Template Synthesis of Nano-Structured Carbons

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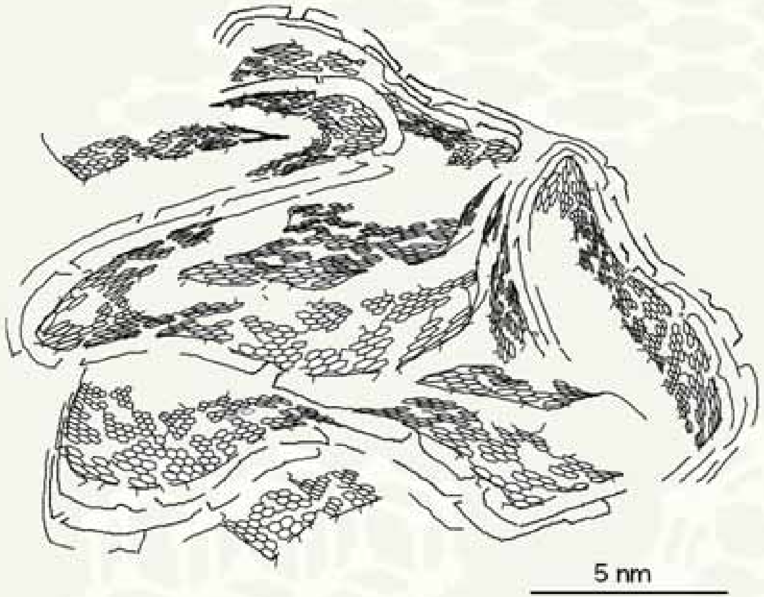
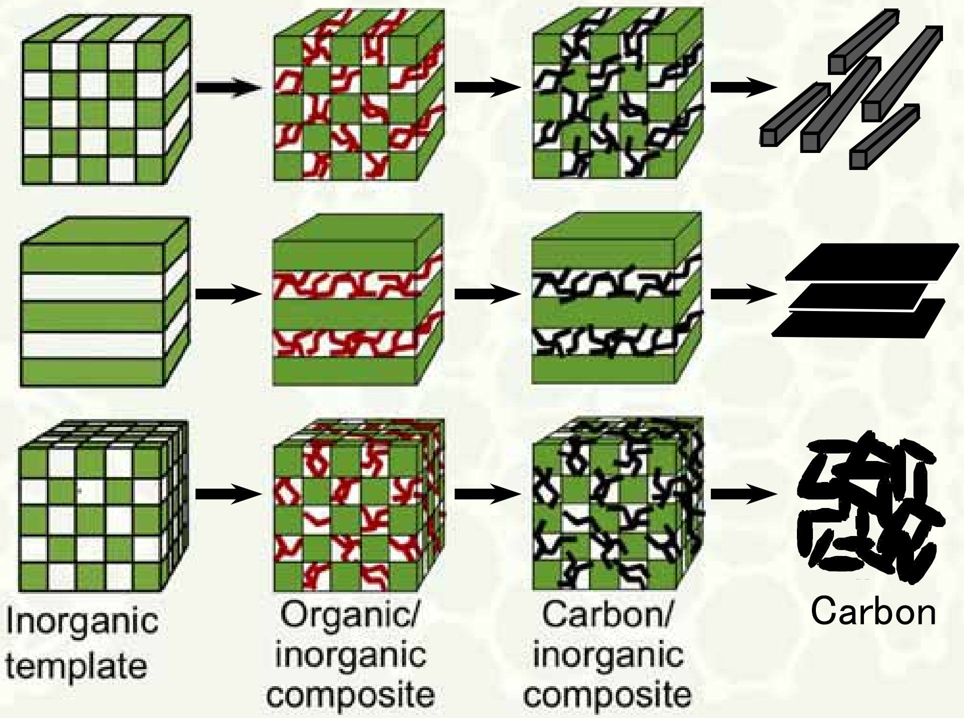
For controlling complicated carbon structure at nanometer level



Structure of activated carbon

Template carbonization technique!!

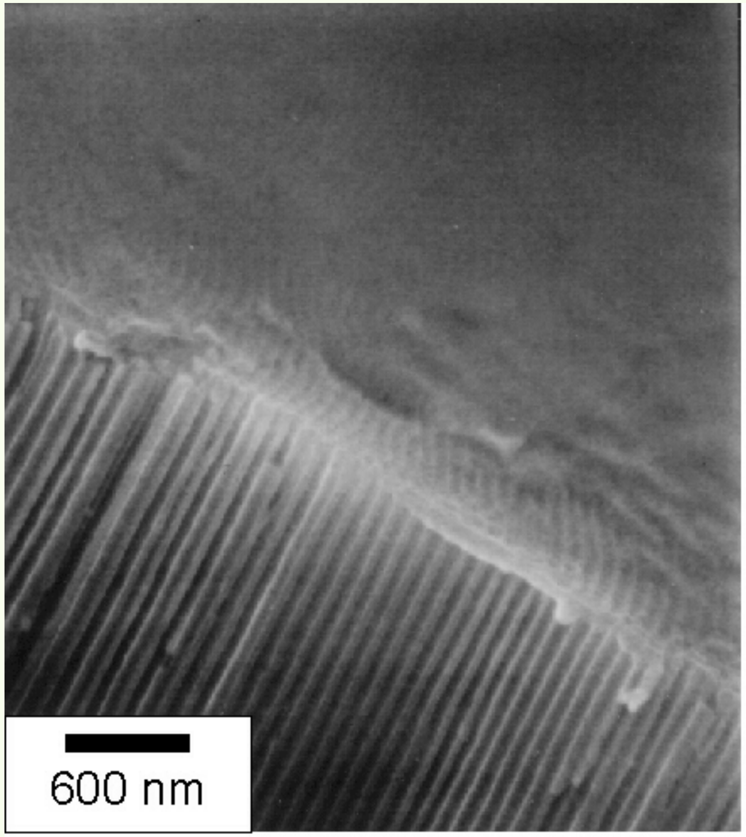


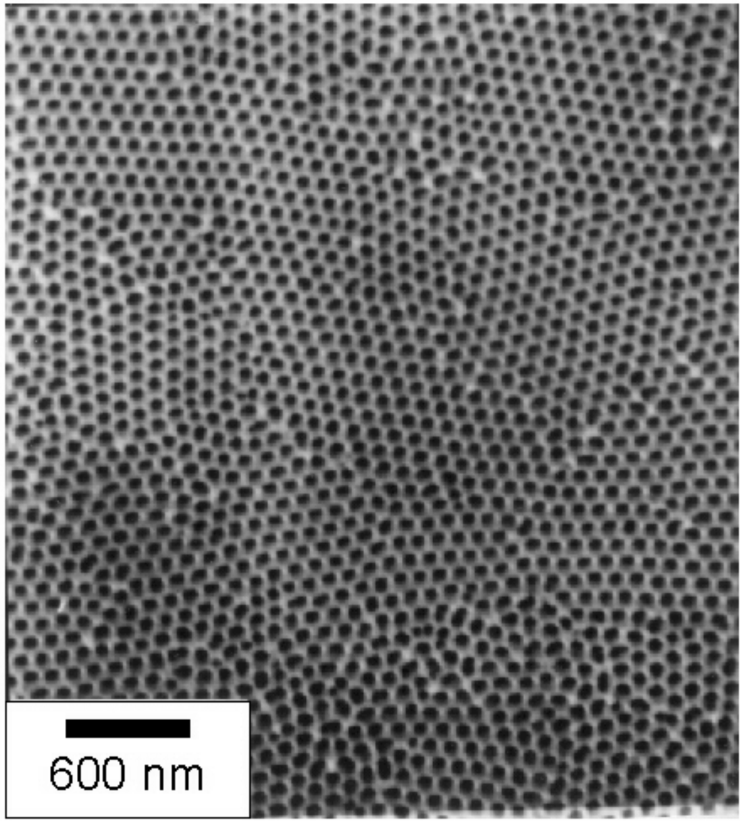
TOC

A. Template synthesis of carbon nano-test tubes and their unique properties

B. Template synthesis of porous carbons and their application to energy storage medium

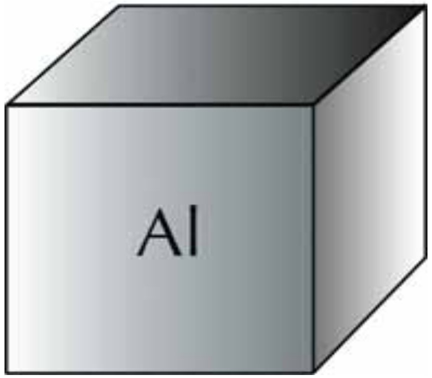
1. Water dispersible carbon nano-test-tubes (CNTTs)





Uniform straight channels in anodic aluminum oxide (AAO) film

Synthesis of carbon nano-test tubes



Al plate

anodic oxidation

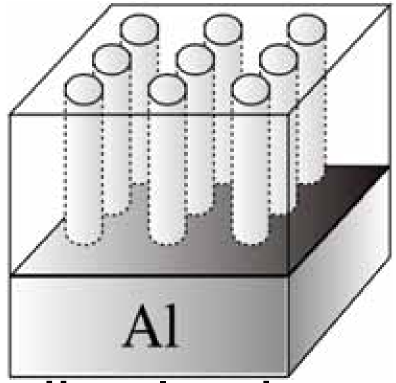
electrolyte: 20 wt% sulfuric acid

voltage: 20 V

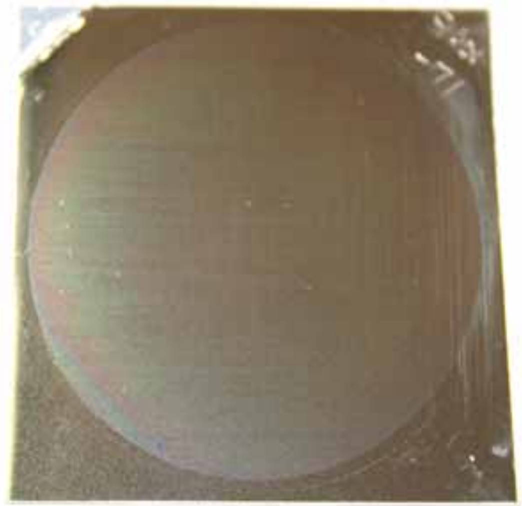
temperature: 10˚C

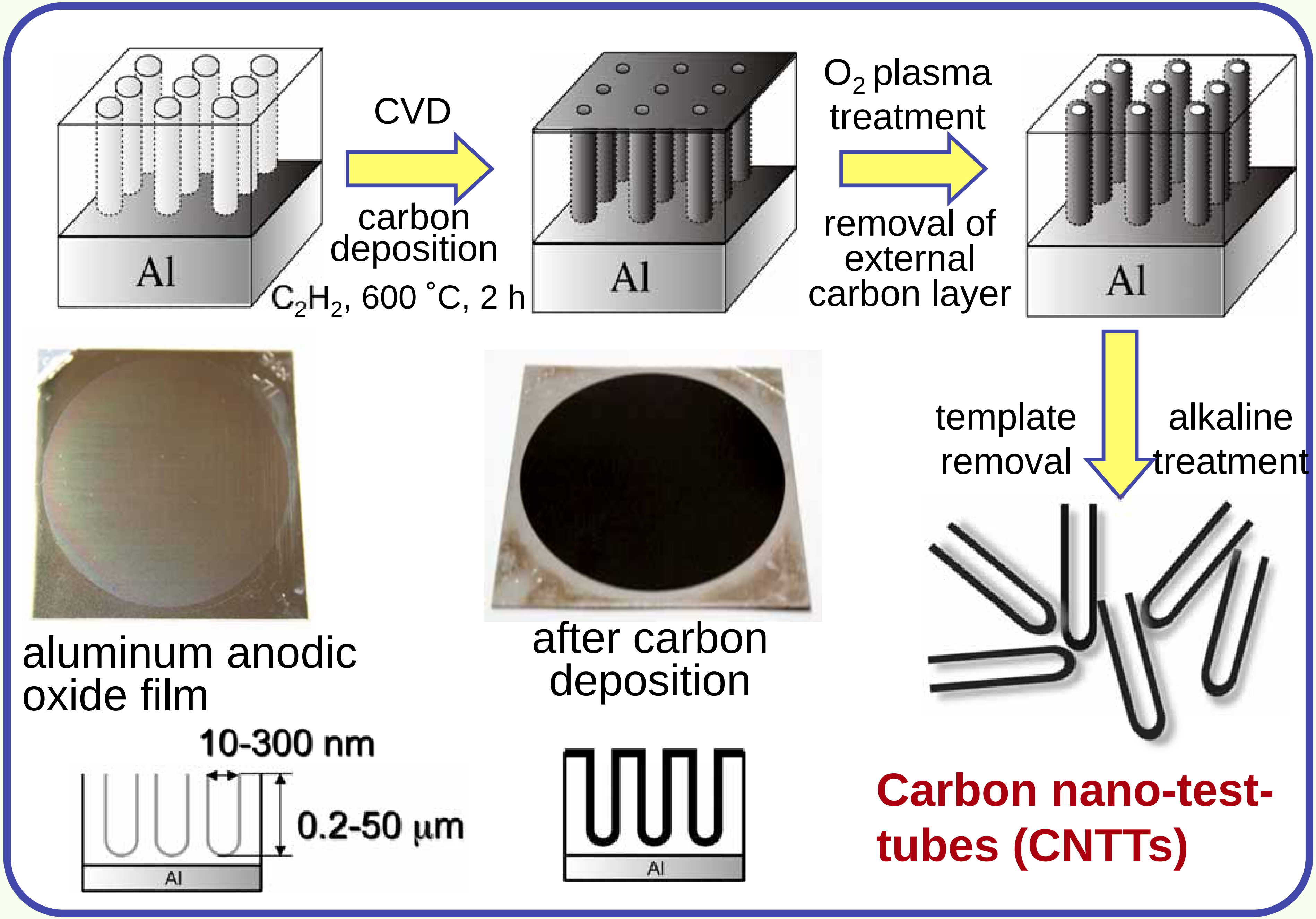
oxidation time: 96 s

diameter 35 nm



anodic aluminum oxide film



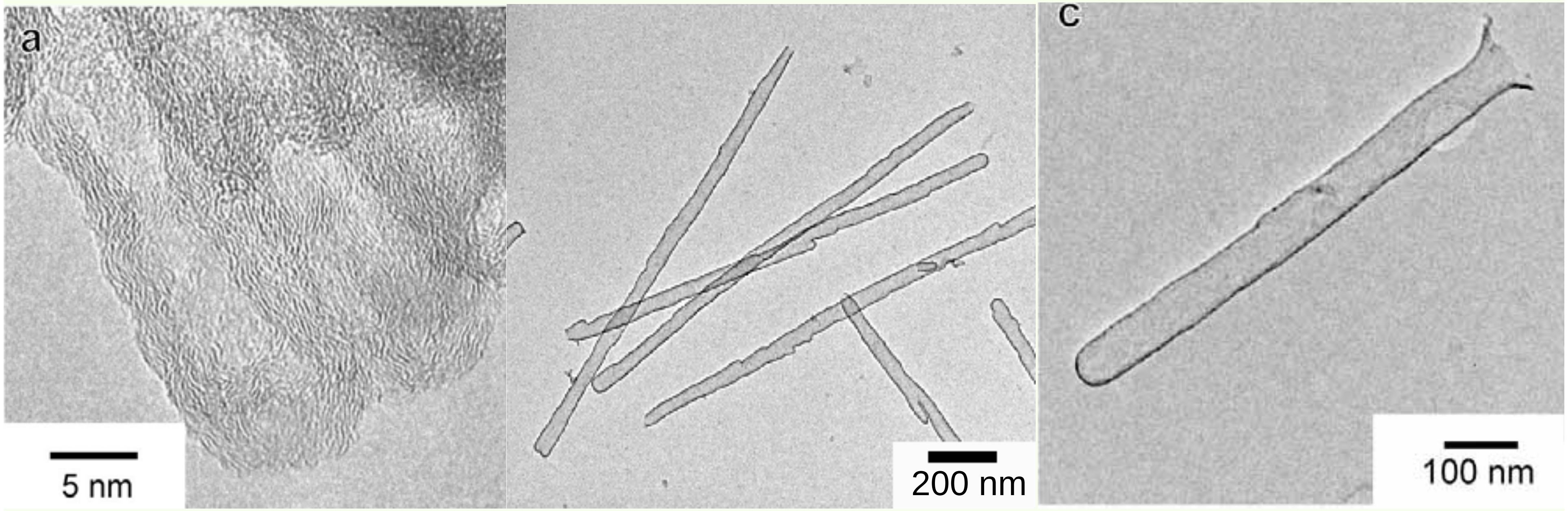


Al
CVD
carbon deposition
C2H2, 600 °C, 2 h
Al
O2 plasma treatment
removal of external carbon layer
Al
template removal
alkaline treatment
aluminum anodic oxide film
10-300 nm
0.2-50 µm
Al
after carbon deposition
Al
Carbon nano-test-tubes (CNTTs)

CNTTs with different diameters

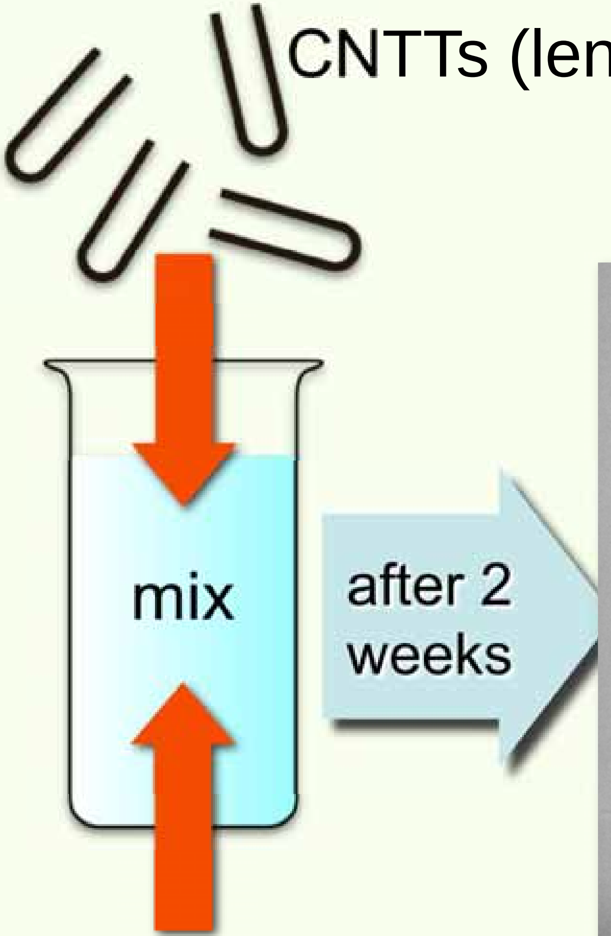
diameter

15 nm 35 nm 60 nm



Test tube shape !
(one of the ends is always closed.)

CNTTs (length: 1 µm)

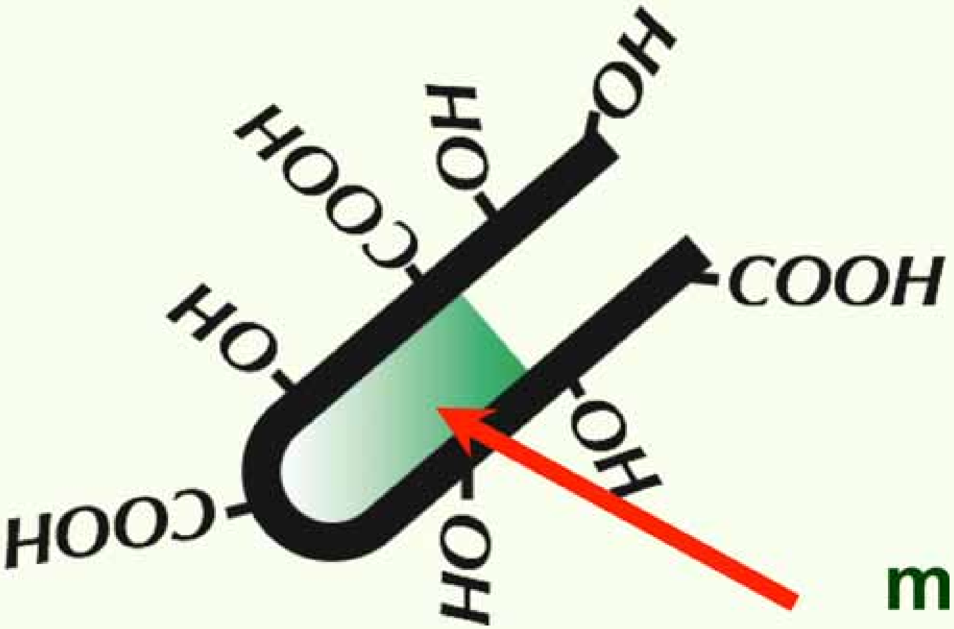


several kinds
of solvents

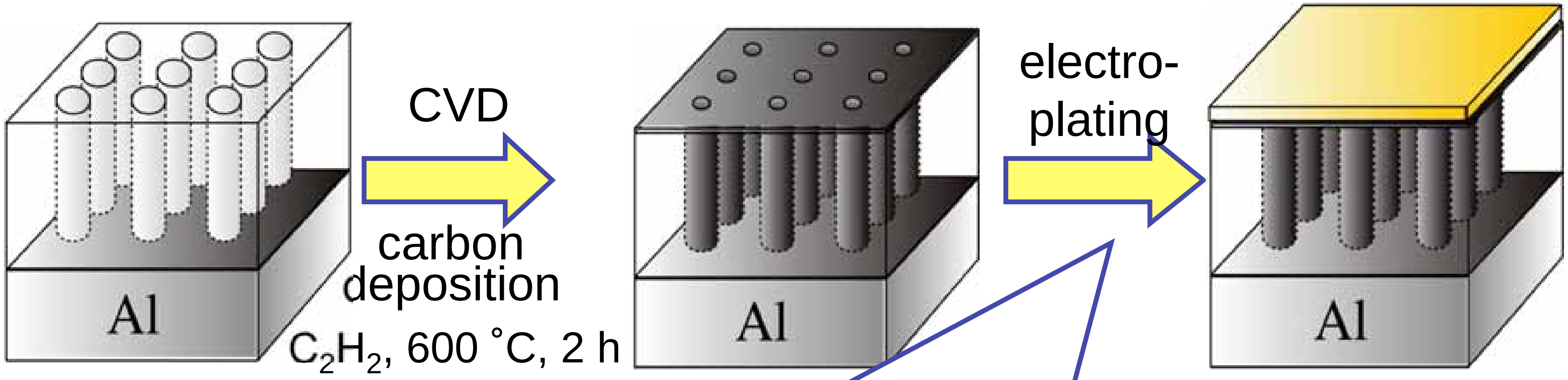
water ethanol chloroform toluene

The “as synthesized” CNTTs are easily dispersed in water without any post treatment!

2. Inclusion of magnetic, organic materials or DNA into carbon nano-test-tubes



magnetic materials, organic polymer or DNA



plating conditions

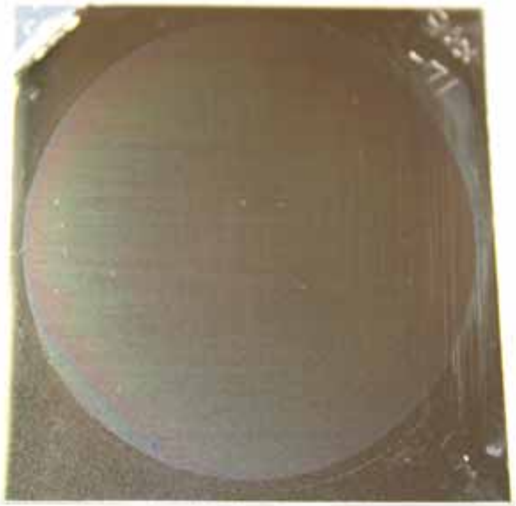
filling metal: NiFe

plating bath : nicl
saccharin, boric a

bath temperature

voltage: 4 V

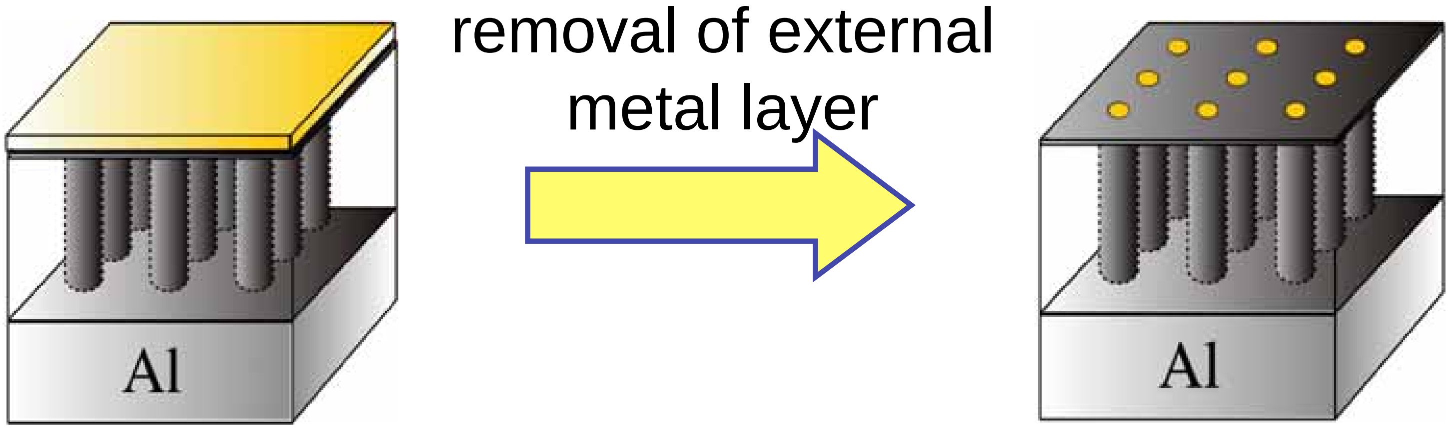
plating time: 30 min



aluminum anodic oxide film

after carbon deposition

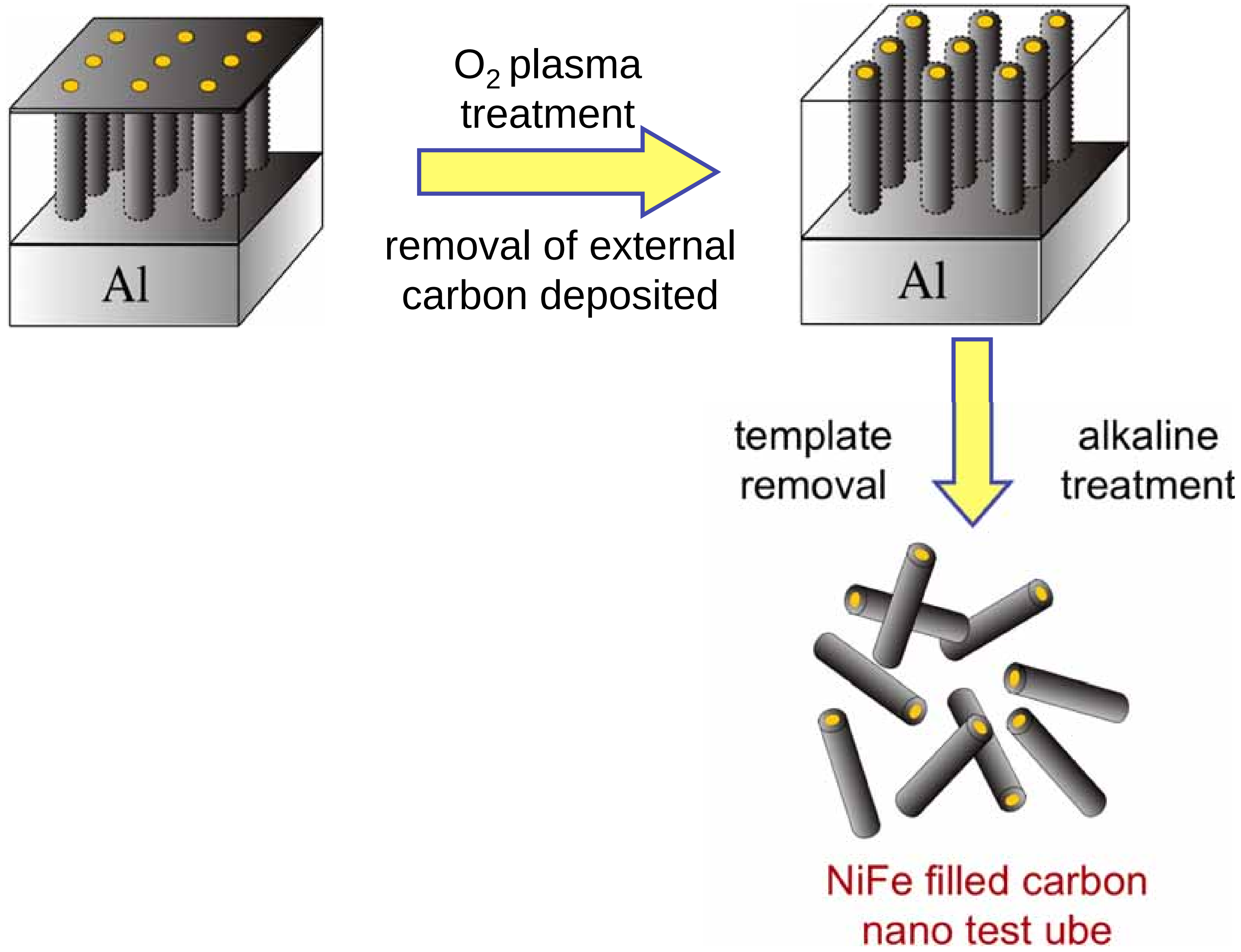
after electroplating



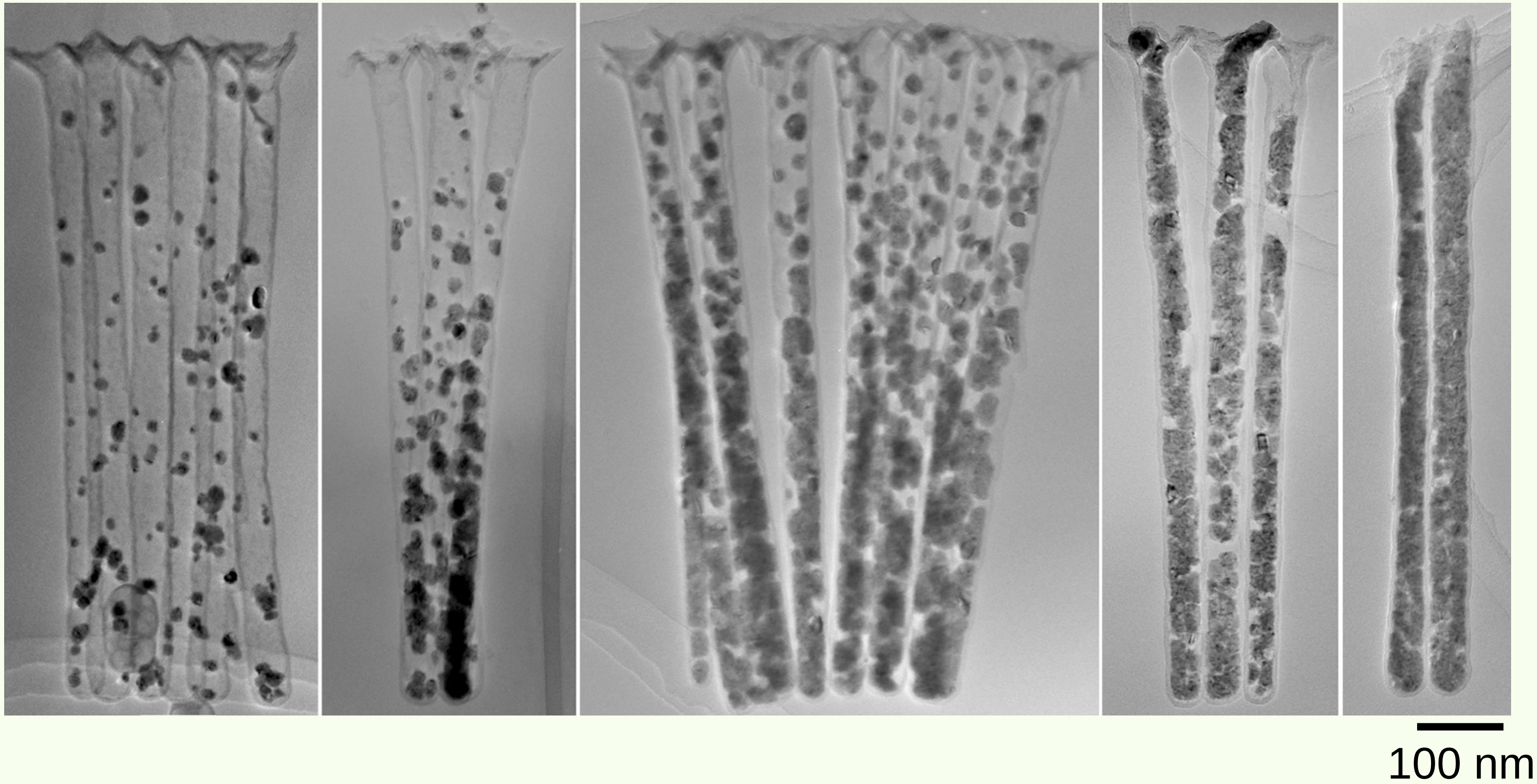
after the plating

during peeling the metal off

after the peeling


Al
O_2 plasma treatment
removal of external carbon deposited
Al
template removal
alkaline treatment
NiFe filled carbon nano test ube

Controlled filling of NiFe alloy into CNTTs



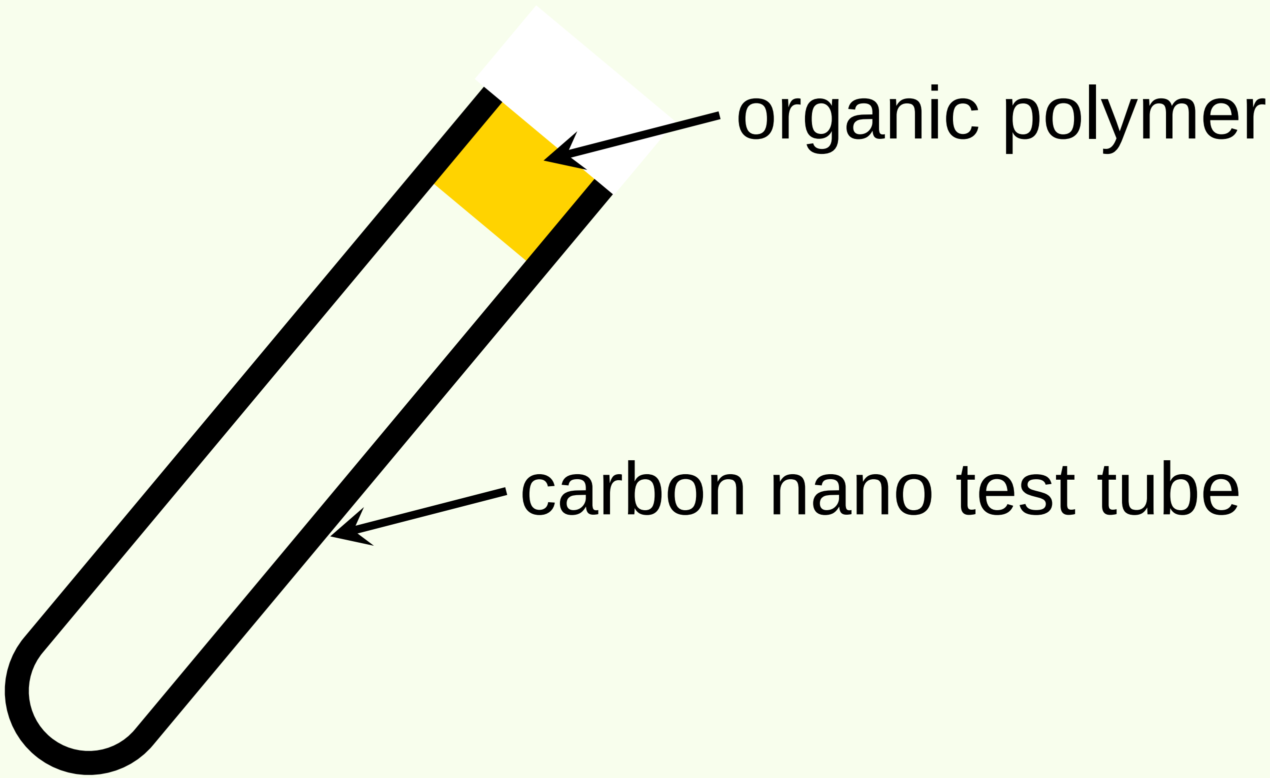
Just by changing the electroplating conditions, the filling of NiFe alloy into CNTs (dia. 40 nm) can be controlled!

What will happen when a magnet is placed just next to this vial?

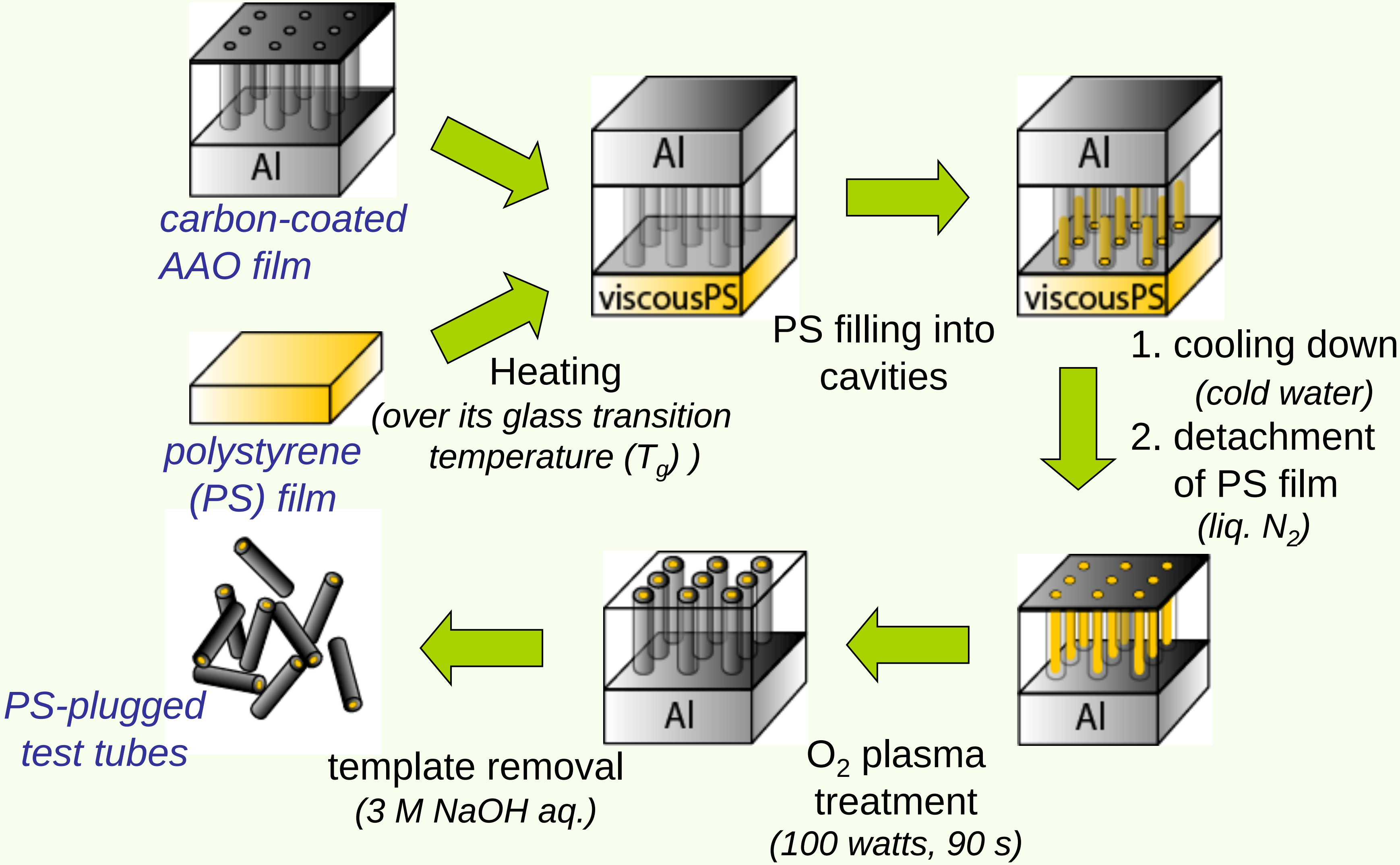
Even magnetic metal filled CNTTs can be dispersed in water!

1 sec = 10 min

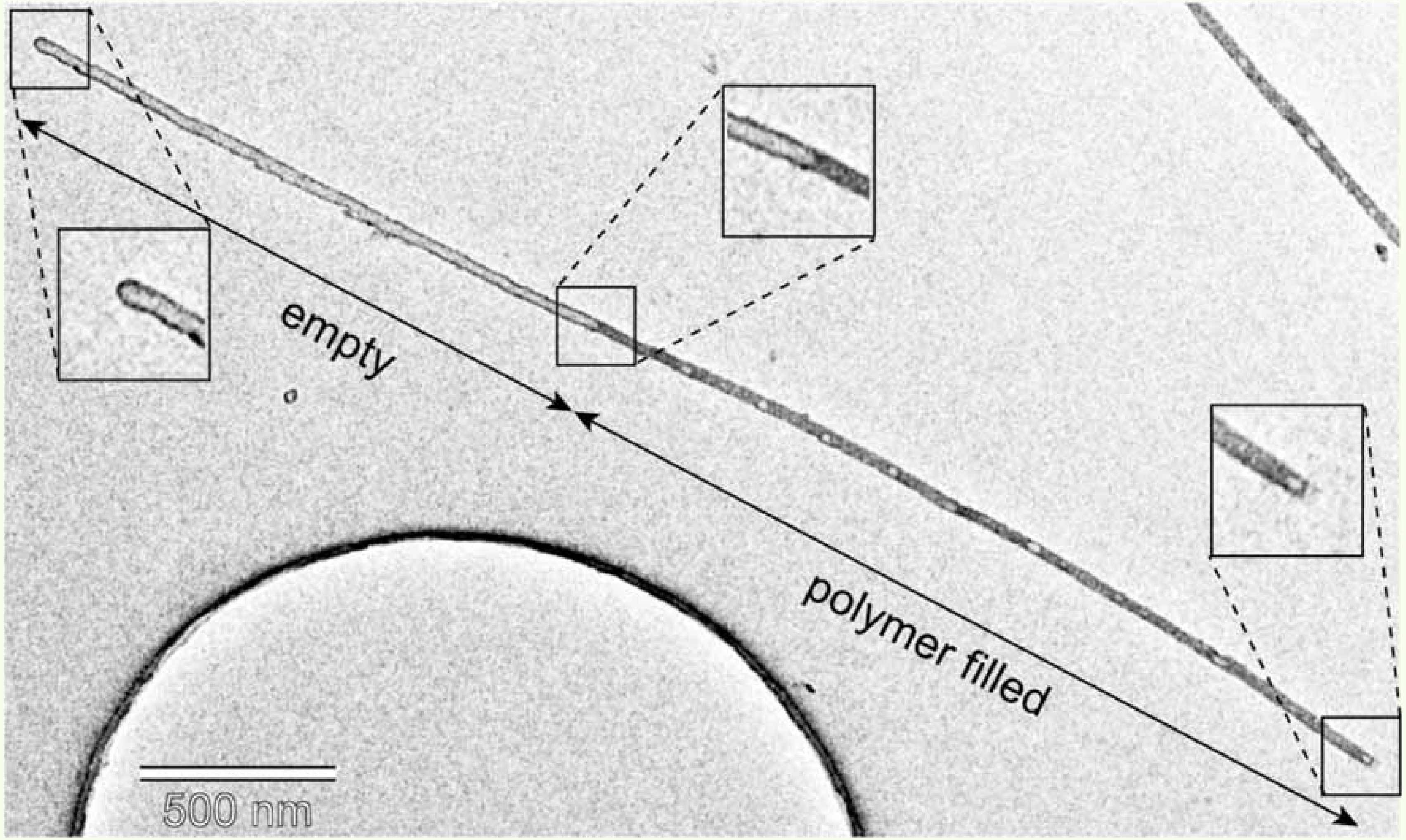
Introduction of organic polymer (polystyrene, PS) into the cavities of carbon nano test tubes to plug the polymer the open mouths of the tubes



Synthesis process of PS-plugged test tubes

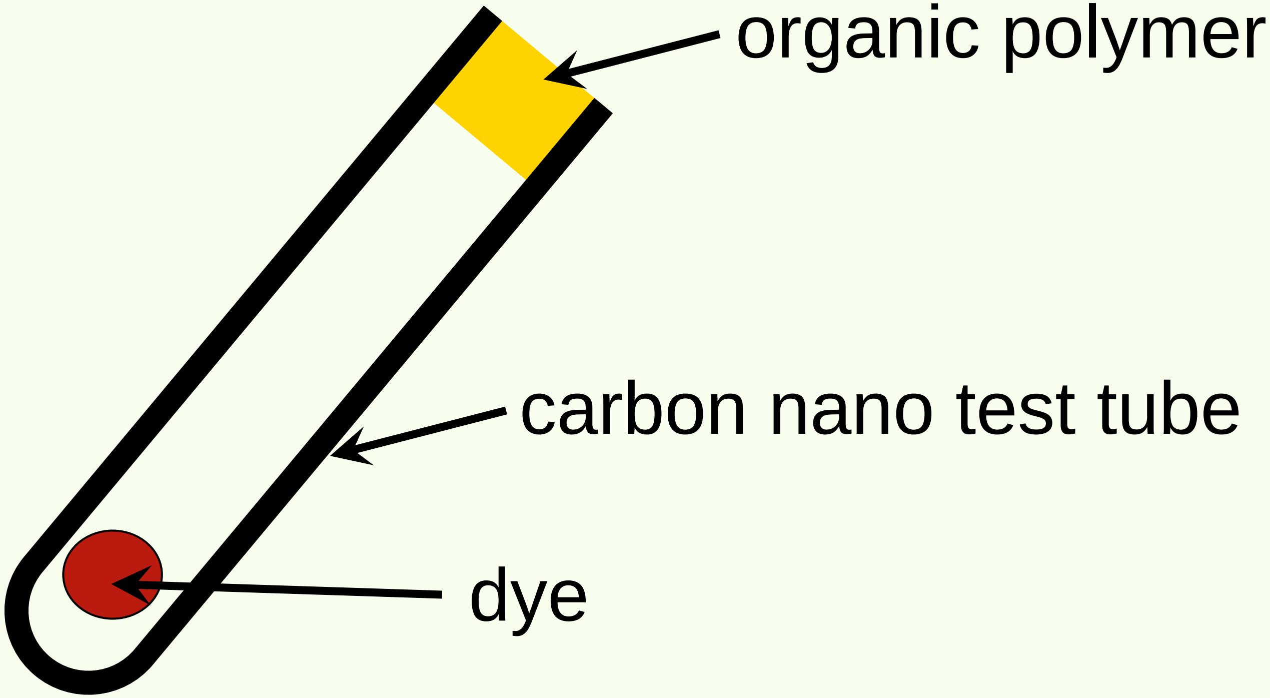


PS filling into the cavities of CNNTs

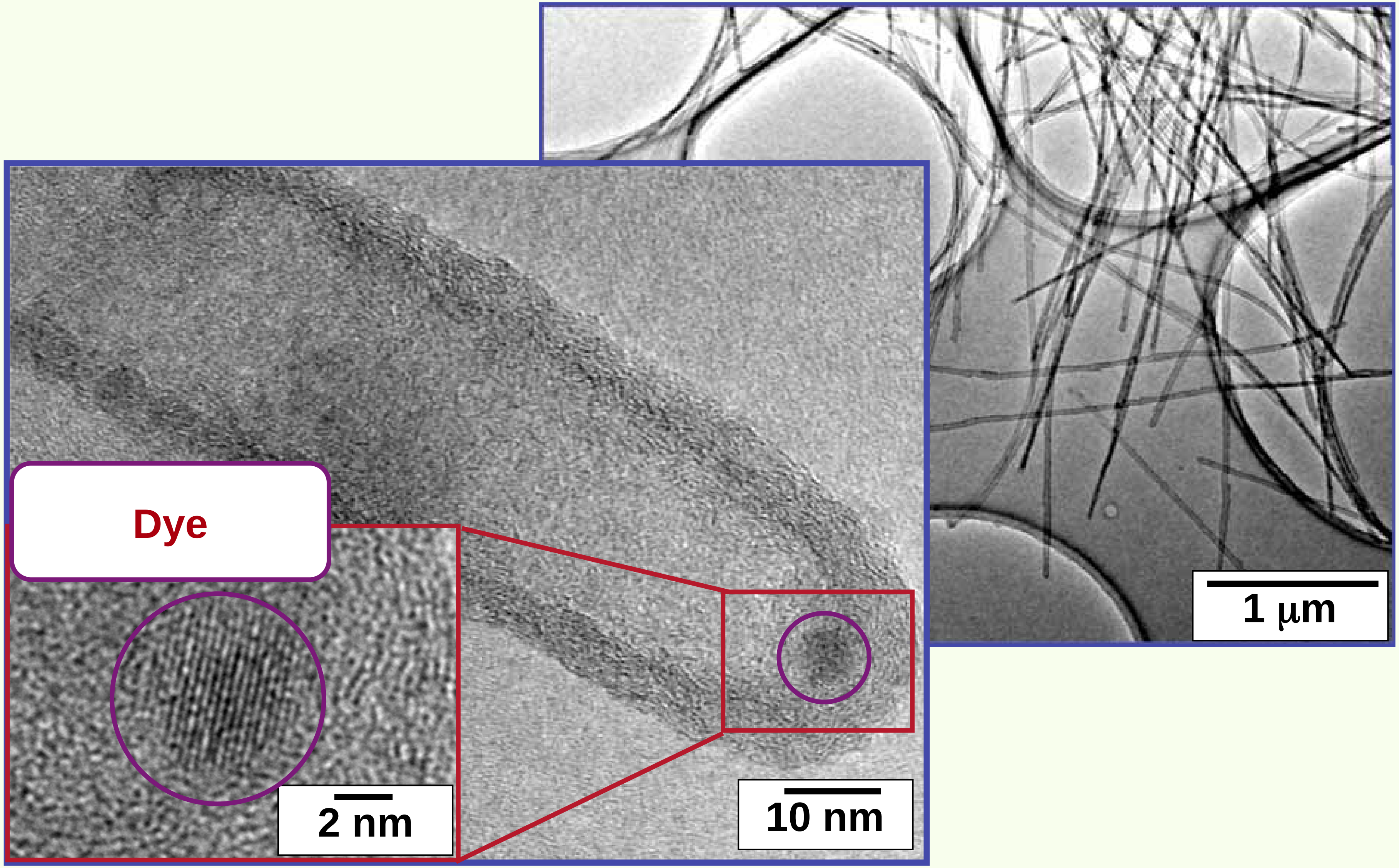


PS-plugged test tubes prepared at heating temperature of 200 ^{o}C and time of 1 min

Introduction of dye (eosin Y) into the cavities of carbon nano test tubes and then plug the open mouths with the polystyrene

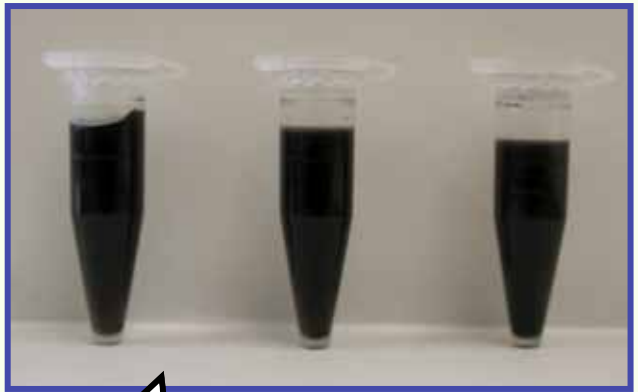


TEM images of dye-encapsulated CNTTs



Dye-encapsulated CNTTs in different solvents

Water *Ethanol* *Acetone*



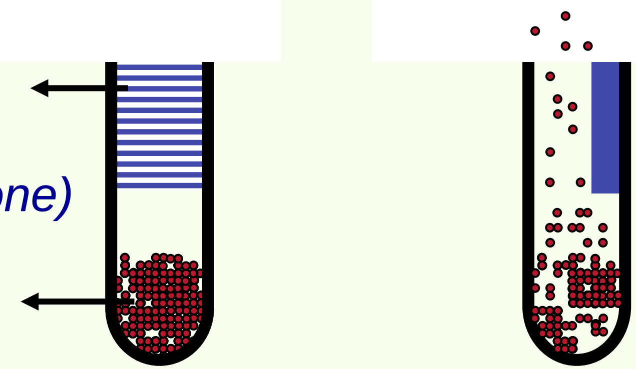
Centrifugation

Water *Ethanol* *Acetone*

Dispersion states were maintained for several weeks after the samples were prepared.

Polystyrene
(-doesn't dissolve in water and ethanol, but dissolve in acetone)

Dye
(soluble in water, ethanol, and acetone)



In water or ethanol

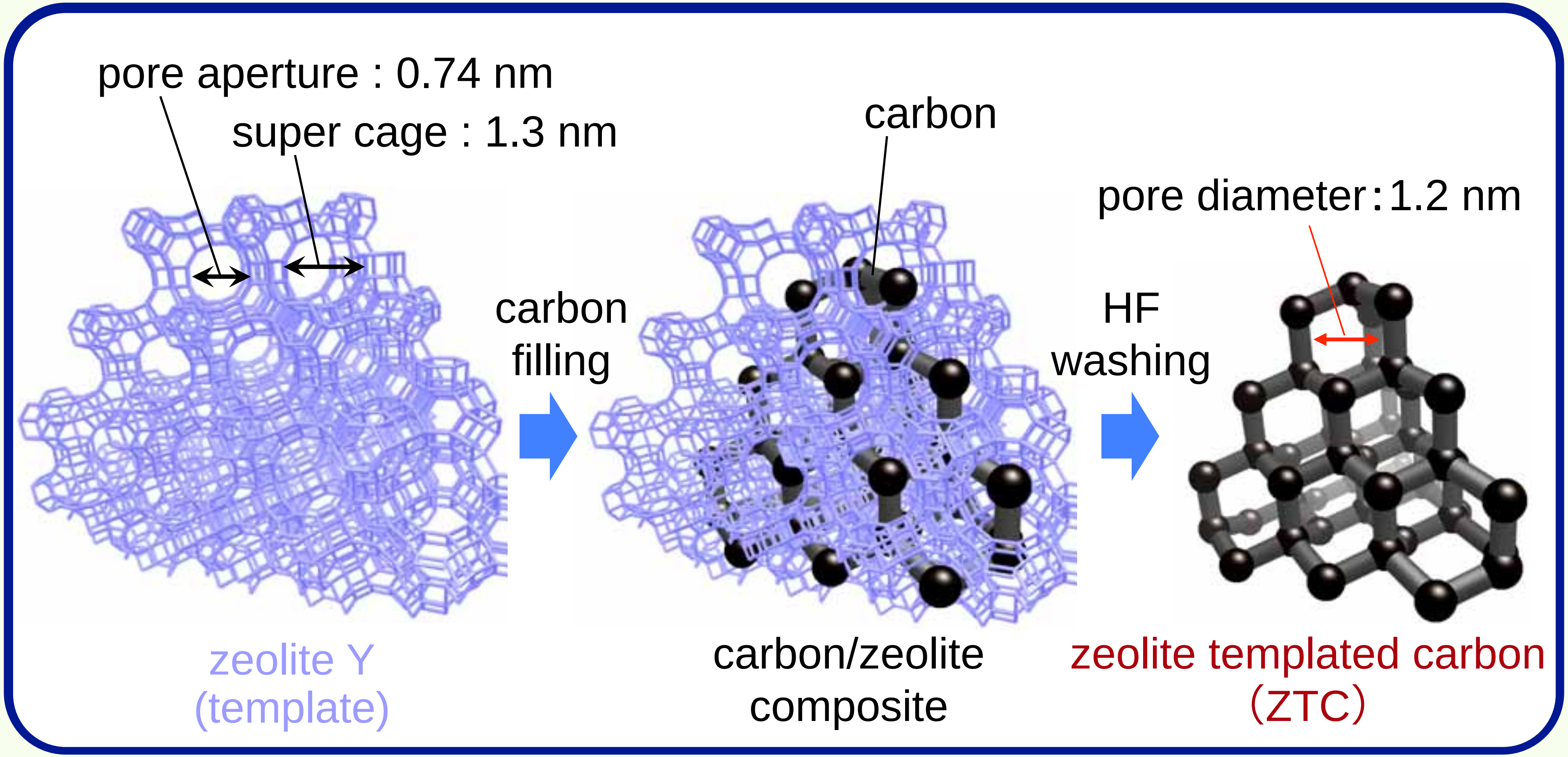
In acetone

Application fields of water dispersible CNTTs

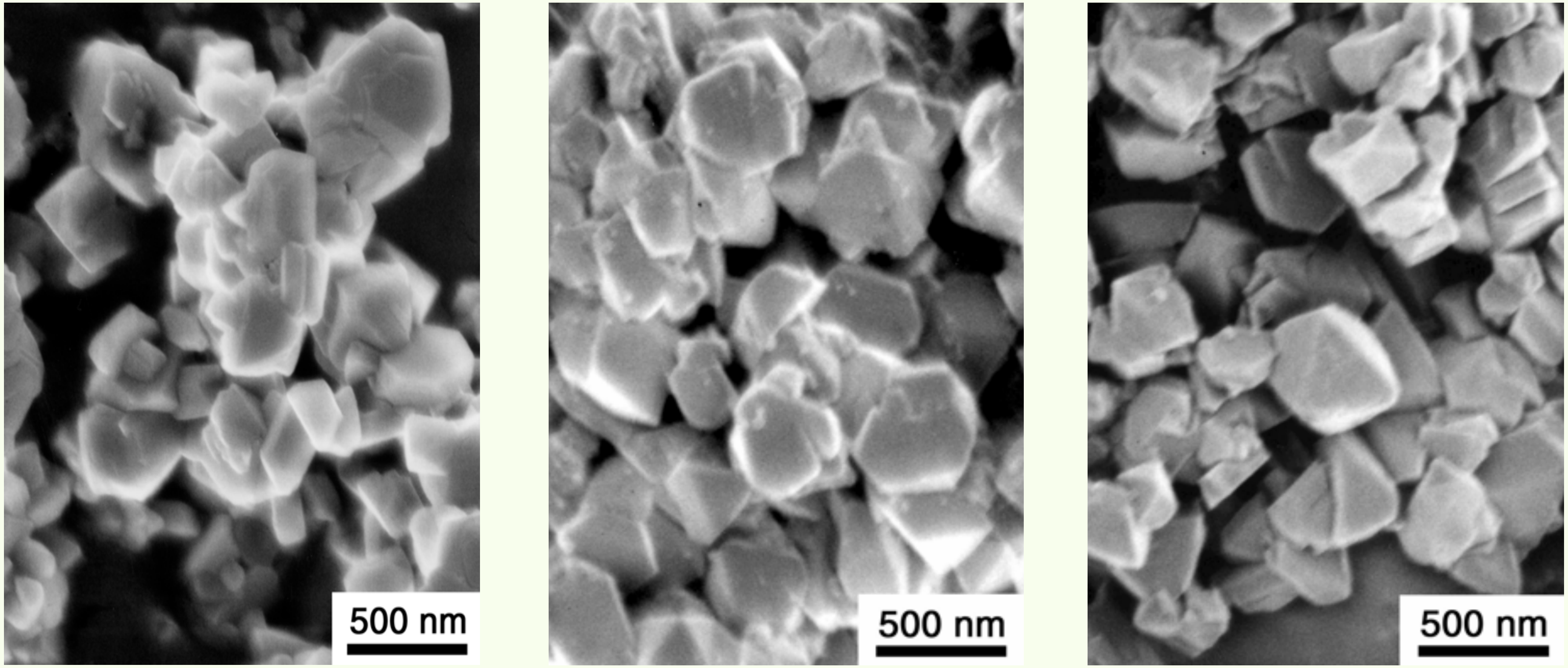
A capsule for D(G)DS (drug or gene delivery system), magnetic separation of biomolecules such as proteins and DNA!?

3. Ordered porous carbon with the regularity of zeolite

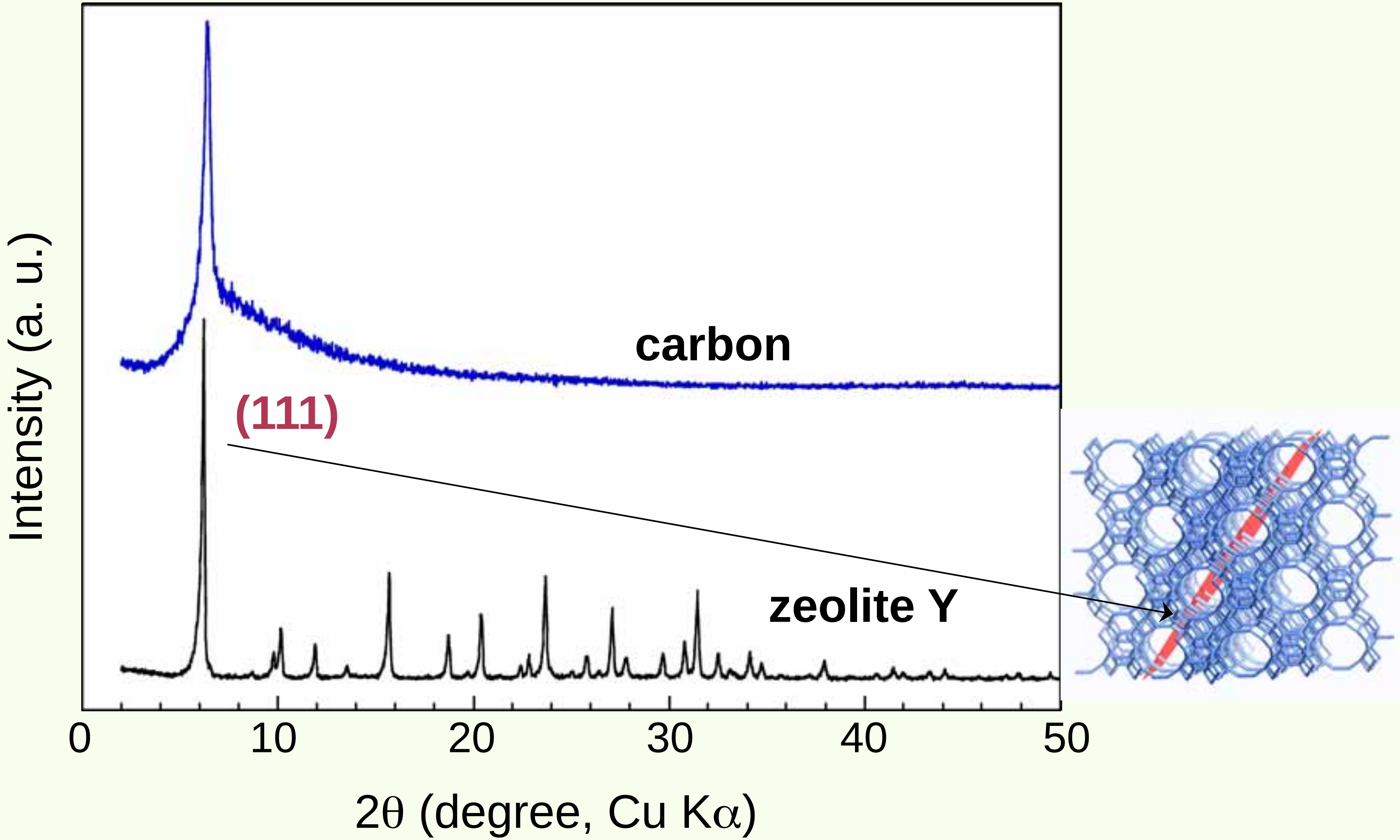
Synthesis of porous carbon from zeolite template



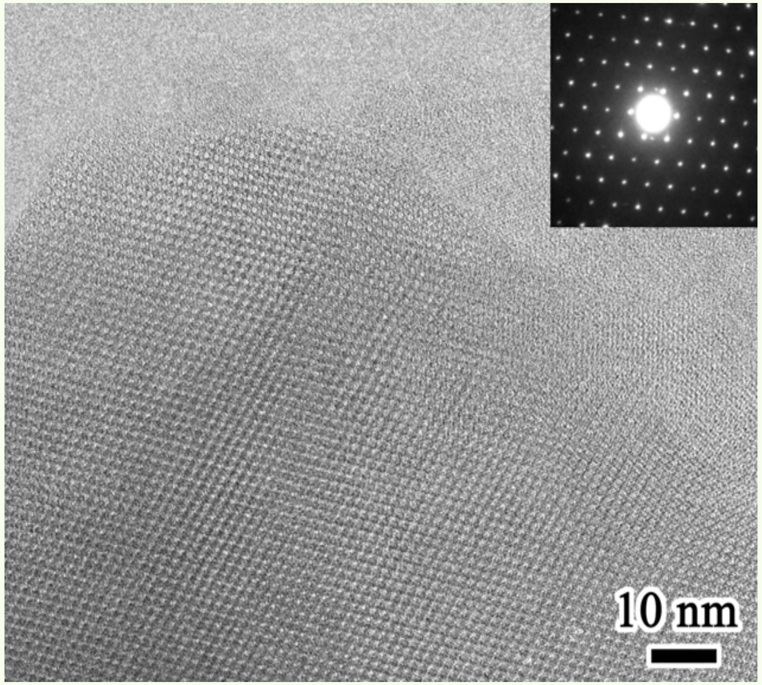
zeolite Y **composite** **carbon**

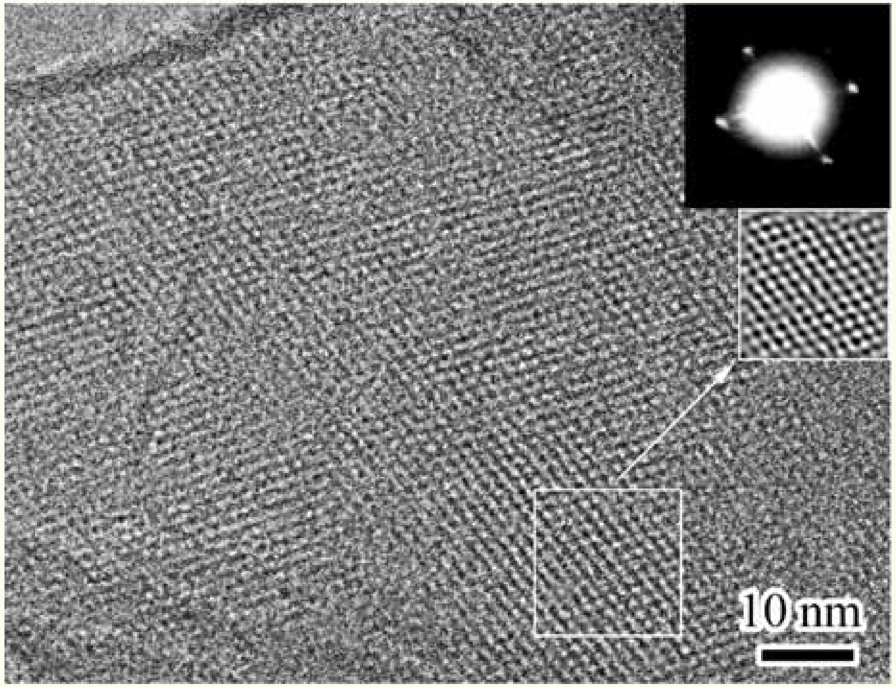


SEM images of zeolite Y, its carbon composite and carbon (ZTC; zeolite templated-carbon)



XRD patterns of zeolite Y and ZTC



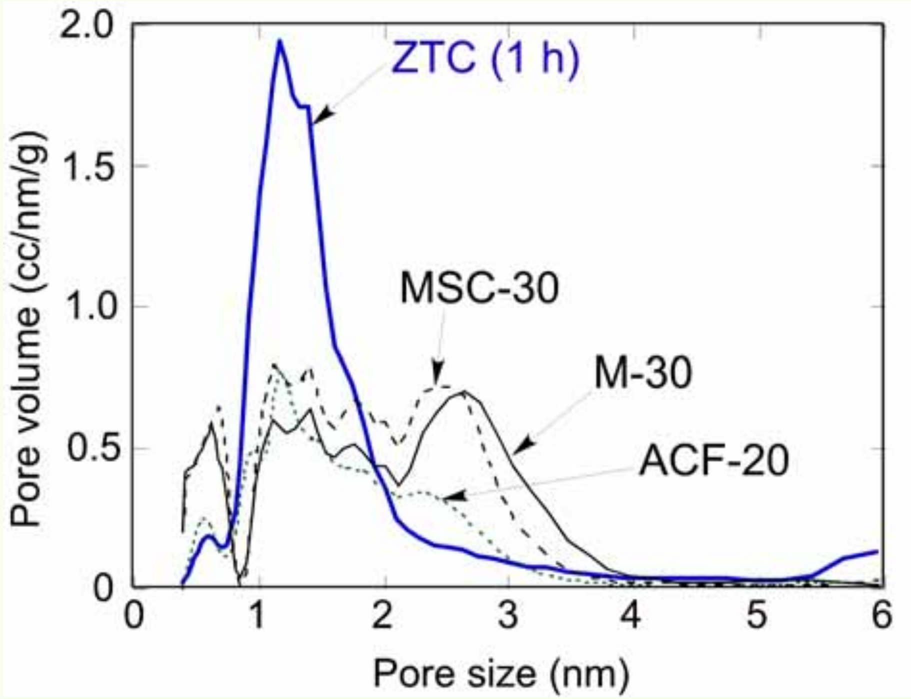


High resolution TEM images of zeolite Y and ZTC

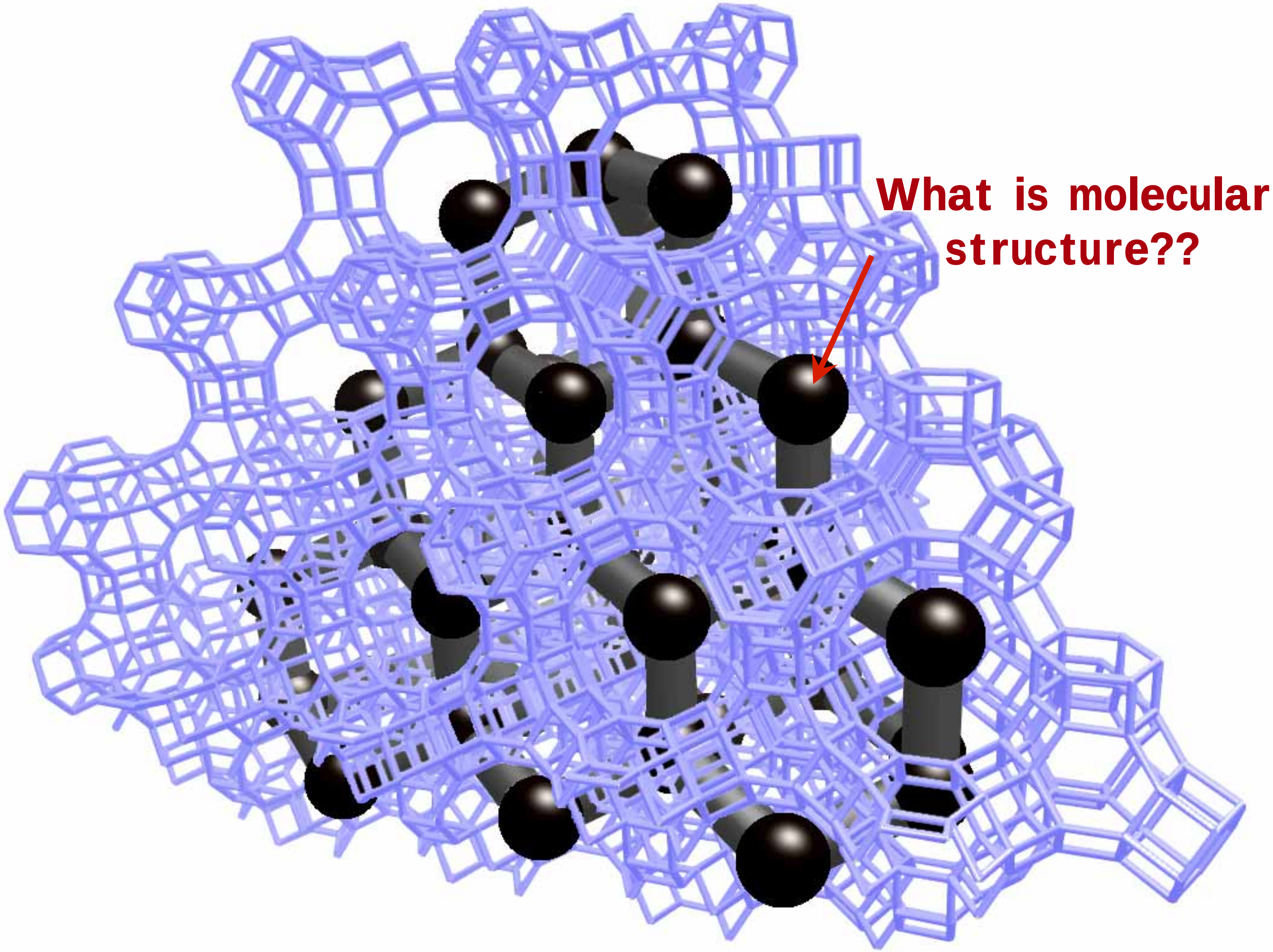
N_2 isotherm, surface area and pore volume for ZTC

Sample	BET-SSA (m^2/g)	Vmicro (cm^3/g)	Vmeso (cm^3/g)
ZTC	4080	1.8	0.2
MSC-30	2770	1.1	0.4
M-30	2410	1.0	0.8
ACF-20	1930	0.7	0.5

MSC-30 (Kansai Coke and Chemicals),
M-30 (Osaka Gas): KOH-activated carbon
ACF-20 (Osaka Gas):activated carbon fiber



Very high microporosity, large surface area (4000 m^2/g) , micropore volume (1.8 cc/g) and uniform micropores (size 1.2 - 1.3 nm)!



Carbon formed in zeolite nanochannels

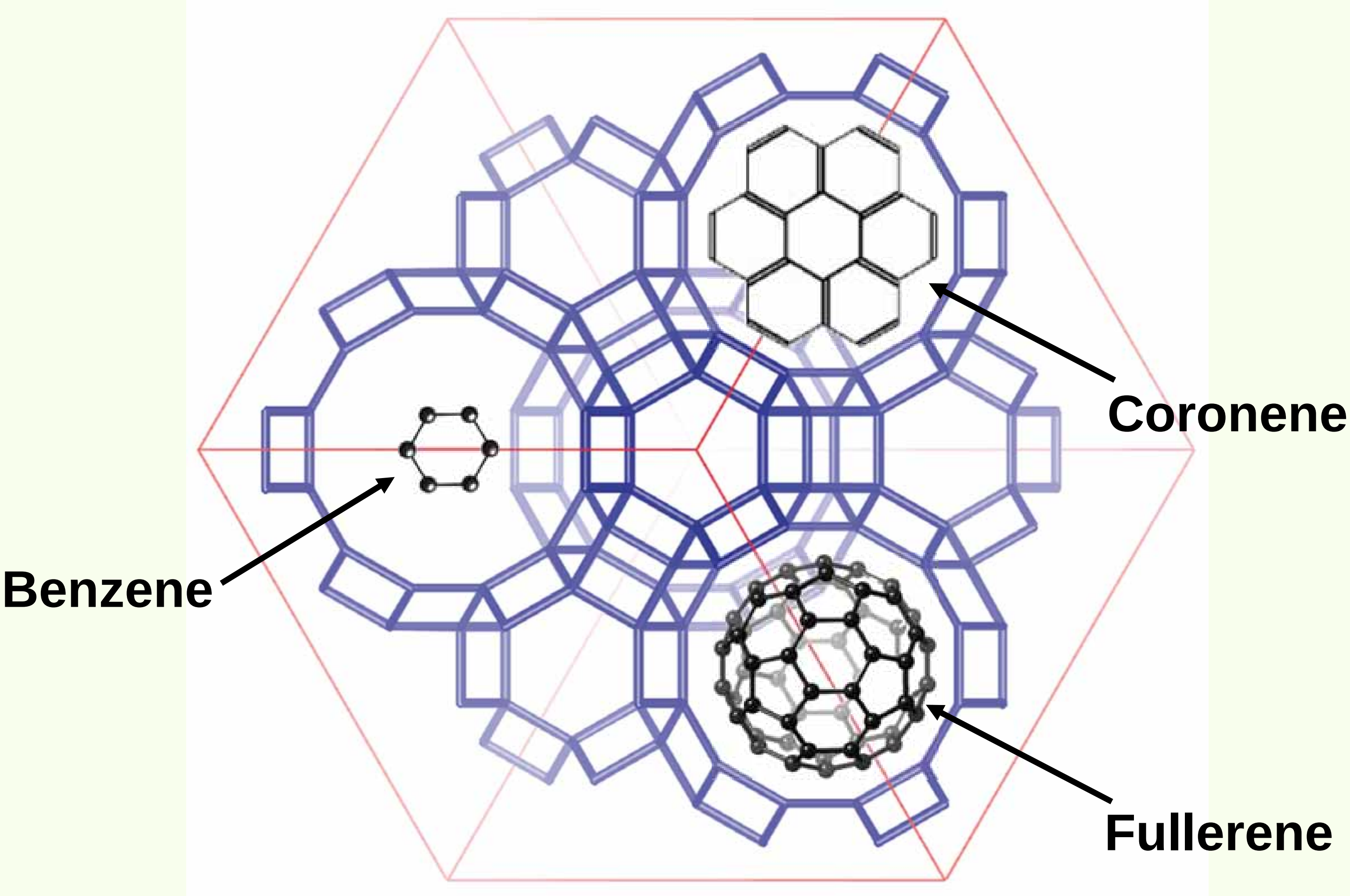


Illustration of the size of supercage compared with that of benzene, coronene and fullerene C_{60}

Average molecular model

XRD
ordered structure,
no (002) diffraction

TEM
ordered structure,
no stacking

^{13}C NMR, EELS
sp^2 carbon

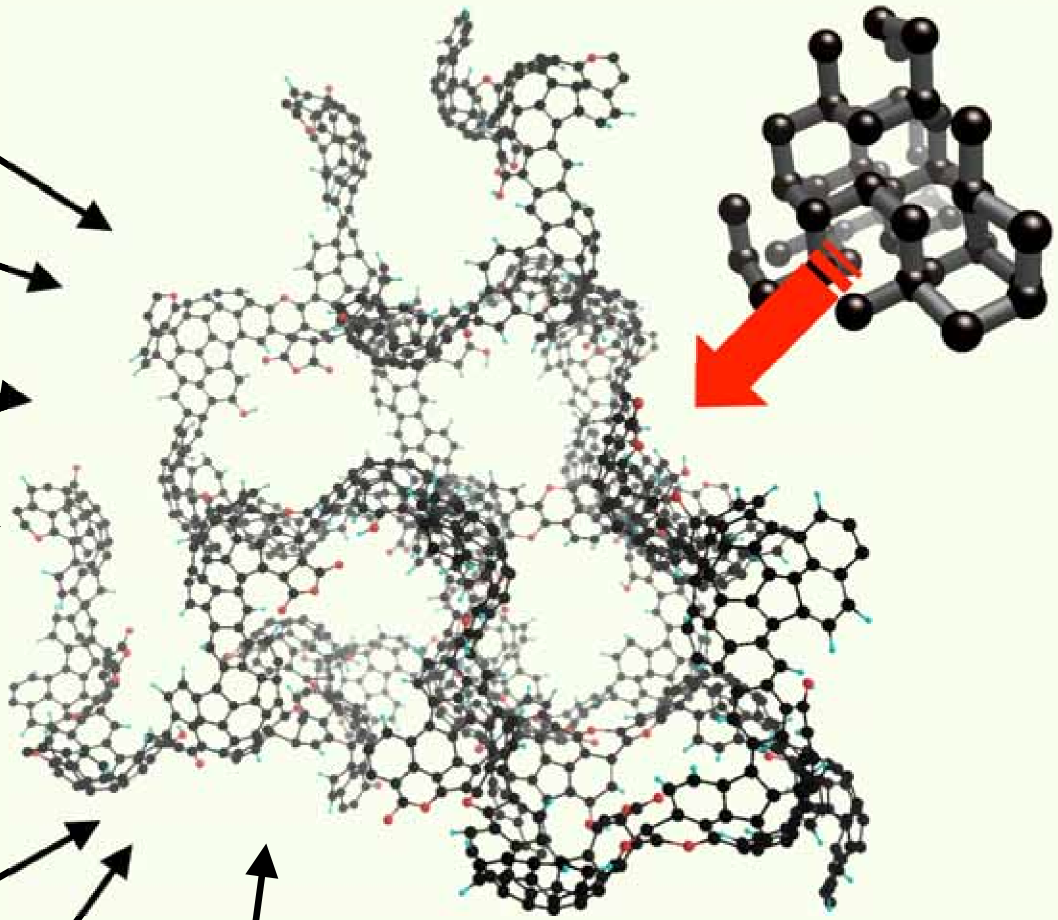
Raman
curved graphene

TG
carbon amount

elemental anaysis
CHO contents

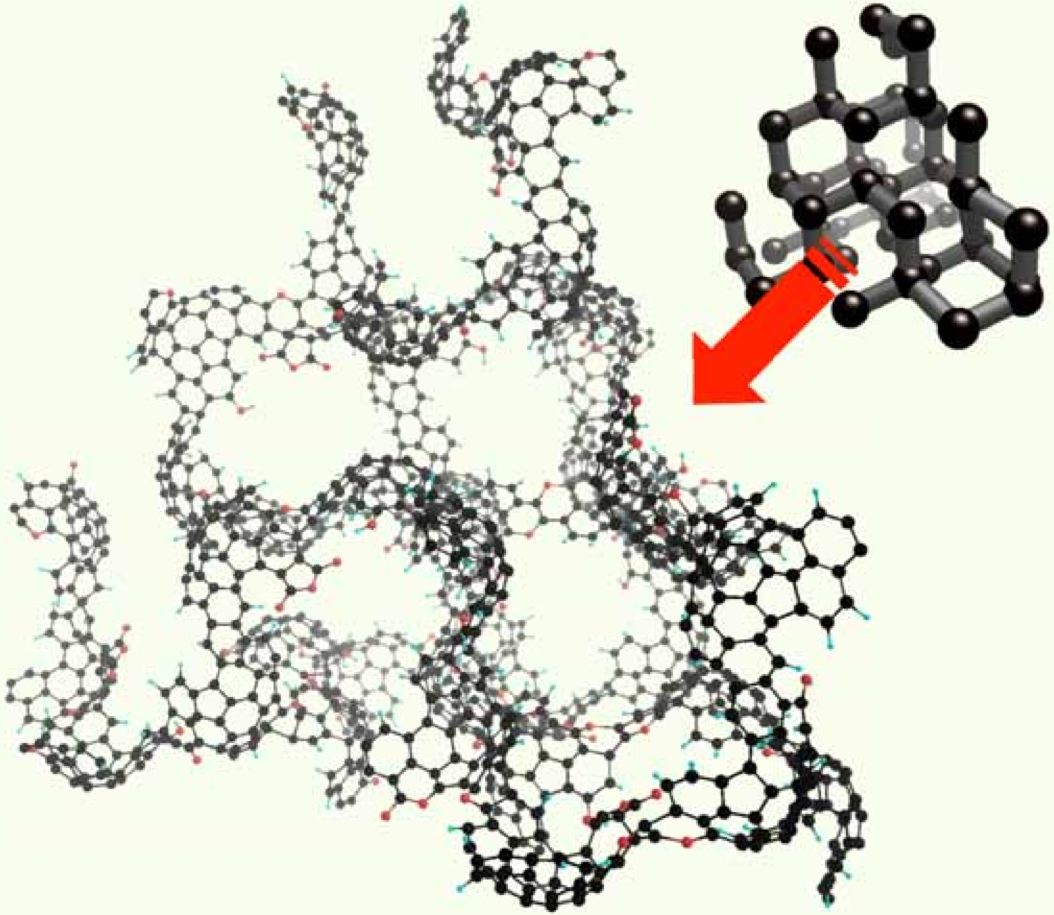
TPD/FT-IR
oxygen functional groups

MO theory
structure optimization



- Carbon atom
- Oxygen atom
- Hydrogen atom

Molecular structure determined from TEM, XRD,TG, Raman, FT-IR and MO theory

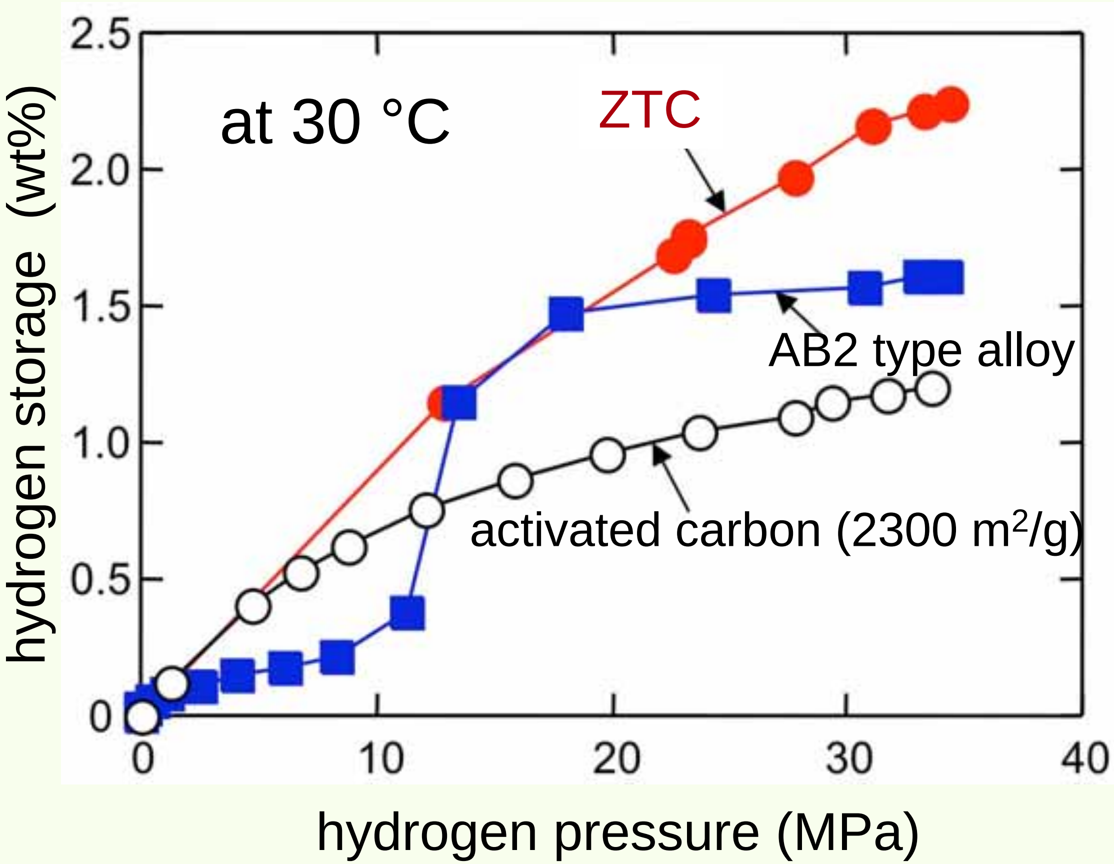


black：carbon atom
red：oxygen atom
blue：hydrogen atom

	expr.	model
carbon content (g/g-zeolite)	0.29 (TG)	**0.30**
frame curvature (nm)	0.5～1.2 (Raman)	**1.0**
pore diameter (nm)	1.0～1.5 (DFT)	**1.1**
surface area (m^2/g)	3730 (α_s)	**3490**
micro pore volume (cm^3/g)	1.8 (DR)	**1.8**

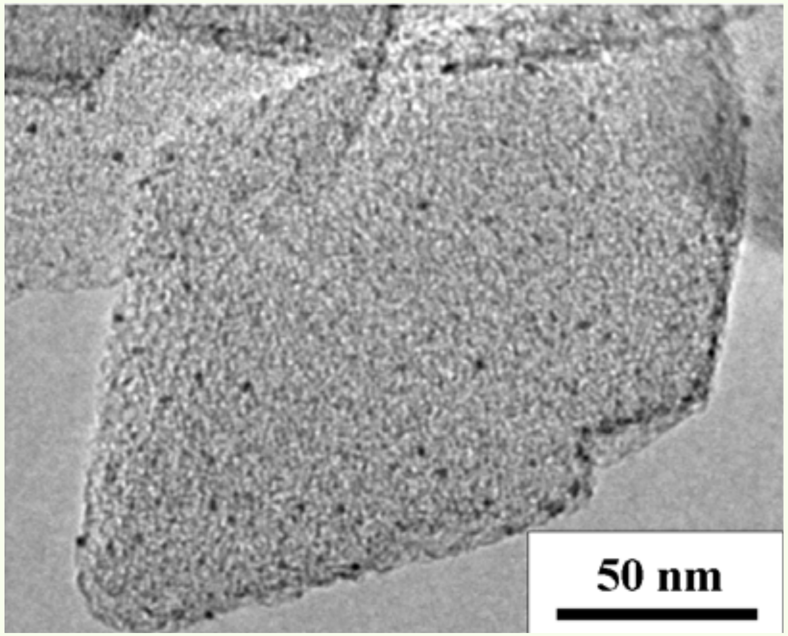
5. Applications of ZTC as energy storage media

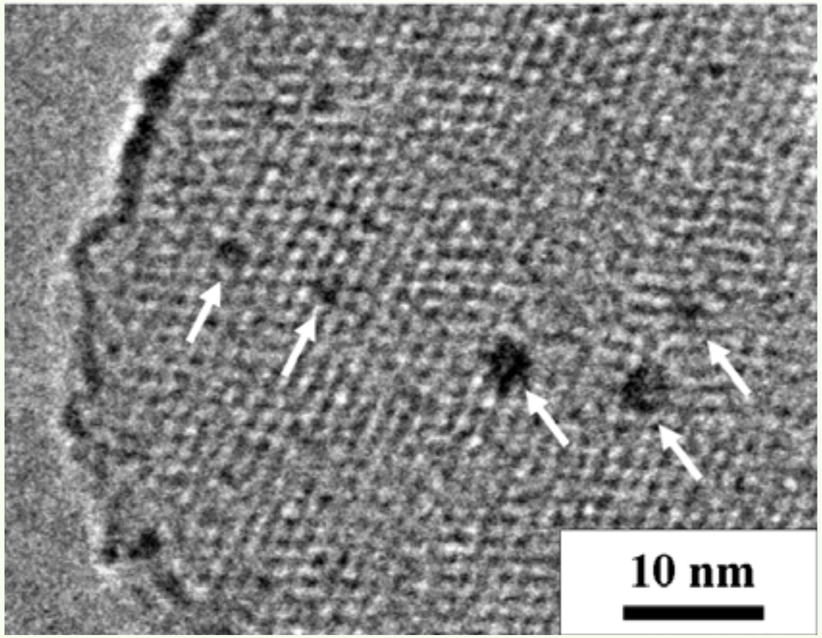
Hydrogen storage performance of ZTC



ZTC shows the largest hydrogen storage capacity as carbon materials!

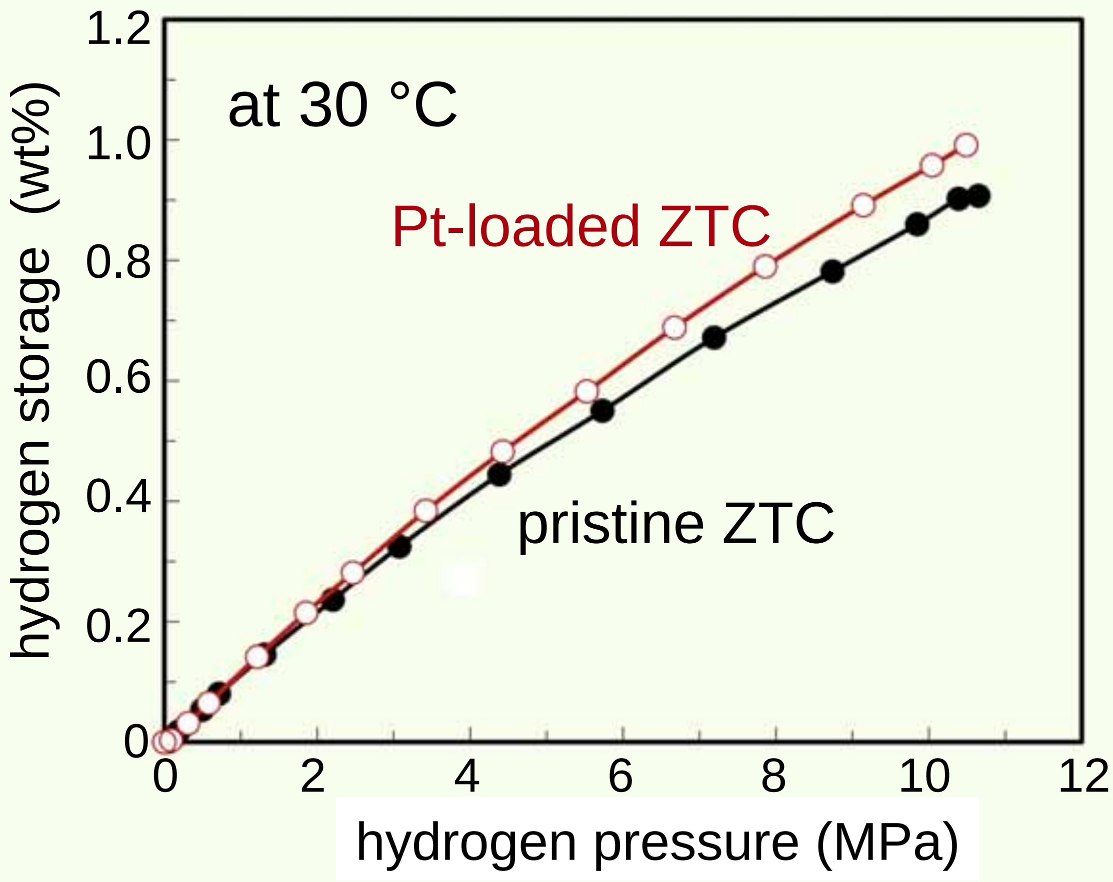
TEM images of the Pt/ZTC





- **Pt amount was 0.2 wt%.**
- **Pt nanoparticles 1~3 nm**

Effect of Pt on the hydrogen storage of ZTC



Enhancement effect was observed even at an amount of Pt loading as small as 0.2 wt%!

Conclusions

Formation of unique carbon nanoforms by template technique;

- Template synthesis of carbon nano tubes
- Water dispersible carbon nano test tubes (CNTTs)
- Inclusion of magnetic, organic materials and DNA into CNTTS
- Ordered porous carbon with the regularity of zeolite
- Control of micropore size by the mechanical compression of ZTC (zeolite templated carbon)
- Applications of ZTC as energy storage media