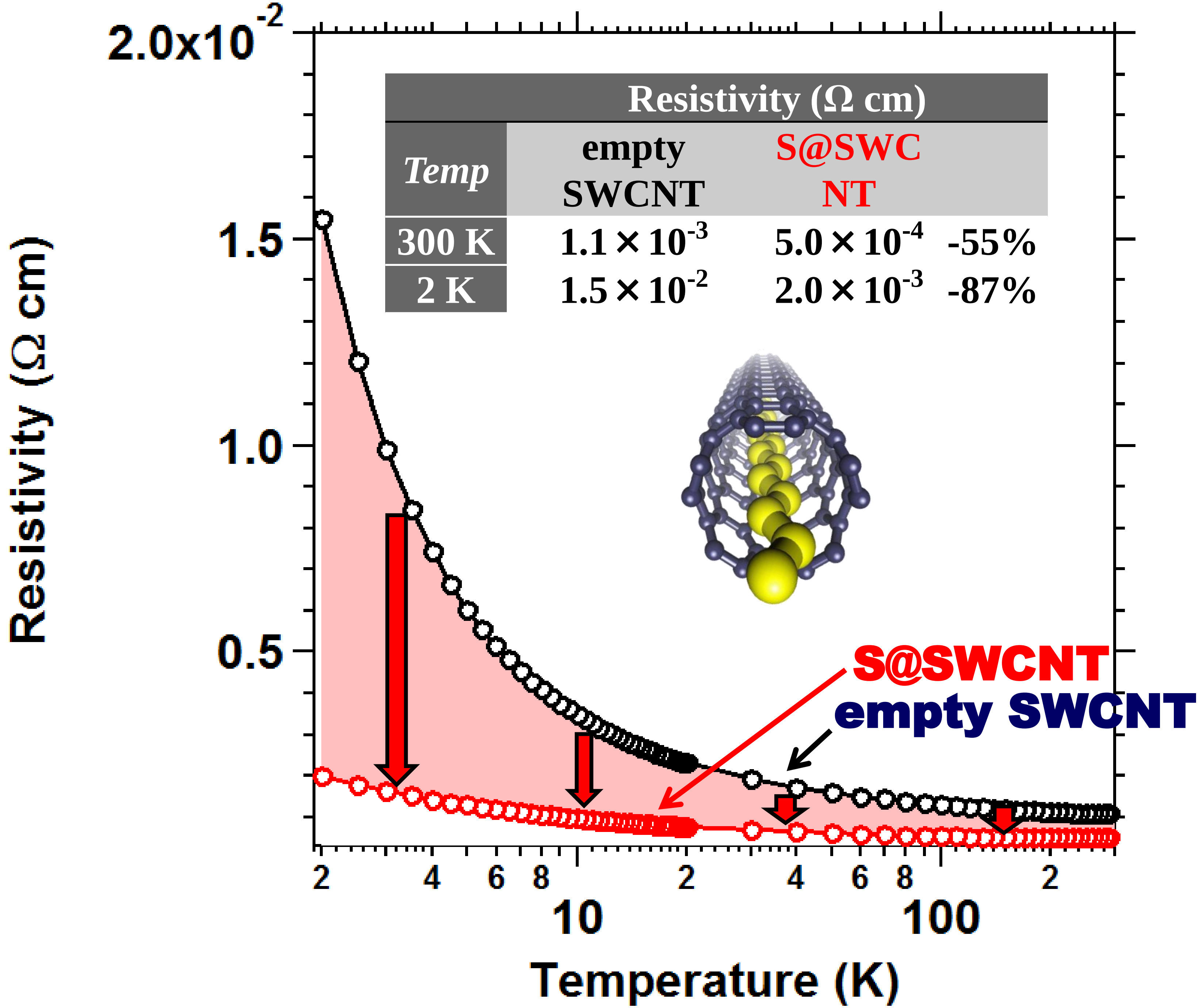
TEM Images



S can form different 1D chain according to the tube diameter (potential)

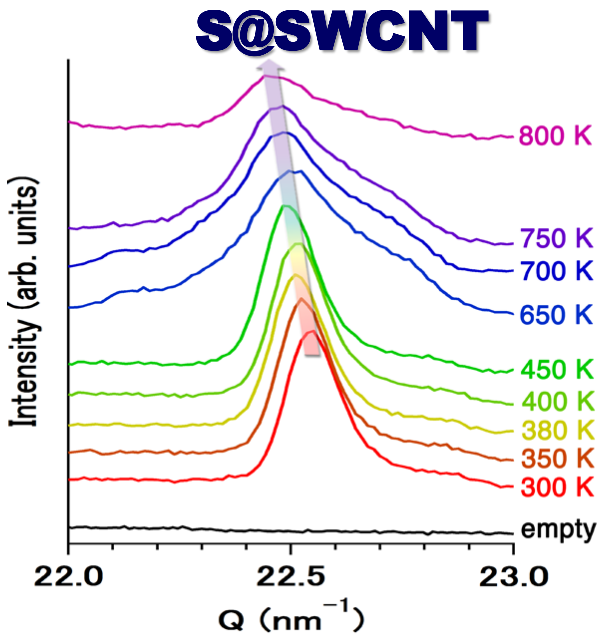
Synchrotron XRD of Atomically 1D-S

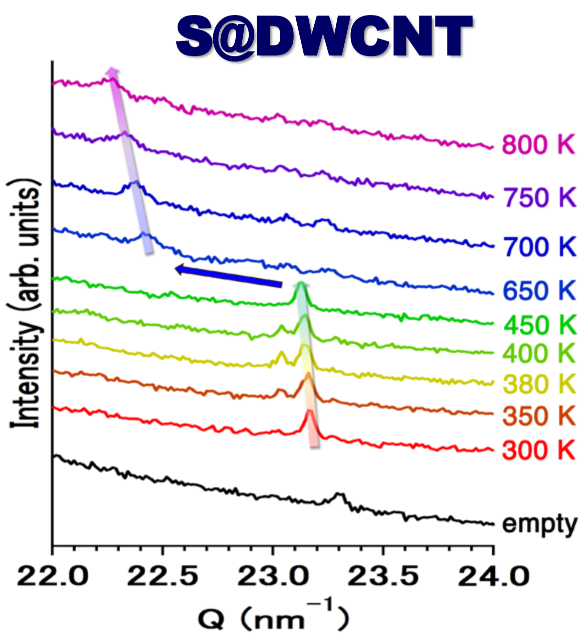


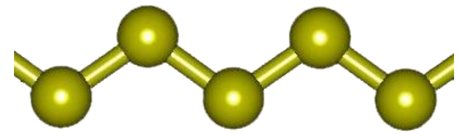


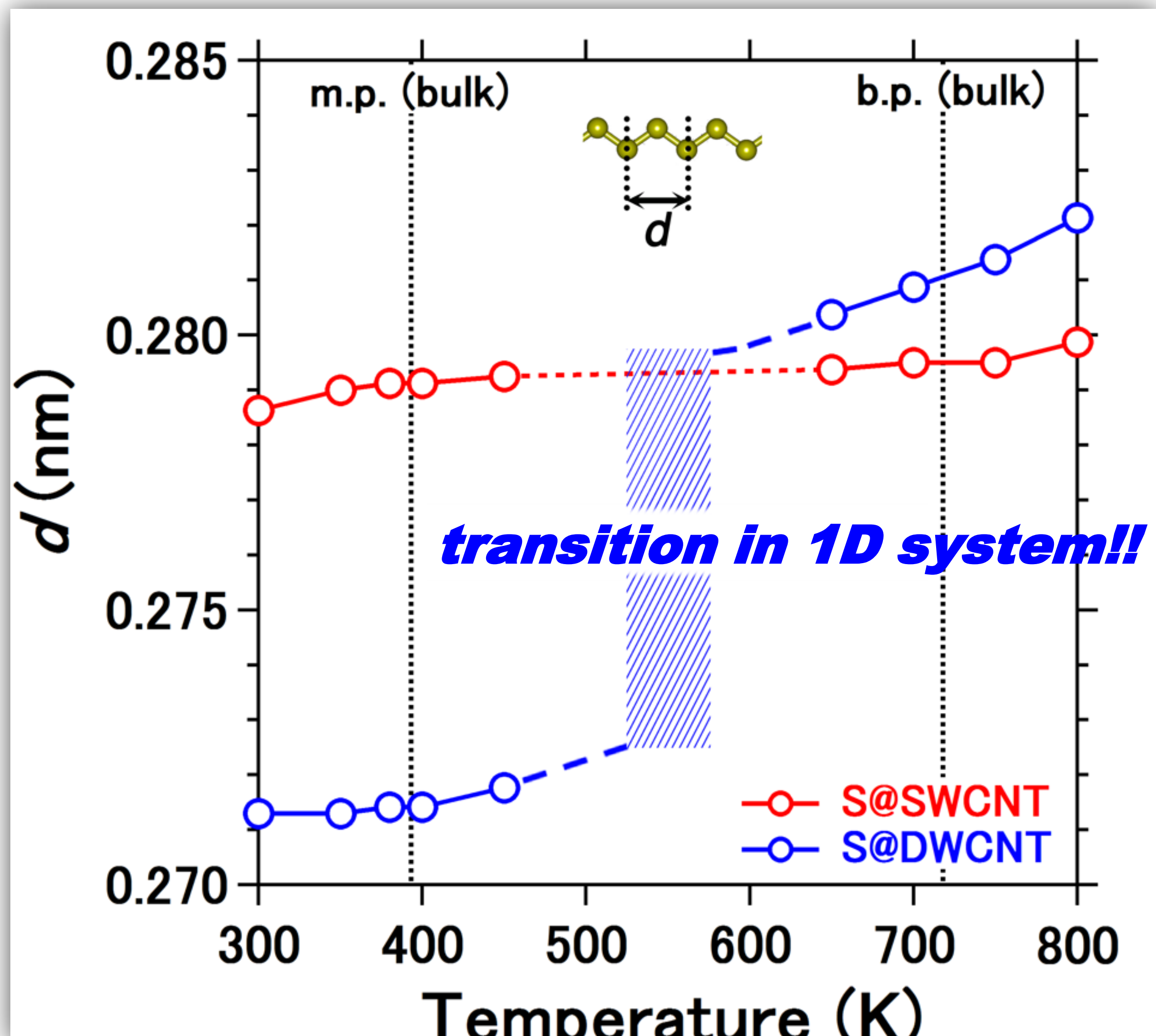
2.0x10^-2
1.5
1.0
0.5
Resistivity (Ω cm)
2
4
6
8
10
2
4
6
8
100
2
Temperature (K)
Resistivity (Ω cm)
Temp
empty SWCNT
S@SWCNT
300 K
1.1×10^-3
5.0×10^-4
-55%
2 K
1.5×10^-2
2.0×10^-3
-87%
S@SWCNT
empty SWCNT

Thermal Stability of 1 D S-Chain





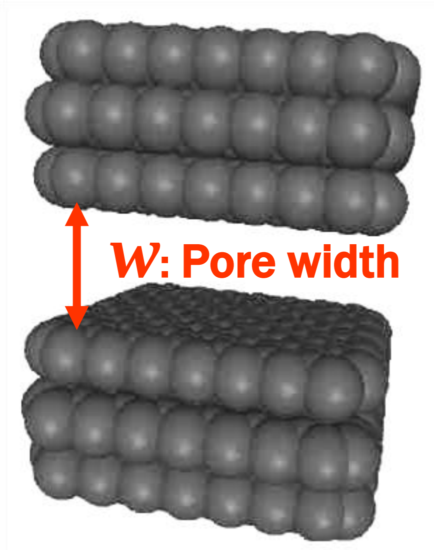




Xe Adsorption on Porous Carbon

Activated carbon fiber 活性炭素繊維

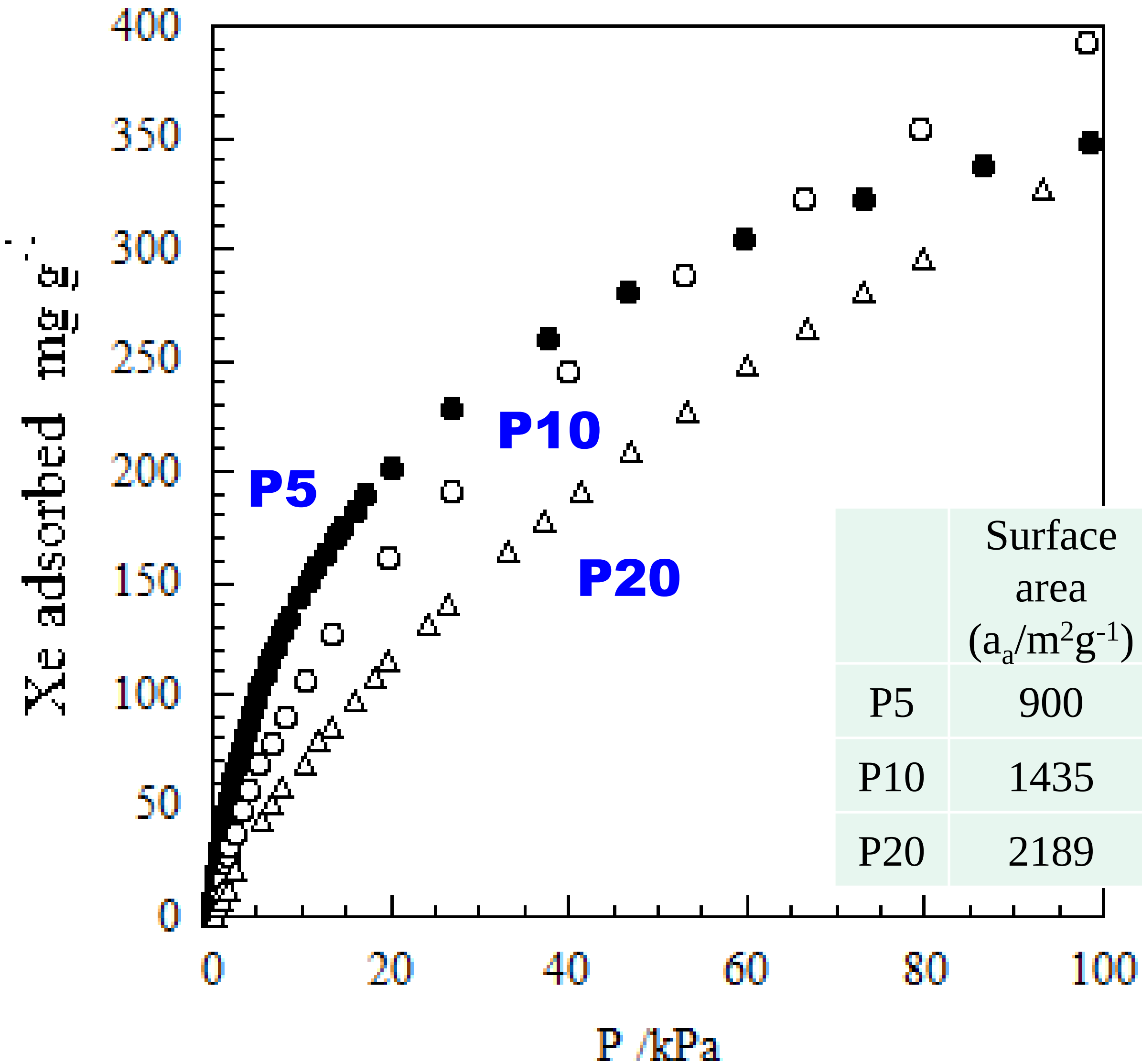
Graphitic nanoscale slit pores



W tunable

0.5 ---- 1.3 nm

Adsorption Isotherms of Xe on ACFs at 300 K



Critical temp. 289.7 K
Boiling temp 161.7 K

LJ size s : 0.396nm
LJ interaction energy
217K k_B

	Surface area (a_a/m^2g^{-1})	Micropore volume (W_0 /ml g^{-1})	Pore width /nm)
P5	900	0.336	0.75
P10	1435	0.614	0.86
P20	2189	1.136	1.05

M.Aoshima et al, J. Colloid Interface Sci. 2000,222, 1790183.

Description of Supercritical Xe Adsorption

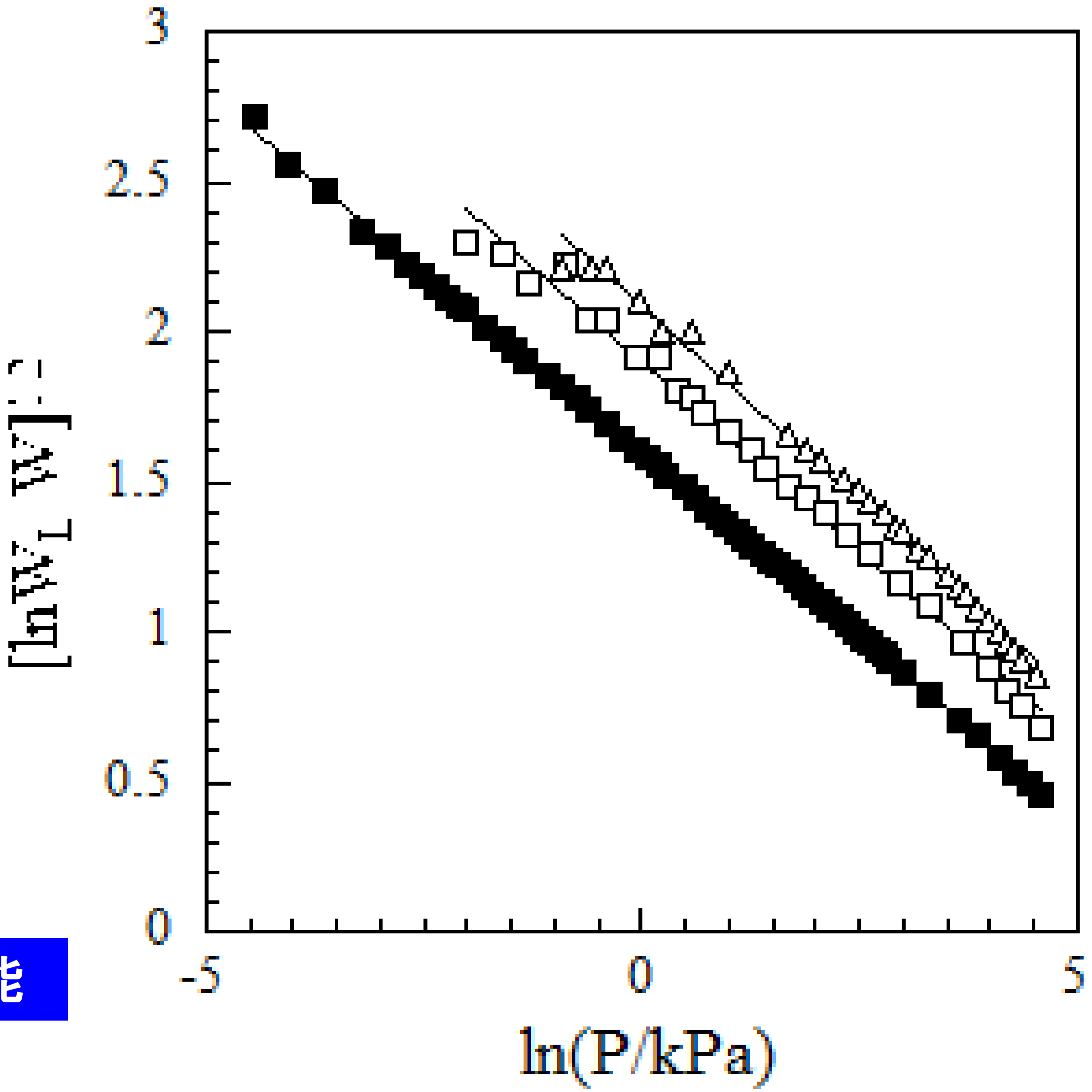
Supercritical DR eq.
by Kaneko

$$[\ln(W_L / W)]^{1/2} =$$
$$(RT / \beta E_0)(\ln P_{0q} - \ln P)$$

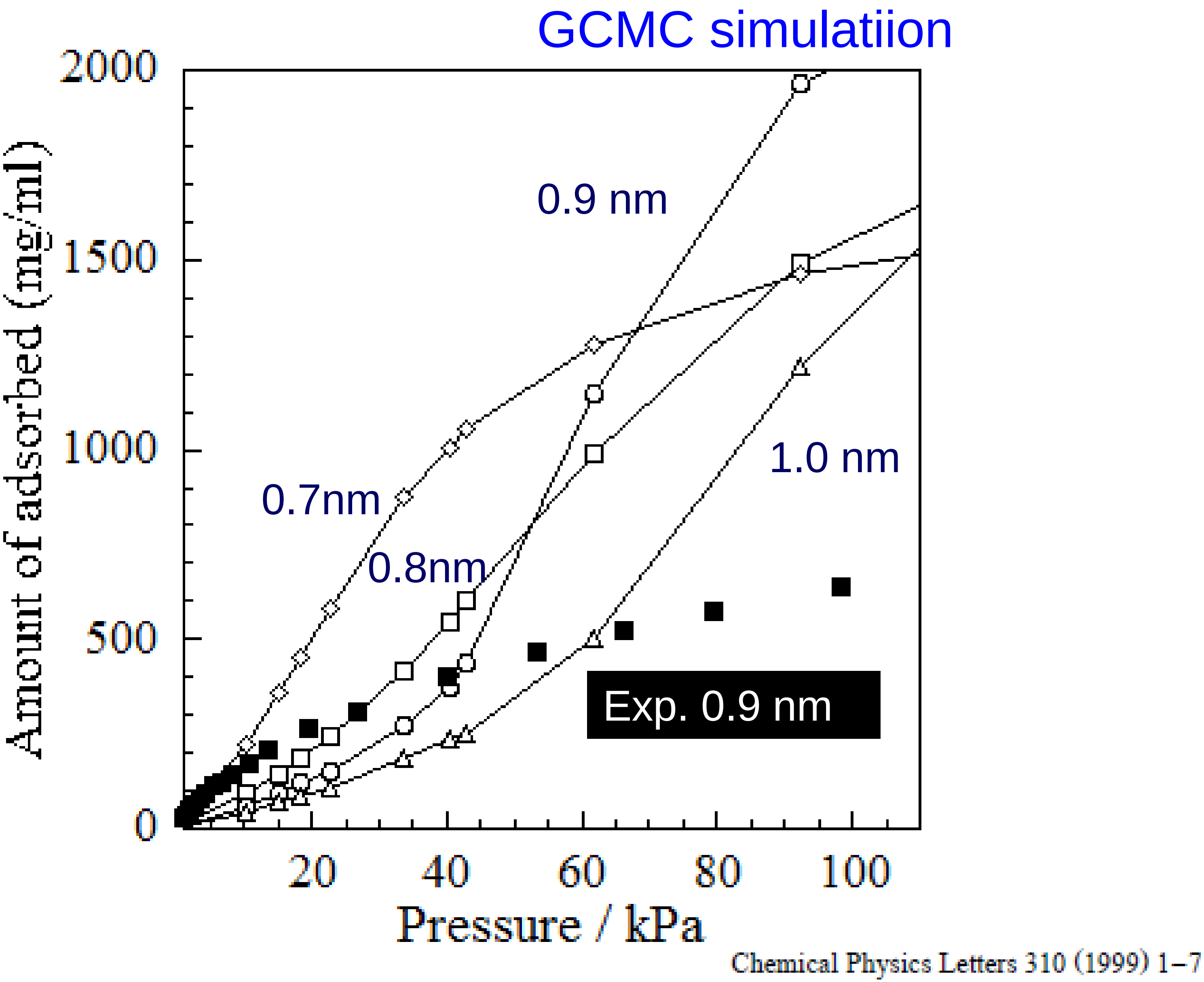
W_L Saturated adsorption

W Adsorption amount at pressure P

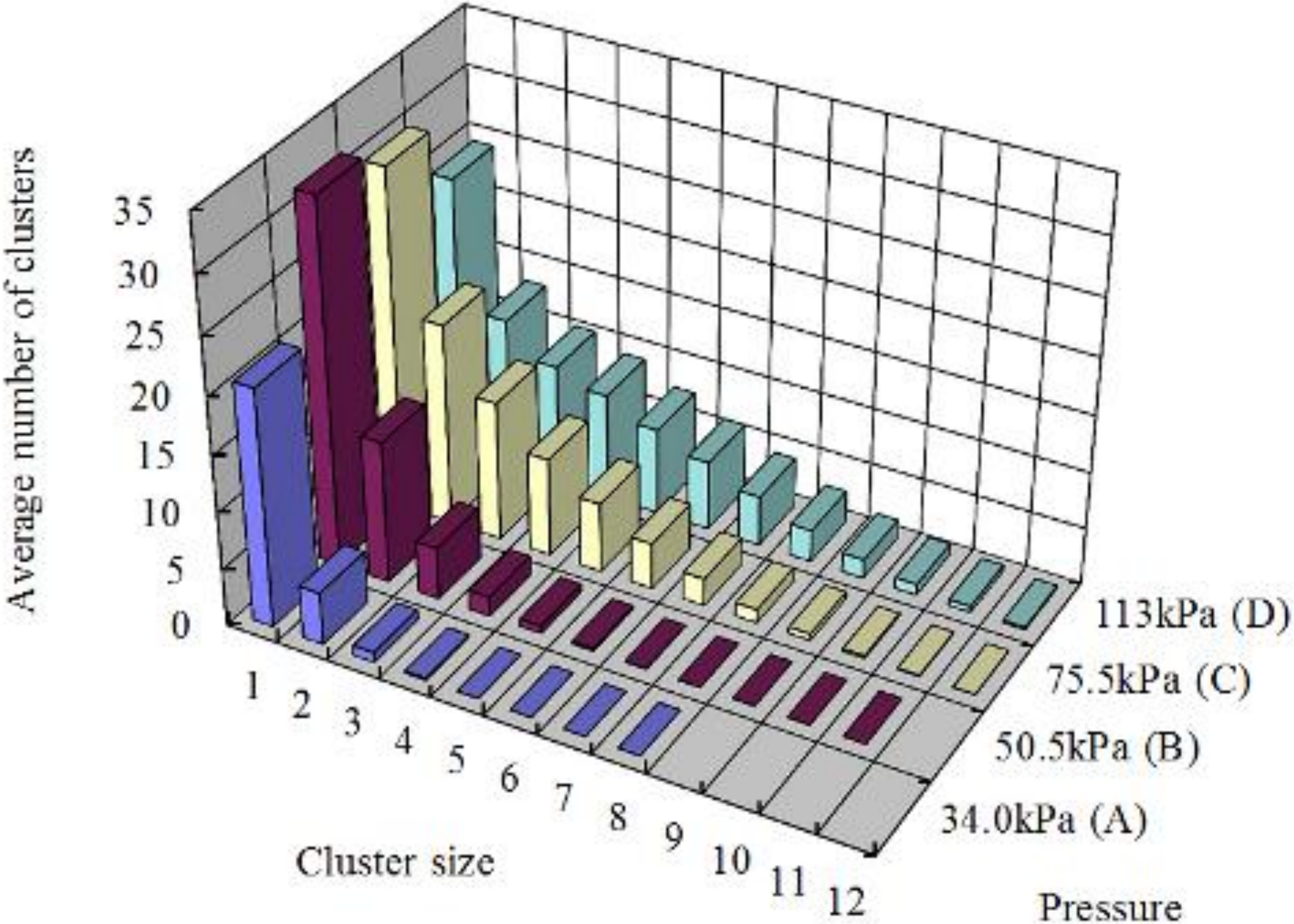
他の条件での吸着予測が可能



Xe Adsorption Isotherms on Graphite Slit Pore at 300 K



Xe Cluster Formation in Pores



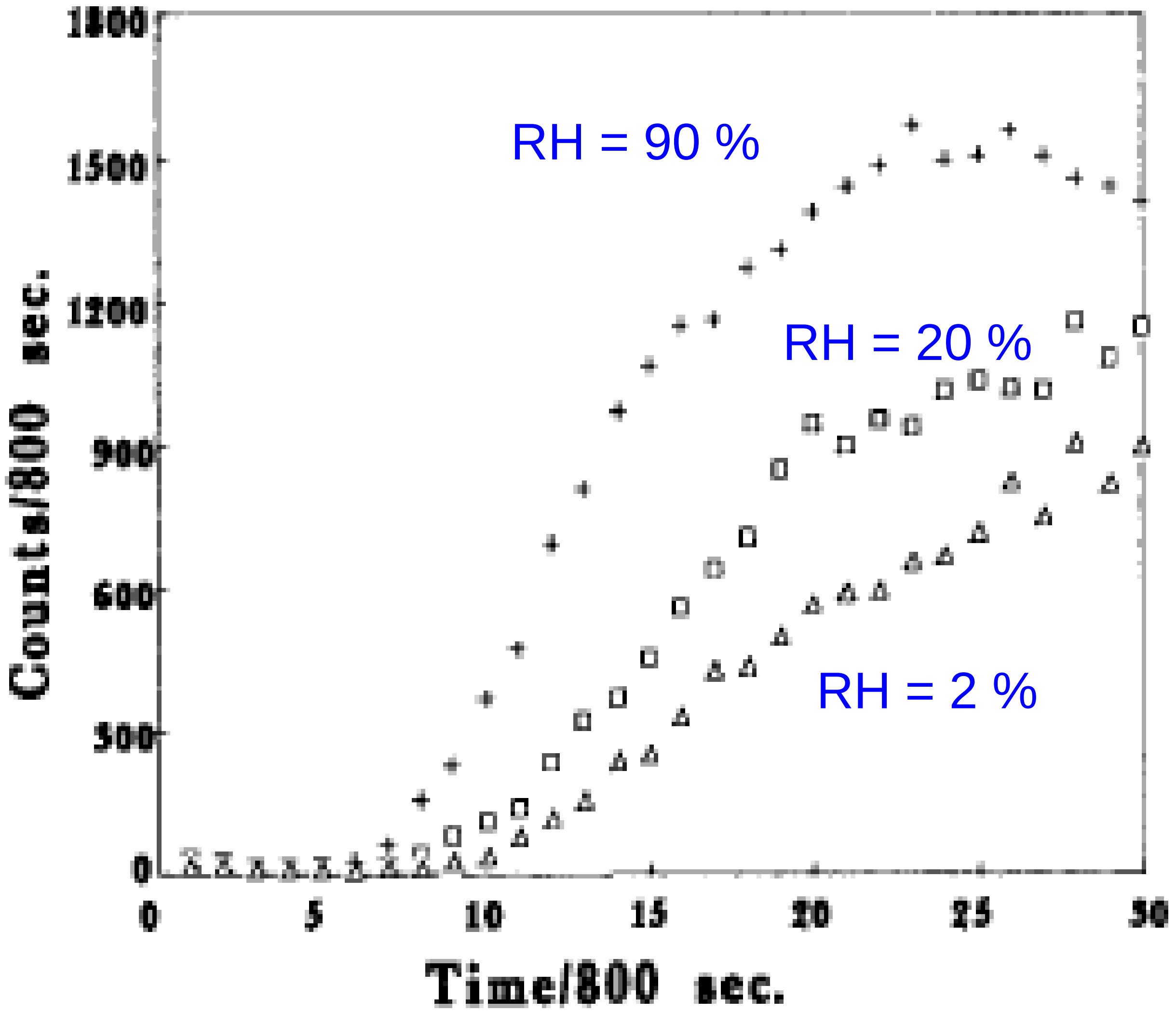
Removal of Rn gas

Adsorption studies on Rn

in the literature

Effect of Humidity on Rn Adsorption on AC

R. Bocanegra, P.K. Hopke、Sci. Total Environ.1988, 76,193-202



How can we remove Rn ?

Removal of Rn gas

Physical adsorption

T_b = 202 K T_c = 377 K

Adsorption at 202 K 〜 377 K   室温附近で可能

Representative physical adsorption

Porous solids

Larger pore volume and surface area

Smaller pore width

> 0.44 nm (> **0. 7nm 1.5 σ (Rn)**)

to avoid the entrance blocking

Issues in Rn Removal

Difficulty in experimental studies

Extremely low concentrated Rn gas in atmosphere

O_2 N_2 Ar CO_2 H_2O Others

Selective adsorptivity of Rn for Rn-CO_2 mixed gas

Adsorption engineering

1 Pre-removal of condensable gases H_2O

Avoiding entrance blocking

2. Selective adsorption removal of Ra around 200 K

without blocking by CO_2

(Pre-removal of CO_2 with amino-modified porous solids, w > 2nm ?)

Critical Temperature of Representative Gases

gas	T_b /K	T_c / K	P_c /Pa	σ_{ff} /nm	ε_{ff} /k_B	multipole moment	magnetism
H_2	20.3	33.0	1.29	0.292	38.0	*qu* $+2.1 \times 10^{-40}$	*dia*
O_2	90.2	154.6	5.04	0.338	126.3	*qu* -1.33×10^{-40}	*para*
N_2	77.3	126.2	3.39	0.363	104.2	*qu* -4.90×10^{-40}	*dia*
NO	121.4	180	6.48	0.347	119	*di* 0.158×10^{-30}	*para*
CO	81.6	132.9	3.50	0.359	110	*di* 0.112×10^{-30}	*dia*
CO_2	194.7	304.2	7.48	0.376	245.3	*qu* -14.9×10^{-40}	*dia*
CH_4	111.6	190.5	4.60	0.372	161.3	*oc*	*dia*
Rn	**202**	**377**					

Promising Adsorbents ?

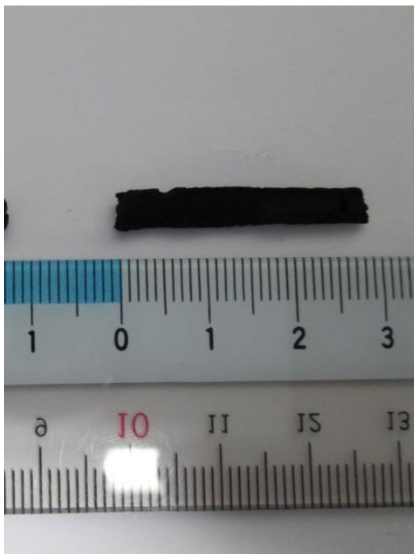
Nanoporous carbons   ACFs

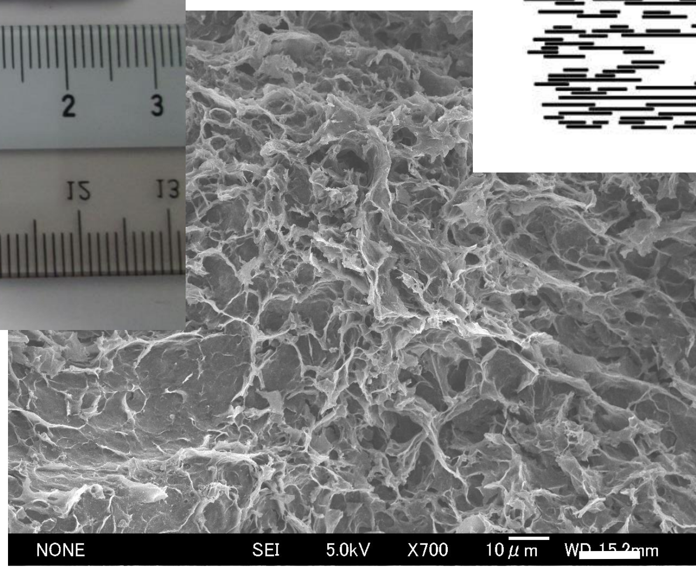
Zeolites or Silica gels   Water

Modified porous solids CO_2

High Surface Area Graphene-based Carbon

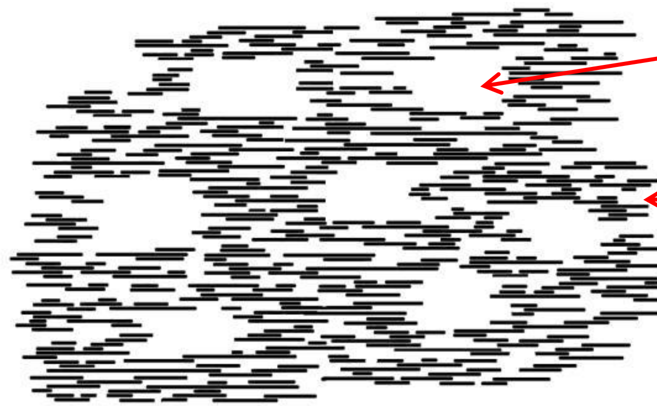
S. Wang et al , Carbon (2014)

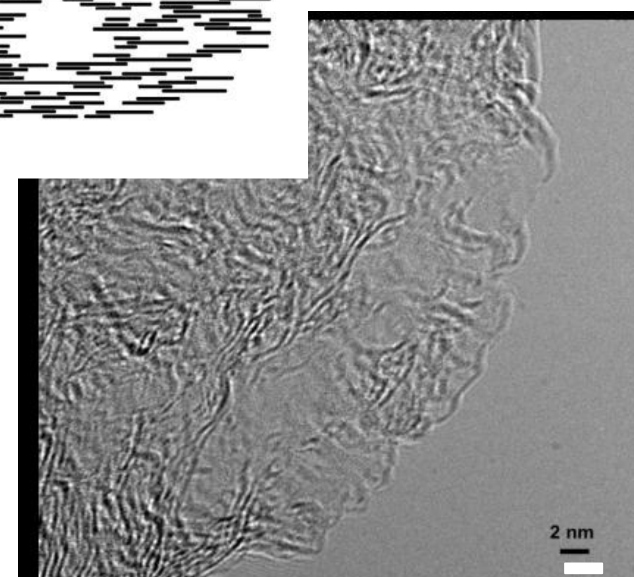




10 μm

SEM image





2nm

TEM image

Acknowledgements

Grant-in-Aid for Scientific Research A (2012-2014)

New chemistry with edge-enriched carbons

JST CREST Project (2013-2019)

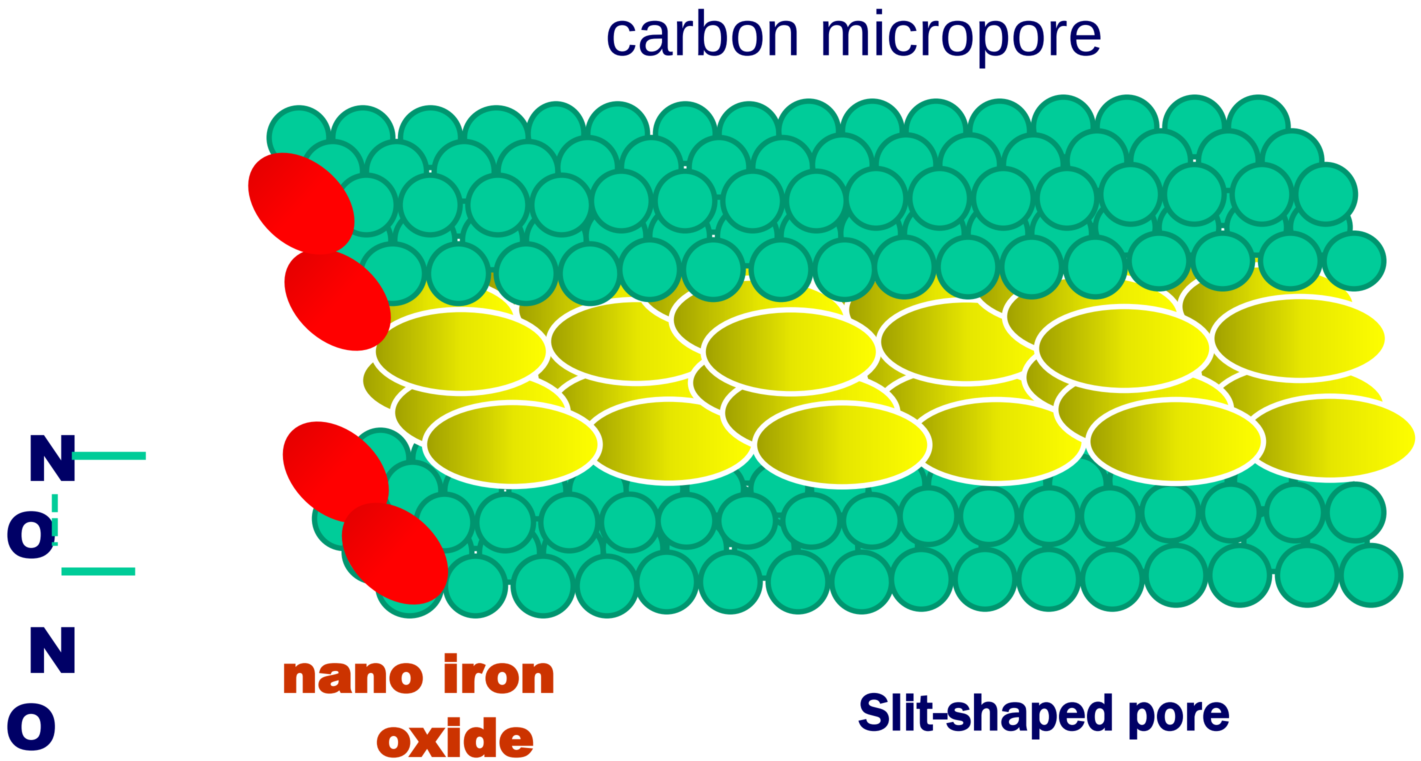
Quantum molecular sieving of isotope molecules

Spring8: Japan Synchrotron Radiation Research Institute; BL02B2 beam line


Thank you

Highly Dense NO-dimer Formation

2 NO → $(NO)_2$



Supercritical NO transforms into vapor with dimerization $(NO)_2$

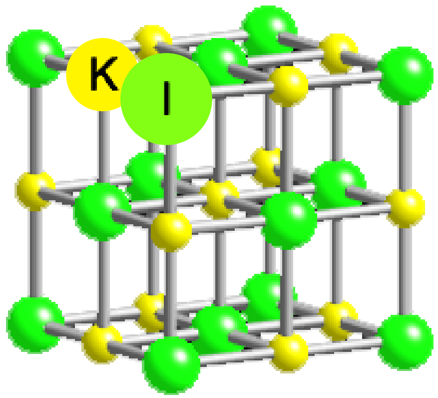
NO adsorption amount **> 30 %** of adsorbent weight

Carbon (1986)   *J. Chem. Phys*. (1987)

KI Solid Phase Trans ion at 1.9 GPa occurs in CNT Spaces below 0.1 MPa

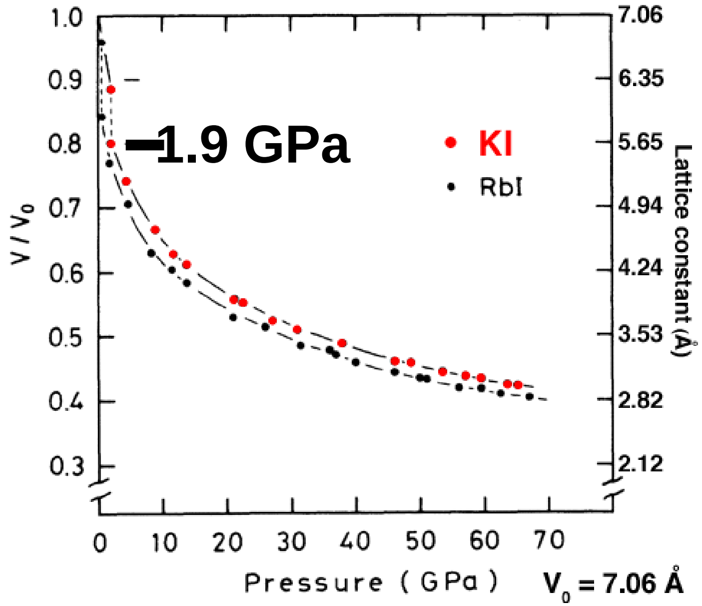
KI

Hygroscopic material

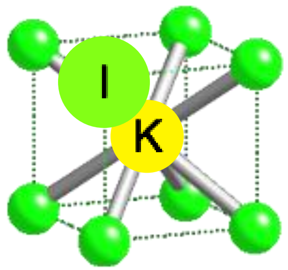


B1

a = 7.06 Å



K. Asaumi et al, PRB (1983)

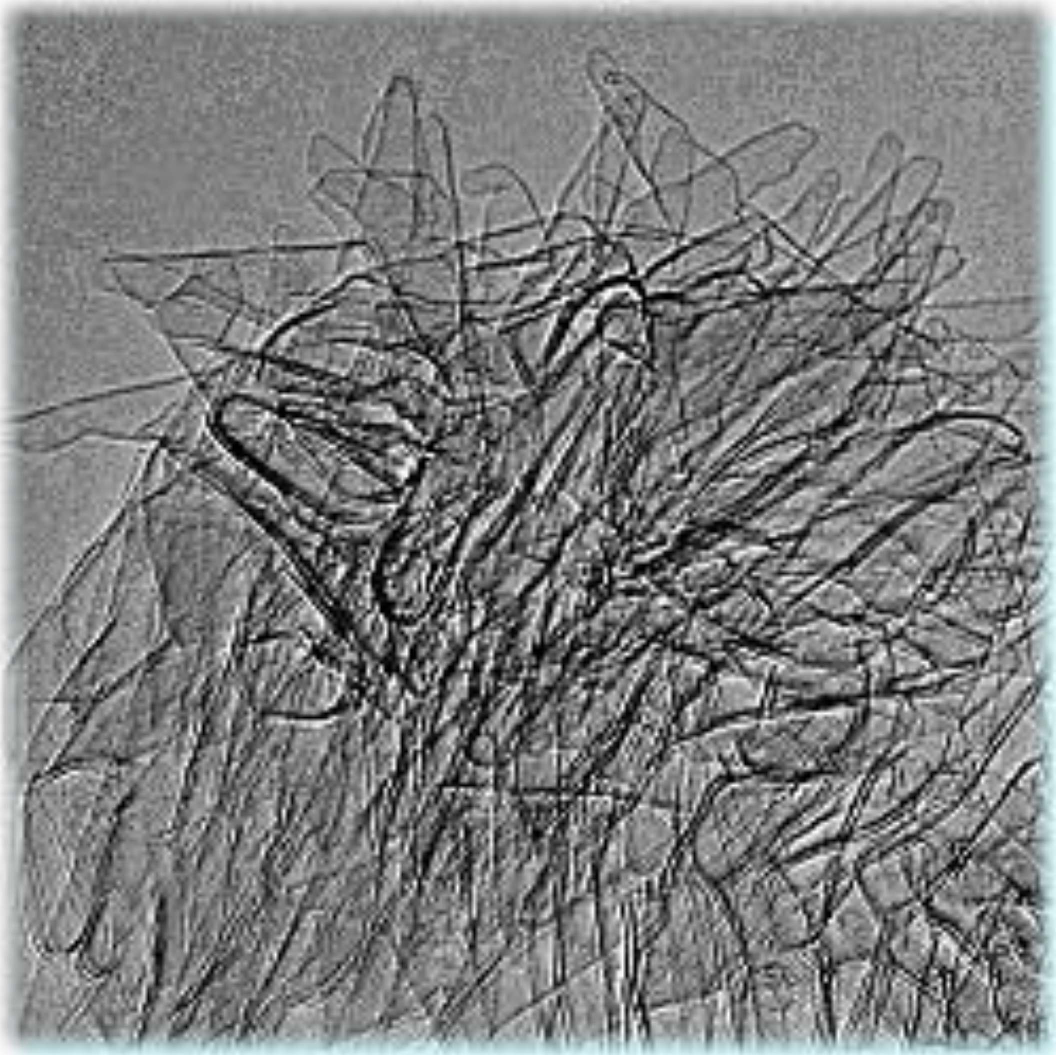


B2

a ≤ 5.65 Å

How about KI assemblies in carbon nanospaces ?

Single Wall Carbon Nanohorn



Single Wall Carbon Nanohorn (SWCNH)

S. Iijima, M. Yudasaka et al, *Chem. Phys. Lett*. (1996)

Merits

Chemically pure (no catalyst)

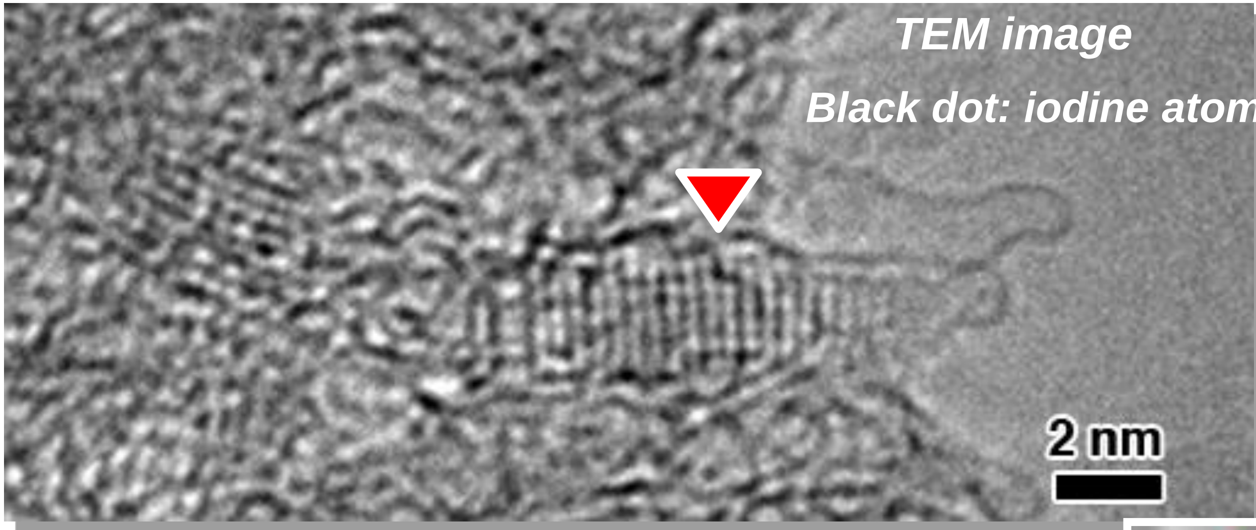
1g-order samples

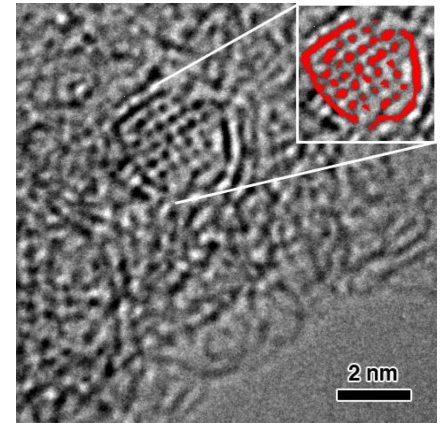
Tuning of nanowindow-size

KI doping

1073 K. < 0.1 MPa

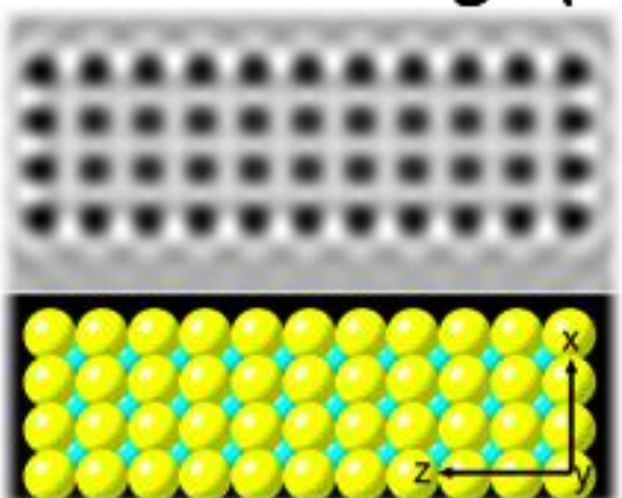
TEM Images of KI on SWCNH B2 Phase





Cross-section

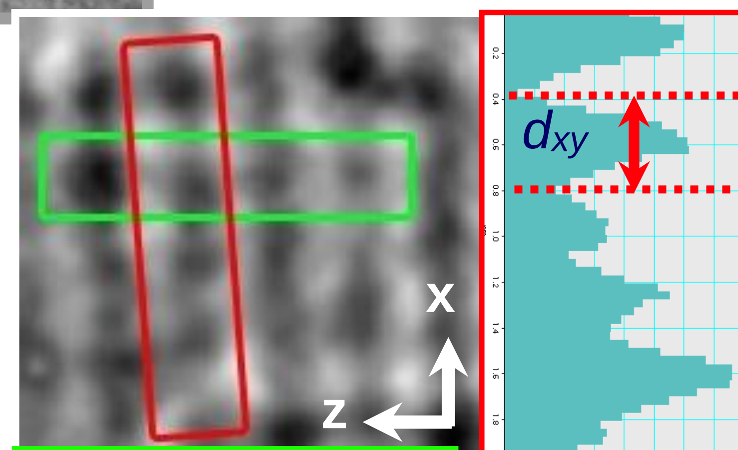
Simulated image (B2)

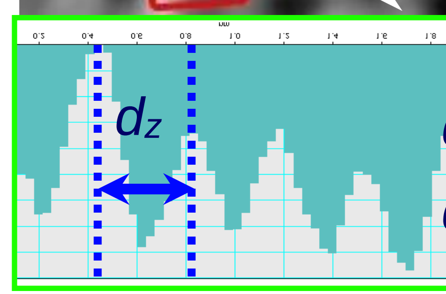


>1.9GPa

a, b ≈ 3.53 Å

c ≈ 3.82 Å

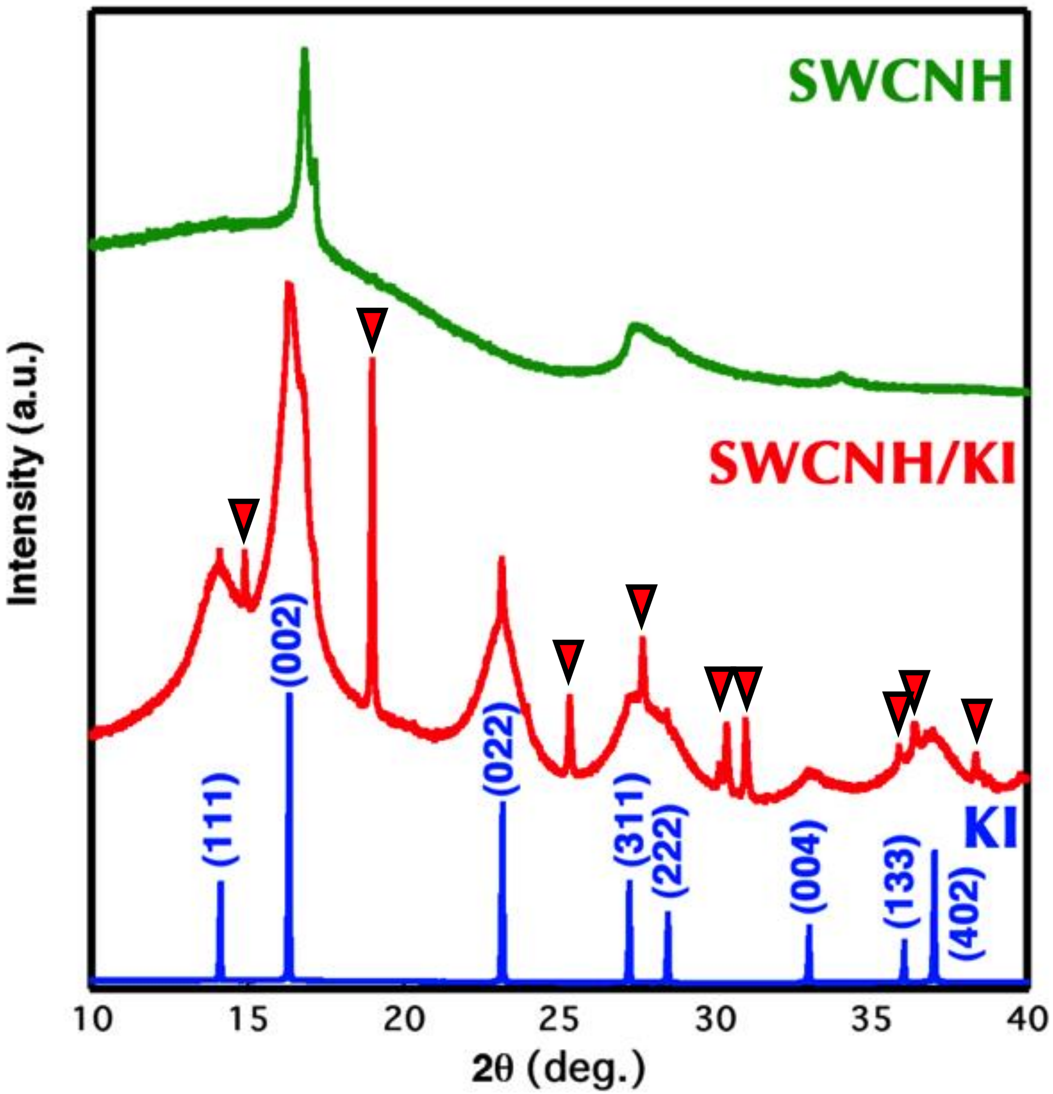




$d_{xy} \approx 3.53$ Å

$d_z \approx 3.82$ Å

X-ray Diffraction Patterns



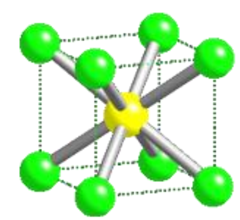
Unknown Peaks

XRD profile of SWCNH/KI

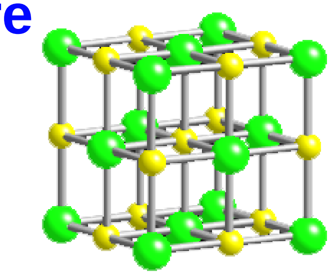
1. Anisotropic growth of B1 structu

2. New sets of XRD pattern

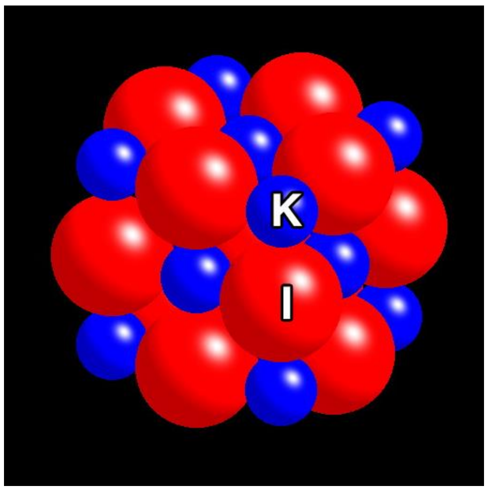
B2 structure



B1 structure

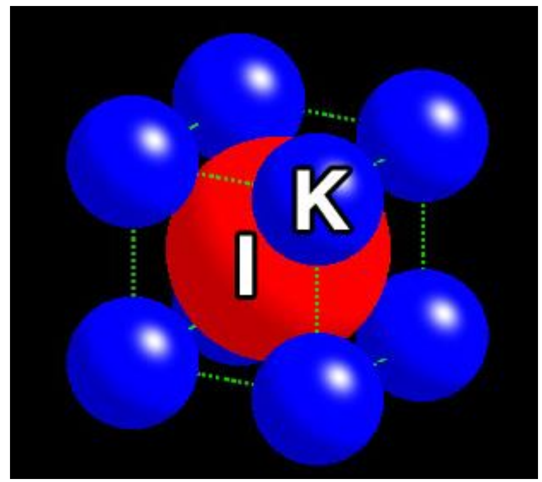


Super high pressure phase is stabilized in nanotube spaces

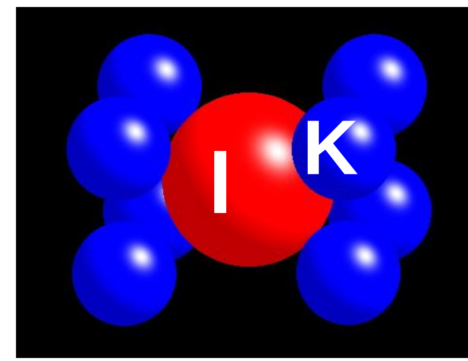


B1 NaCl type

>1.9 GPa



B2 CsCl type



Tetragonal

The structure of high-pressure phase can be formed in nanospaces below 0.1 MPa.

Urita et al, *J. Amer.Chem. Soc.* **133**, 10344 (2011)