새로운 메조포러스 나노백금 / 탄소 복합체 합성, 특성 분석 및 응용

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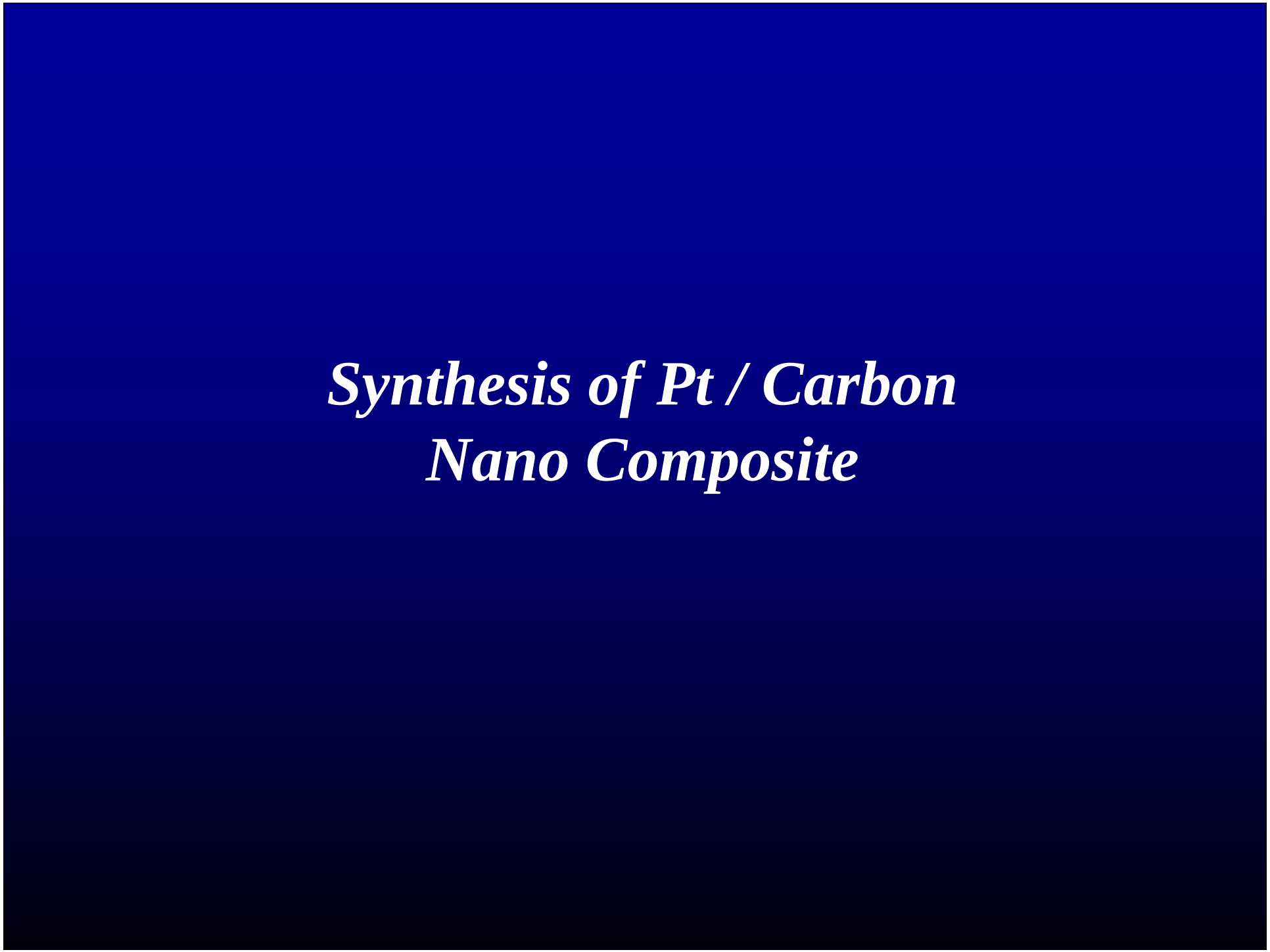

Synthesis of Pt / Carbon
Nano Composite

Synthesis of mesoporous silica template(SBA-15)

The cooperative assembly

between surfactant micelles and inorganic species

- Organic structure-directing agent
  Pluronic P123($PEO_{20}PPO_{70}PEO_{20}$)
- Silica source : TEOS(tetraethoxy silane)
  $Si(OCH_2CH_3)_4$

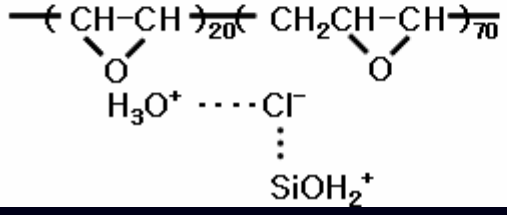
Surfactant solution

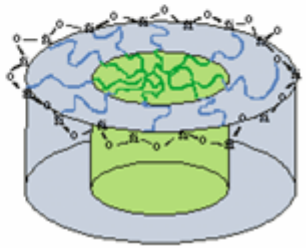
$$REO_m + yHCl \xrightarrow{H_2O} REO_{m-y}[(EO)\cdot H_3O^+]_y \cdots yCl^-$$

Adding TEOS

$$Si(OEt)_4 + nH_3O^+ \xrightarrow[Ph<2]{hydrolysis} Si(OEt)_{4-n}(OH_2^+)_n + nEtOH$$

$$REO_{m-y}[(EO)\cdot H_3O^+]_y \cdots yCl^- \cdot\cdot SiOH_2^+$$





Preparation of surfactant solution

Pluronic P123 in 1.6M HCl solution

↓

Adding TEOS at 35℃

↓

mixing at 35℃

↓

Reaction at 35℃ for 12h

Subsequently reaction at 100℃ for 24h

↓

Filtering & drying

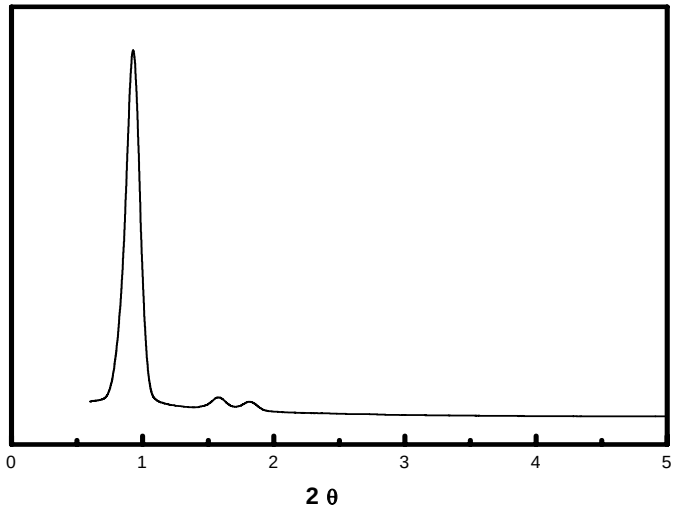
↓

Removal of surfactant

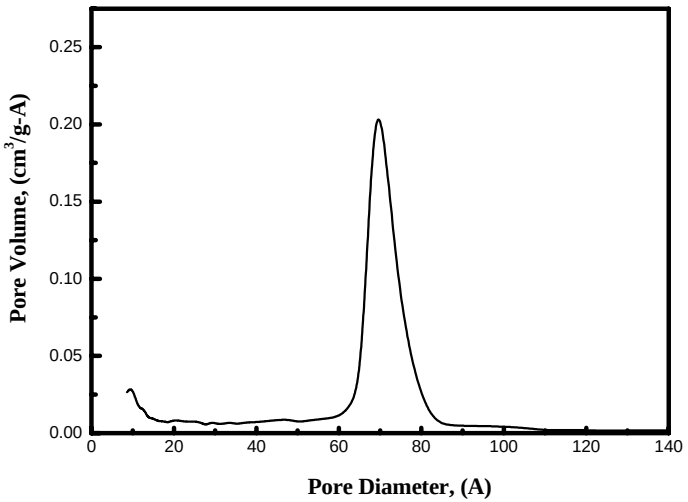
Solvent extraction with EtOH

Calcination at 400 ℃

Characterization of SBA-15

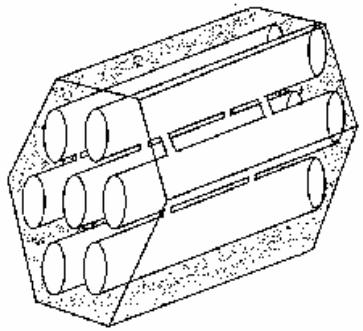


Small angle X-ray diffraction pattern

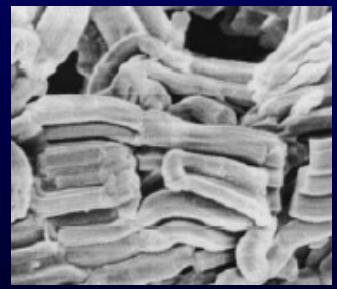


Pore size distribution

- XRD pattern
  characteristic of highly ordered periodic material
  2-D hexagonal mesophase(space group p6mm)
  indexed as (100), (110), and (200)
- Pore size distribution
  exhibit a uniform mesopore size of 7.3nm
  pore less than 3nm : interconnecting pore
- Brunauer-Emmett-Teller specific area
  : 947.32 m^2g^{-1}
- total pore volume : 1.23 cm^3g^{-1}
- rope-like domains
  : relatively uniform size of ~1μm



Mesoporous silica template
SBA-15



Science, Vol,279, Iss.23,
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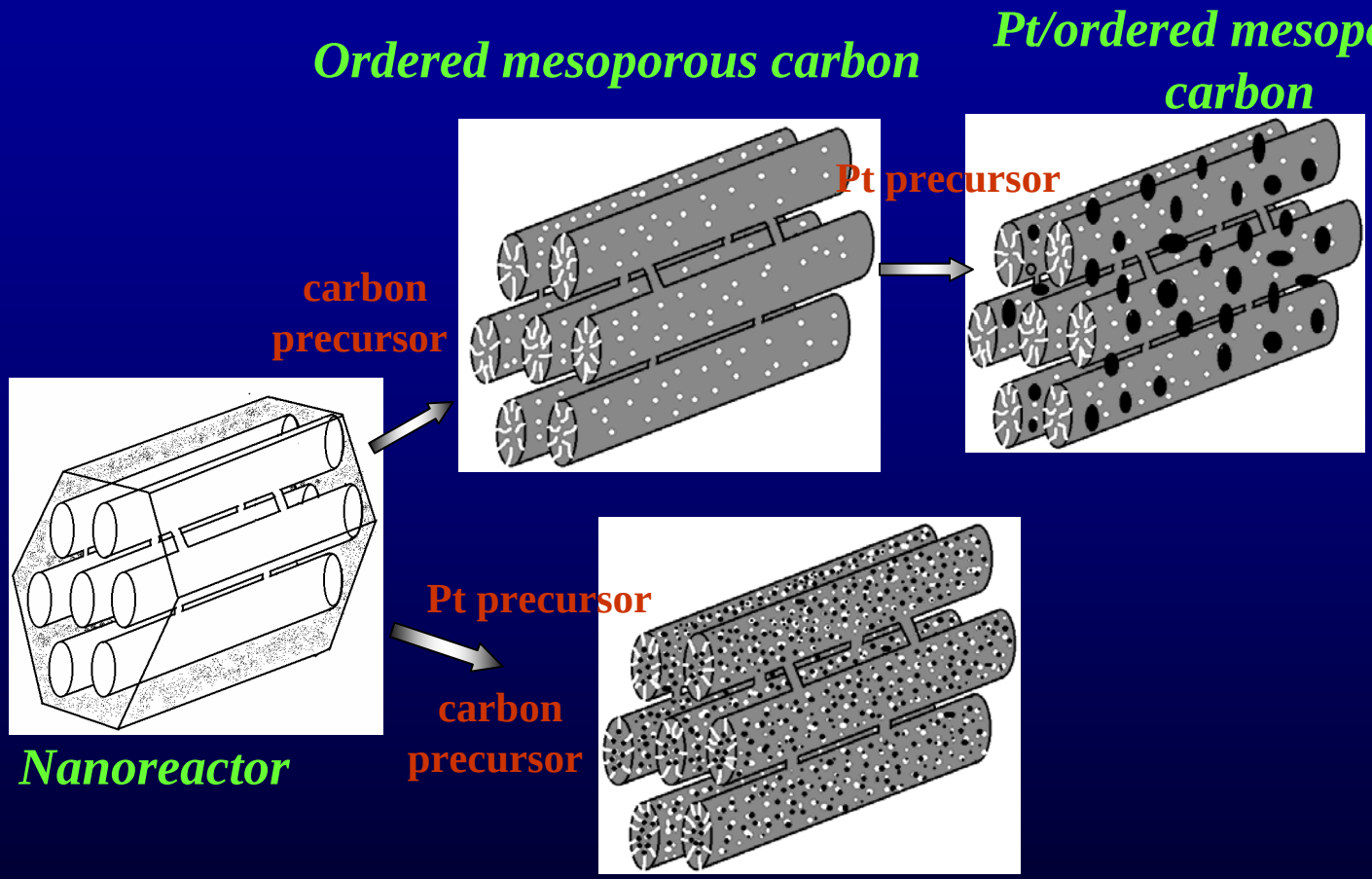
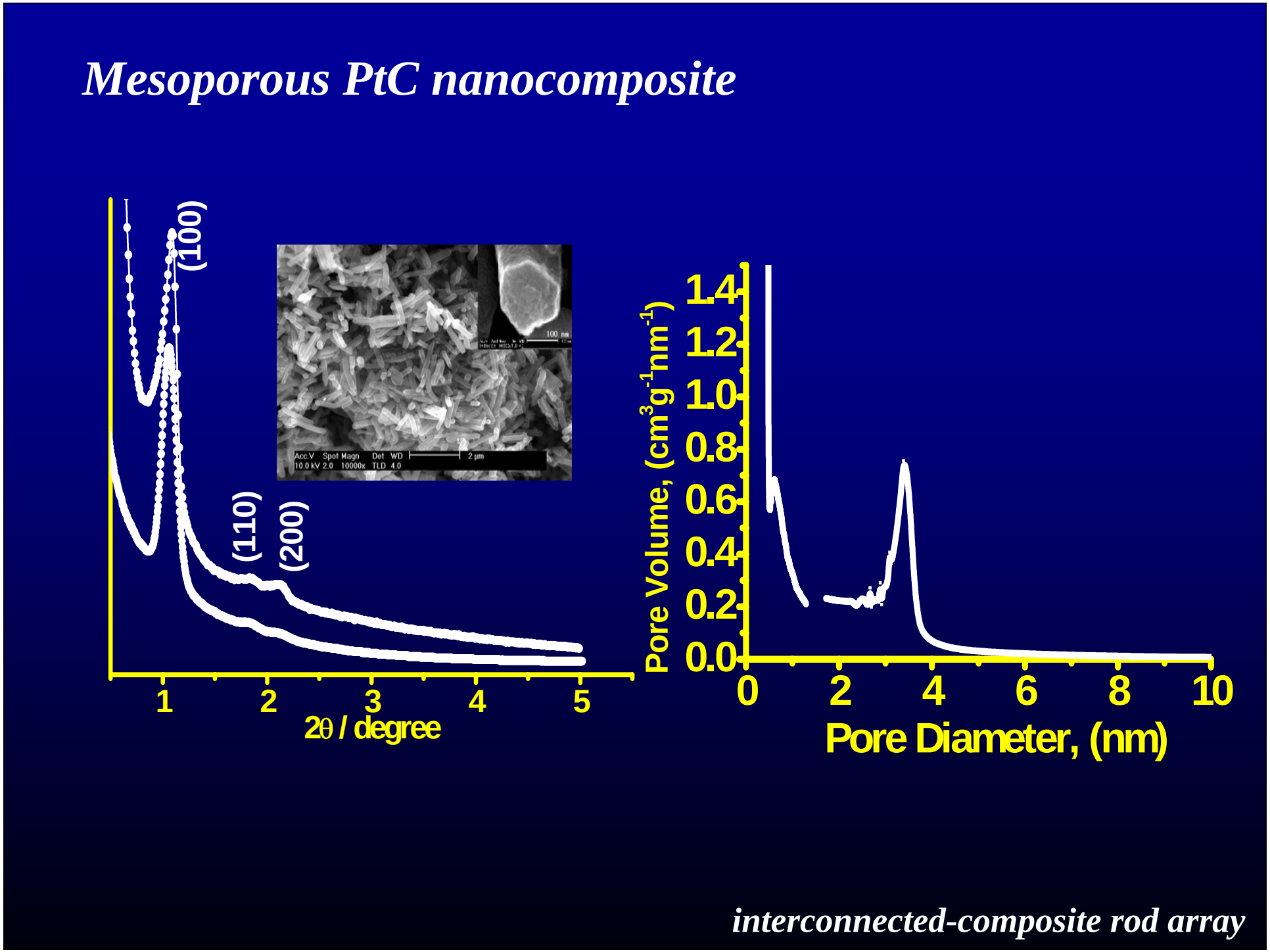
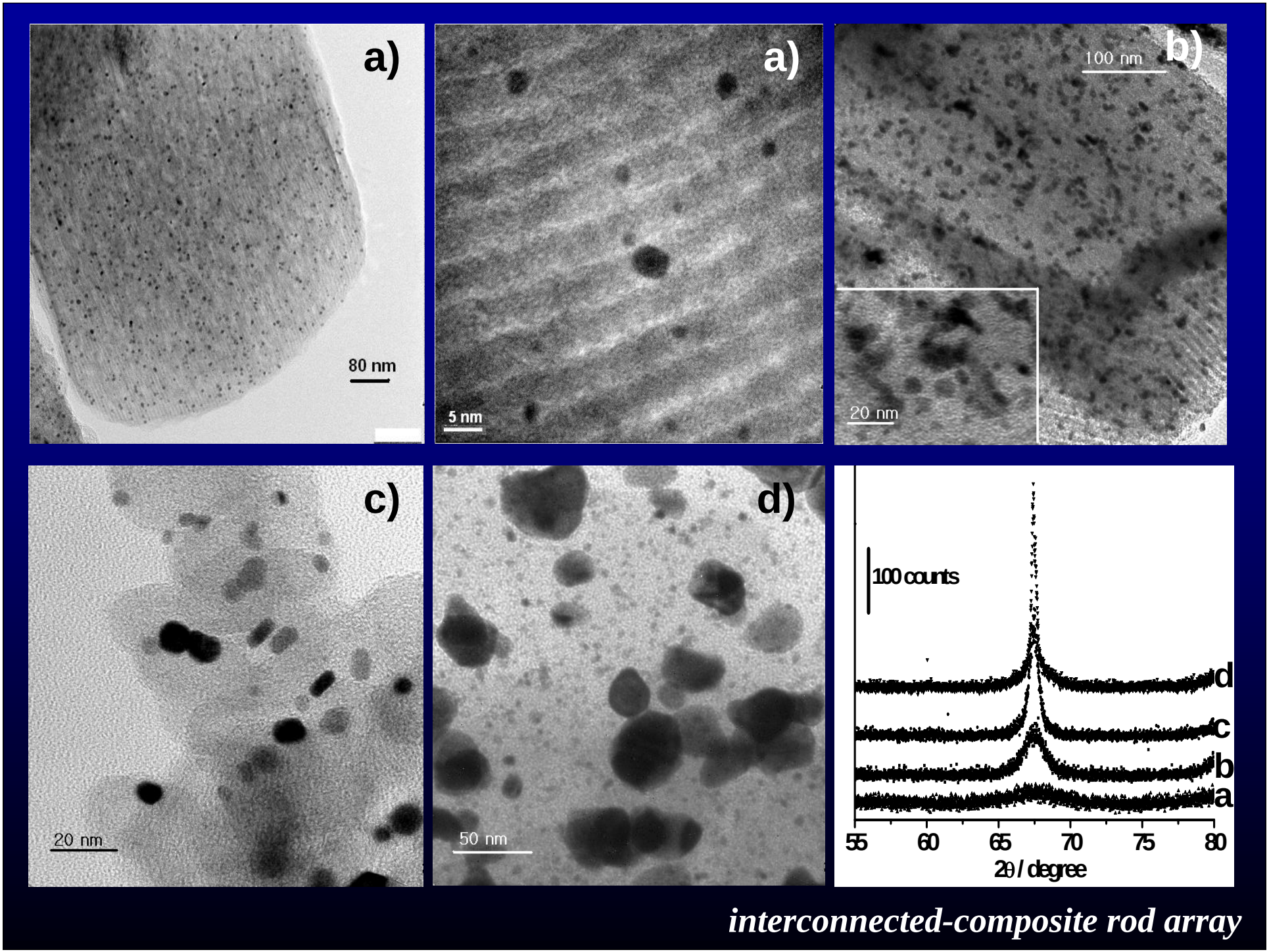
Synthetic route: interconnected-composite rod array



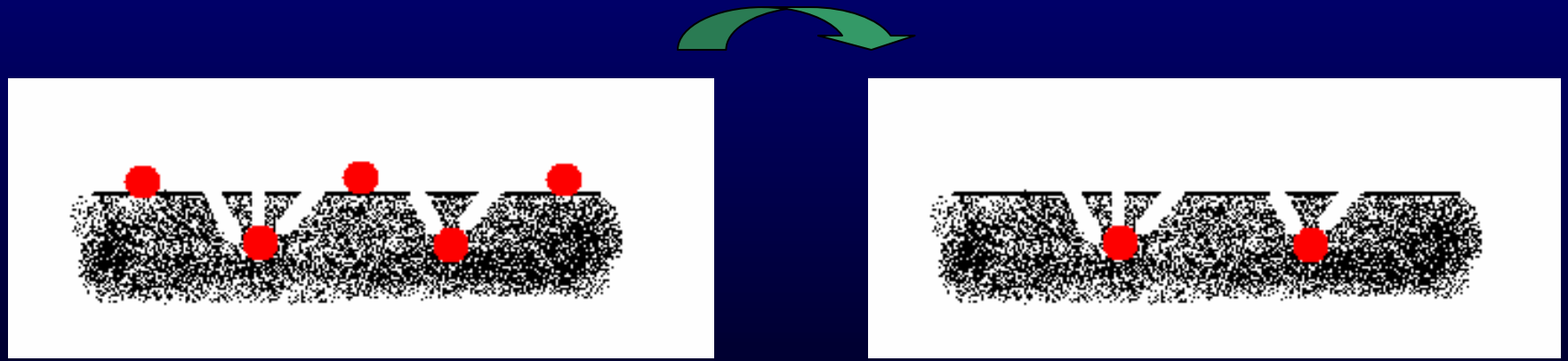
Characterization of Pt / Carbon Nano Composite


Mesoporous PtC nanocomposite
(100)
(110)
(200)
1
2
3
4
5
2θ / degree
Pore Volume, (cm3g-1nm-1)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
0
2
4
6
8
10
Pore Diameter, (nm)
interconnected-composite rod array

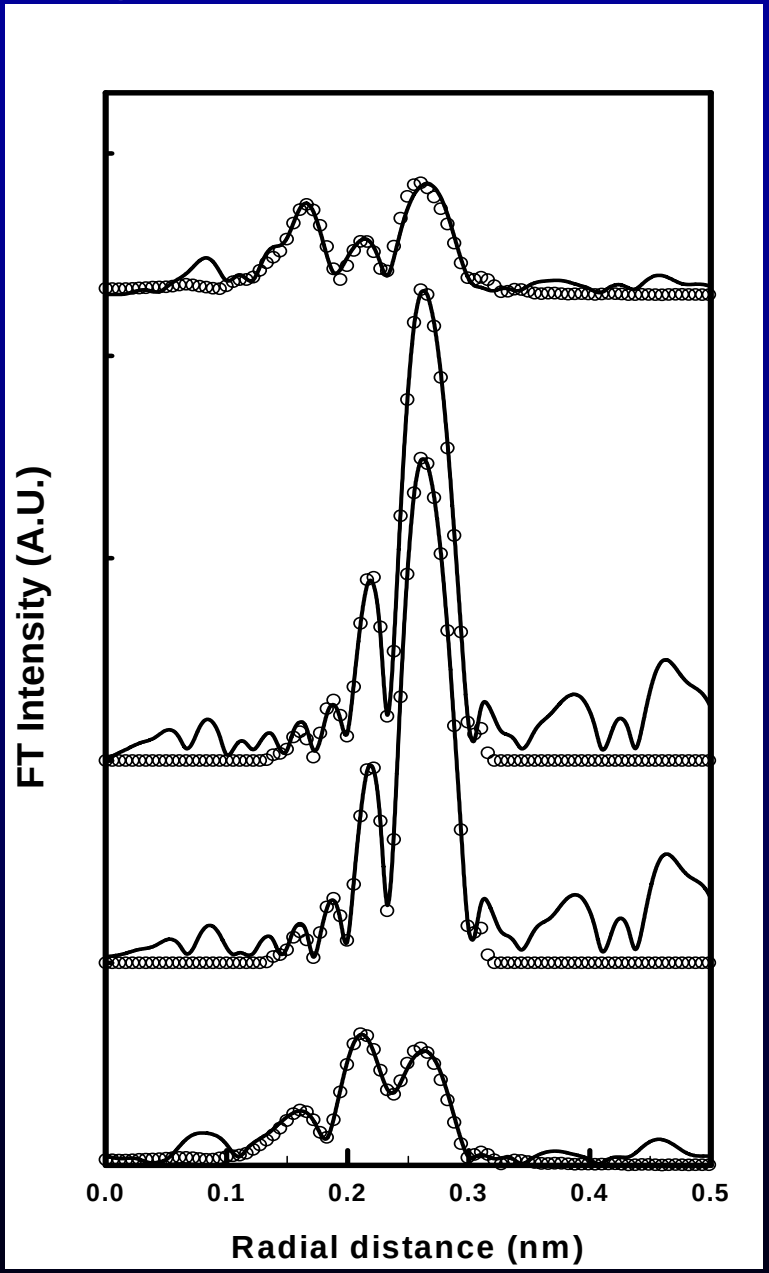

a)
80 nm
a)
5 nm
b)
100 nm
20 nm
c)
20 nm
d)
50 nm
100 counts
d
c
b
a
55
60
65
70
75
80
2θ / degree
interconnected-composite rod array

Accessible Pt nanoparticles in micropores

- ✓ Bromide solution
  : Br_2 + $(C_2H_5)_4N•Br$ + acetonitrile
- ✓ Kinetic diameter of $(C_2H_5)_4N•Br$, 0.8nm
- ✓ Dissolving Pt in mesopores or micropores (> 0.8nm)



EXAFS analysis



PtC nanocomposite
CN (Pt-Pt), 4.31
R (Pt-C), 0.204 nm

Pt/CMK-3
CN (Pt-Pt), 9.58

Pt/Vulcan
CN (Pt-Pt), 9.71

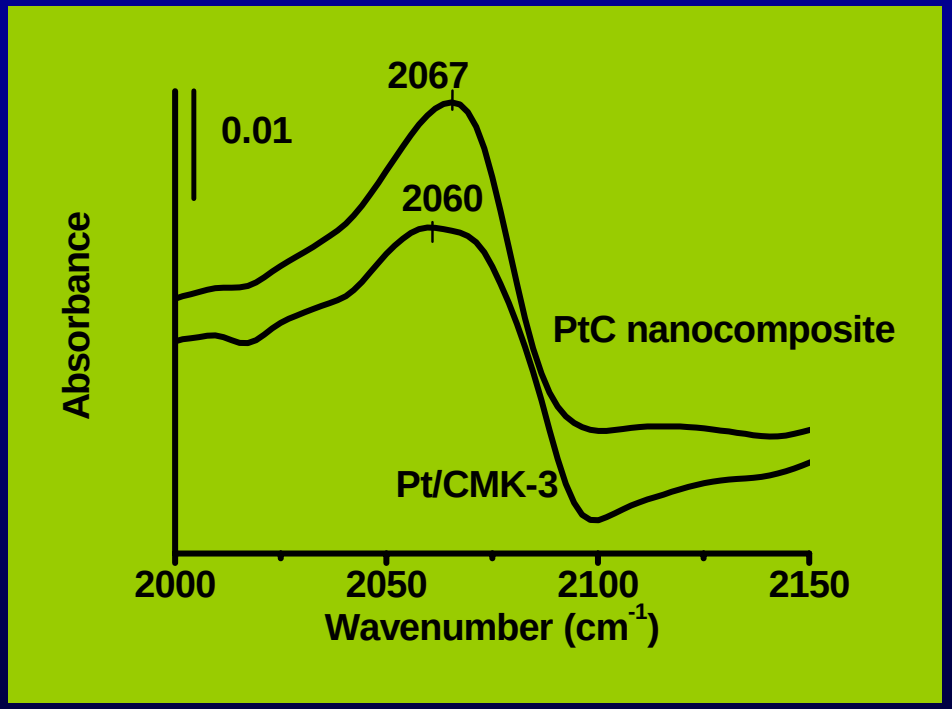
PtC nanocomposite (Br treatment)
CN (Pt-Pt), 2.78
R (Pt-C), 0.201 nm

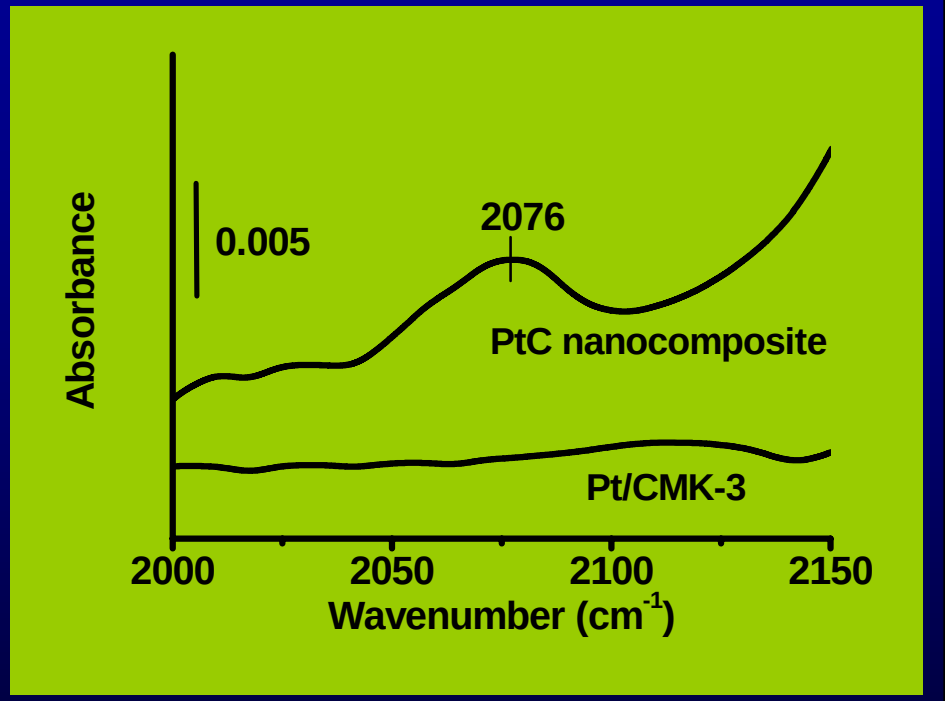
interconnected-composite rod array

Structural parameters from EXAFS

Samples (Pt content, wt%)	Mass activity (A/g Pt) 0.96 V	0.76 V	Structural parameters* Pair	CN	R (Å)	σ^2 (nm)	χ^2 (%)
PtCN arrays (24)	5.9	56.5	Pt-C Pt-Pt	2.73±0.03 4.31±0.05	2.041±0.0008 2.735±0.0006	48.9±1.6 73.5±0.9	13.8
Pt/CMK-3 (24)	4.8	23.8	Pt-Pt	9.58±0.11	2.757±0.0004	50.1±0.1	4.2
Pt/Vulcan XC-72 (24)	4.8	22.6	Pt-Pt	9.71±0.03	2.757±0.0002	48.0±0.1	3.1
PtCN arrays treated with bromide solution (8.5)	13.8	80.9	Pt-C Pt-Br Pt-Pt	2.12±0.03 0.99±0.03 2.78±0.005	2.014±0.0010 2.437±0.0005 2.736±0.0005	69.3±2.1 38.4±1.7 55.5±1.2	7.9

FTIR analysis (CO adsorption)

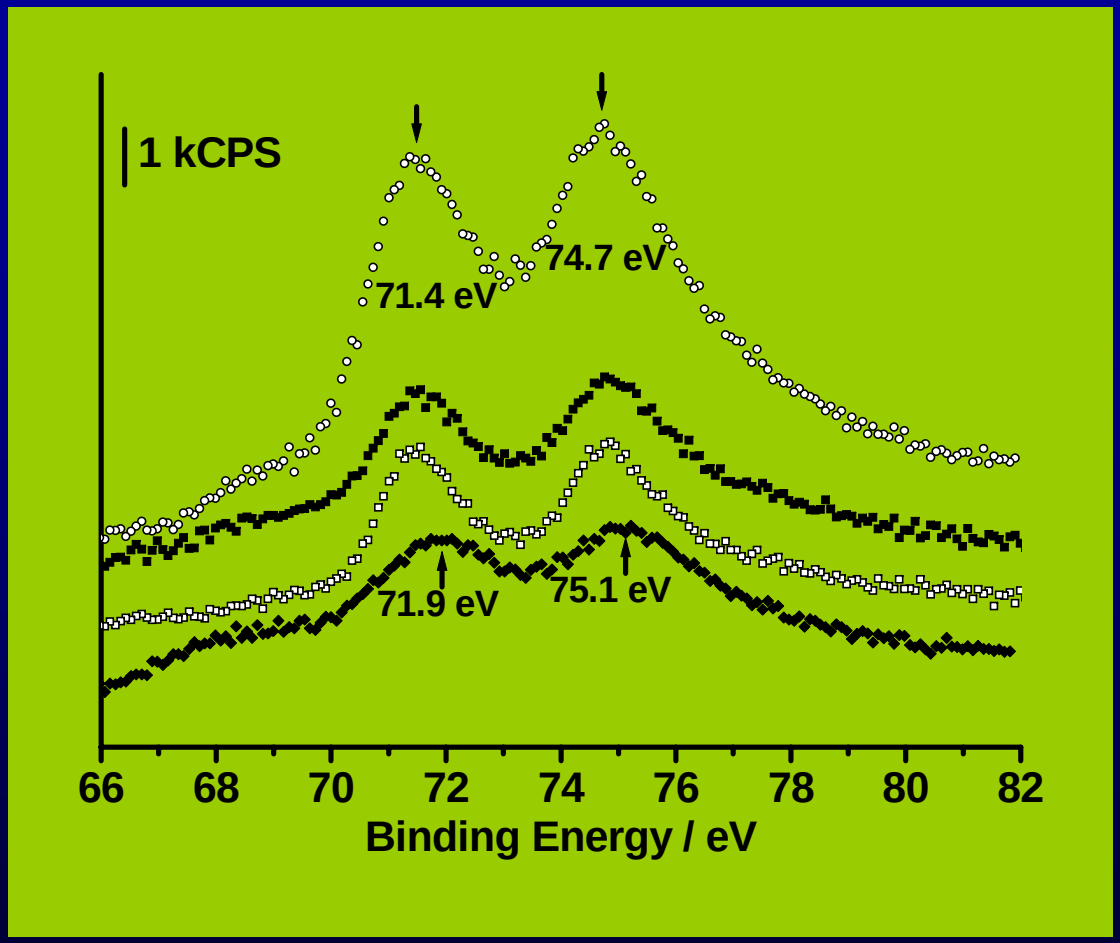




Before Br-treatment

After Br-treatment

XPS analysis



PtC nanocomposite

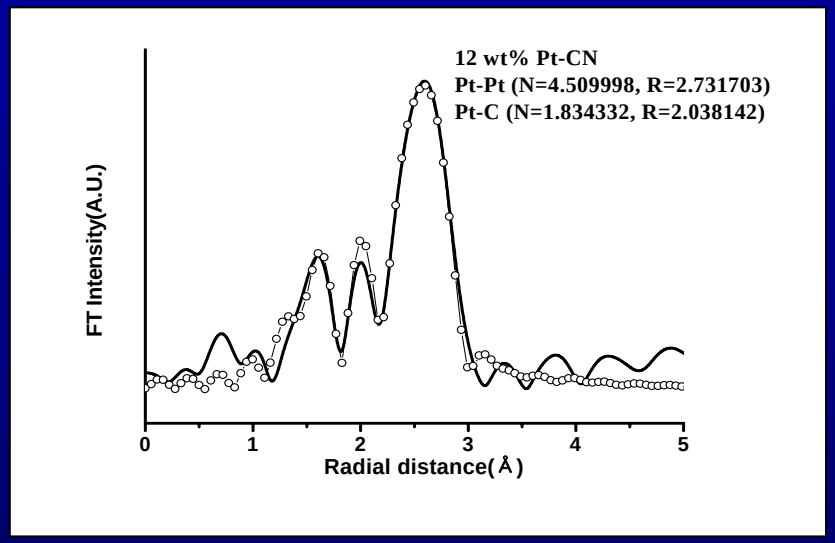
Pt/CMK-3

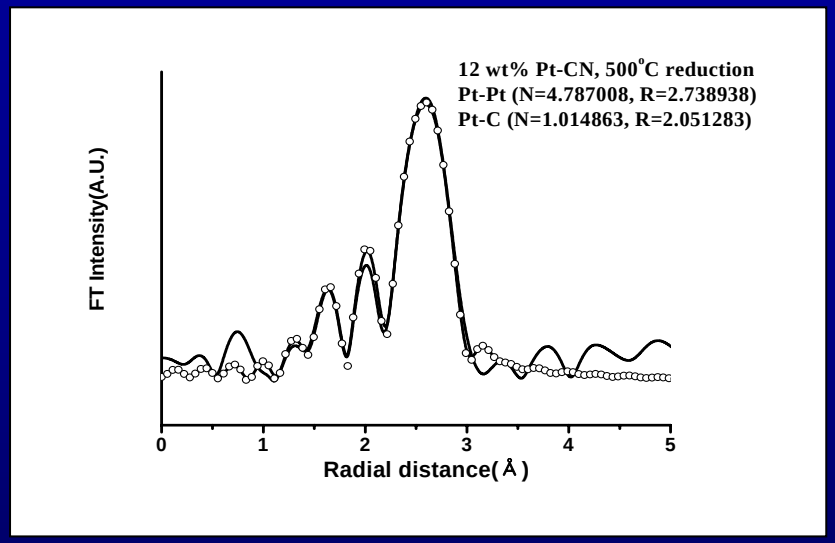
Pt/Vulcan

PtC nanocomposite
(Br treatment)

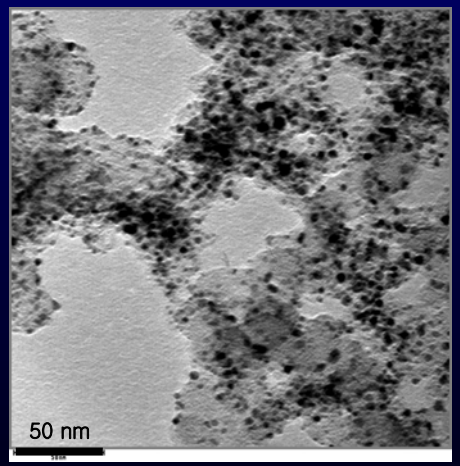
Stability of Pt-clusters in nano composite and commercial catalysis

12wt% Pt-CN

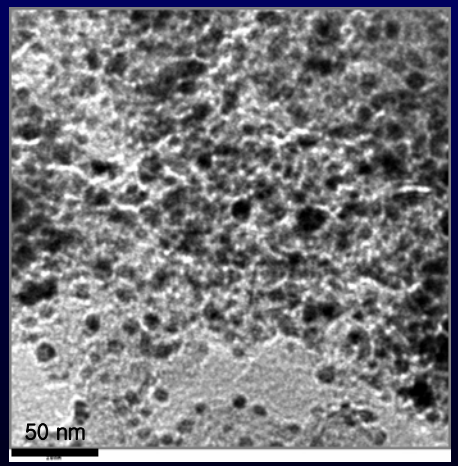




Commercial Pt/C (20 wt% Pt)



Before reduction
(Avg. Particle size 2~3nm))



After reduction
(Avg. Particle size 6~7nm))

Application of Pt/Carbon nano composite :

Direct Methanol Fuel Cell (DMFC)

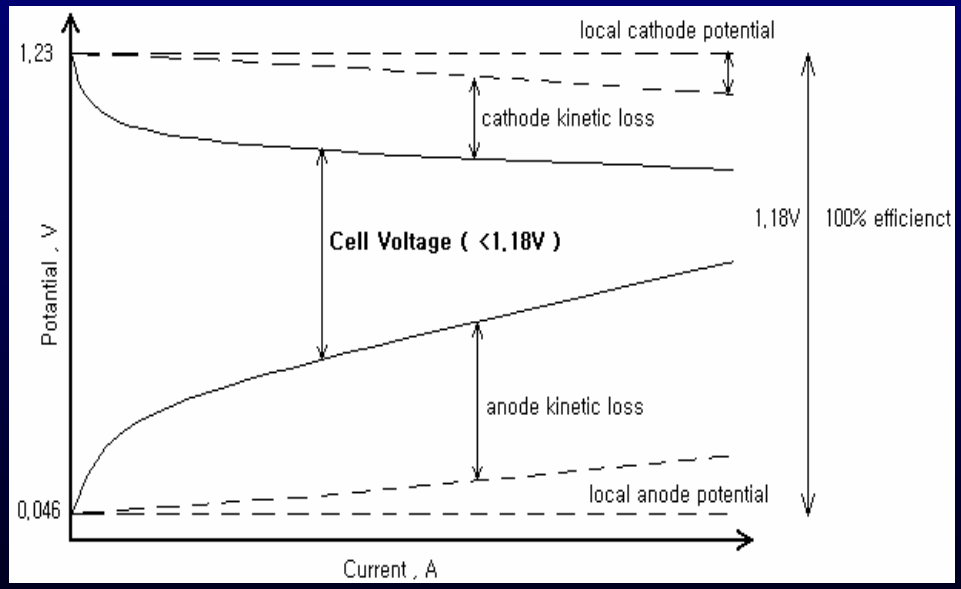
Electrochemical reaction of DMFC

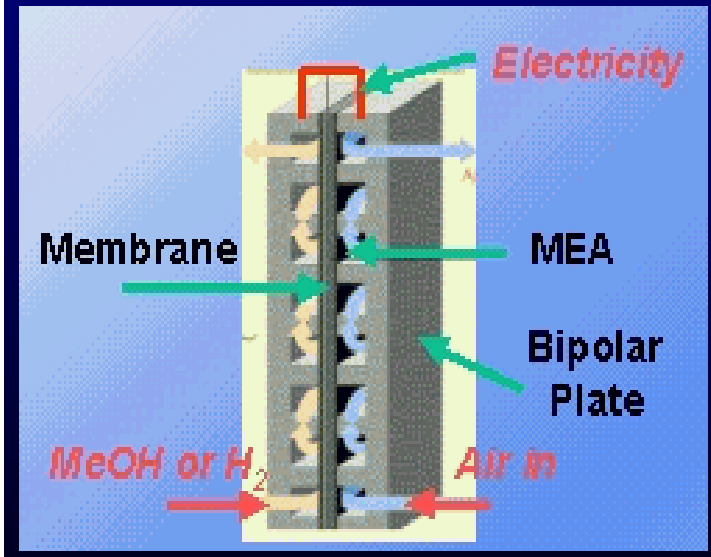
1. Half-cell reaction for the anodic oxidation

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$$

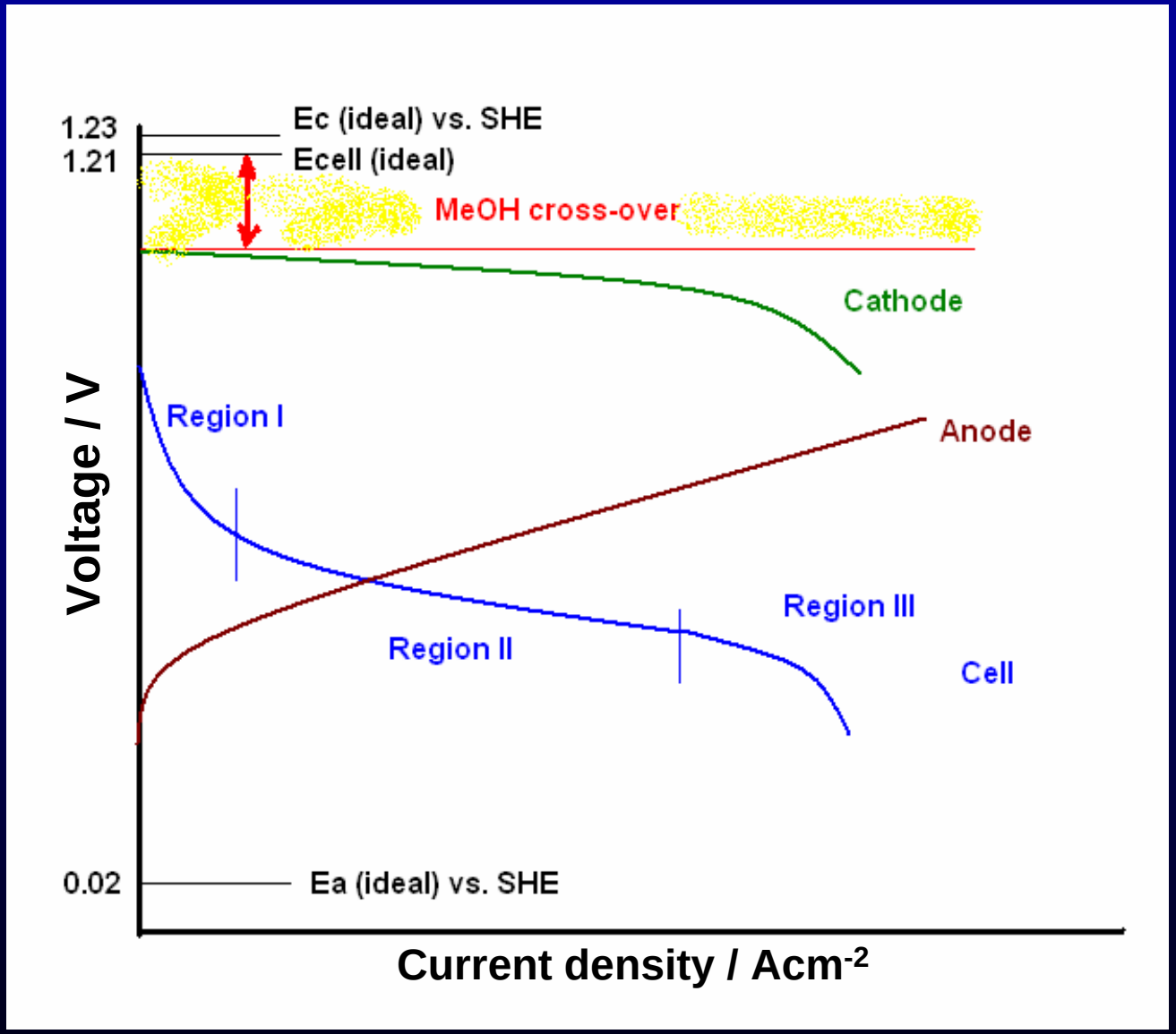
2. Half-cell reaction for the cathodic reduction

$$6H^+ + 3/2O_2 + 6e^- \rightarrow 3H_2O$$



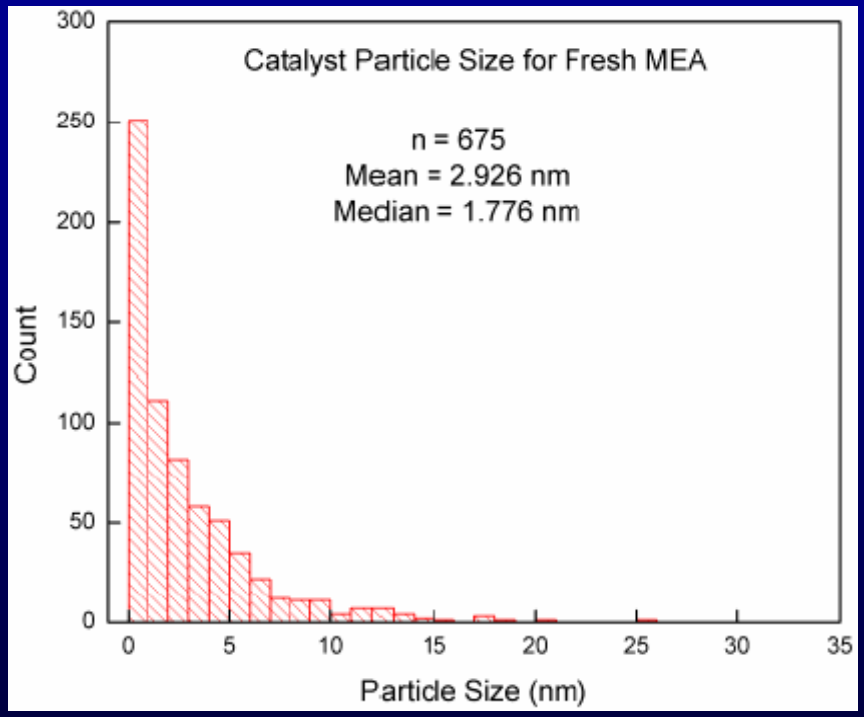


Methanol cross-over

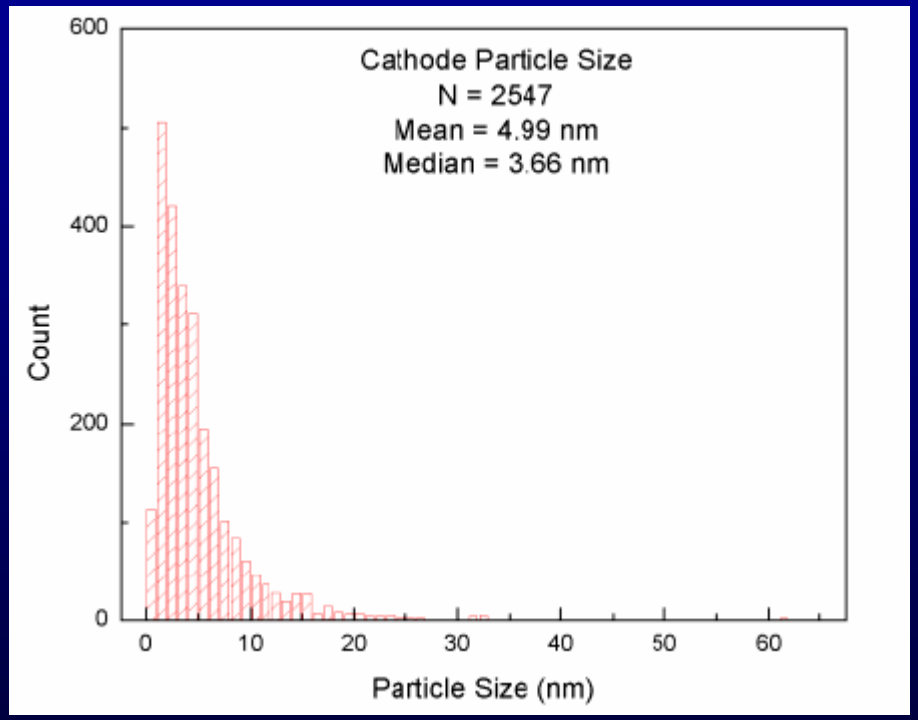


Pt particle size distribution

Fresh MEA



Failed MEA: Cathode



After 1200 hrs

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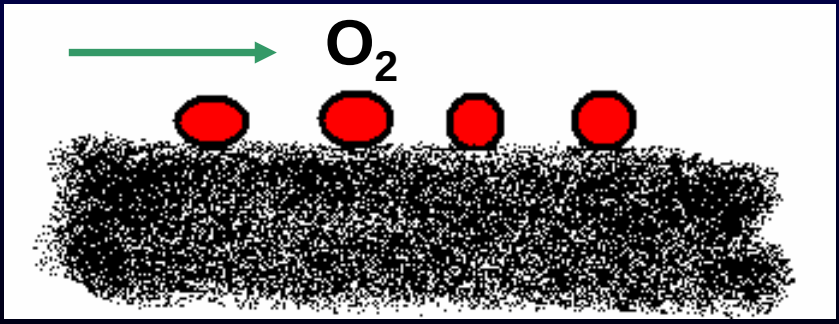
U. S. DEPARTMENT OF ENERGY

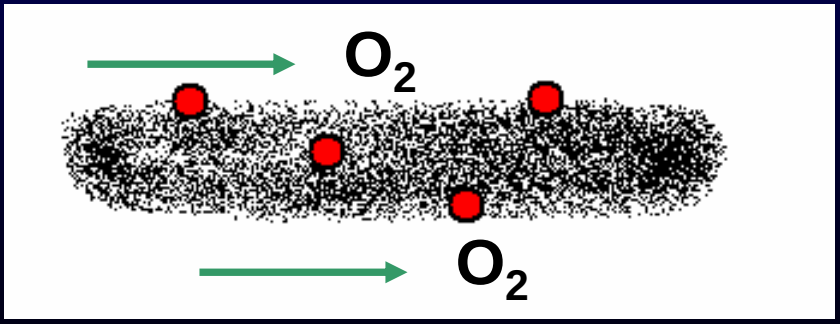
Approach in this study

- ✓ Pt particle size *vs.* Pt(110) / [Pt(100) & Pt(111)]
  - →Pt(110), methanol oxidation
  - →Pt(100) & Pt(111), oxygen reduction

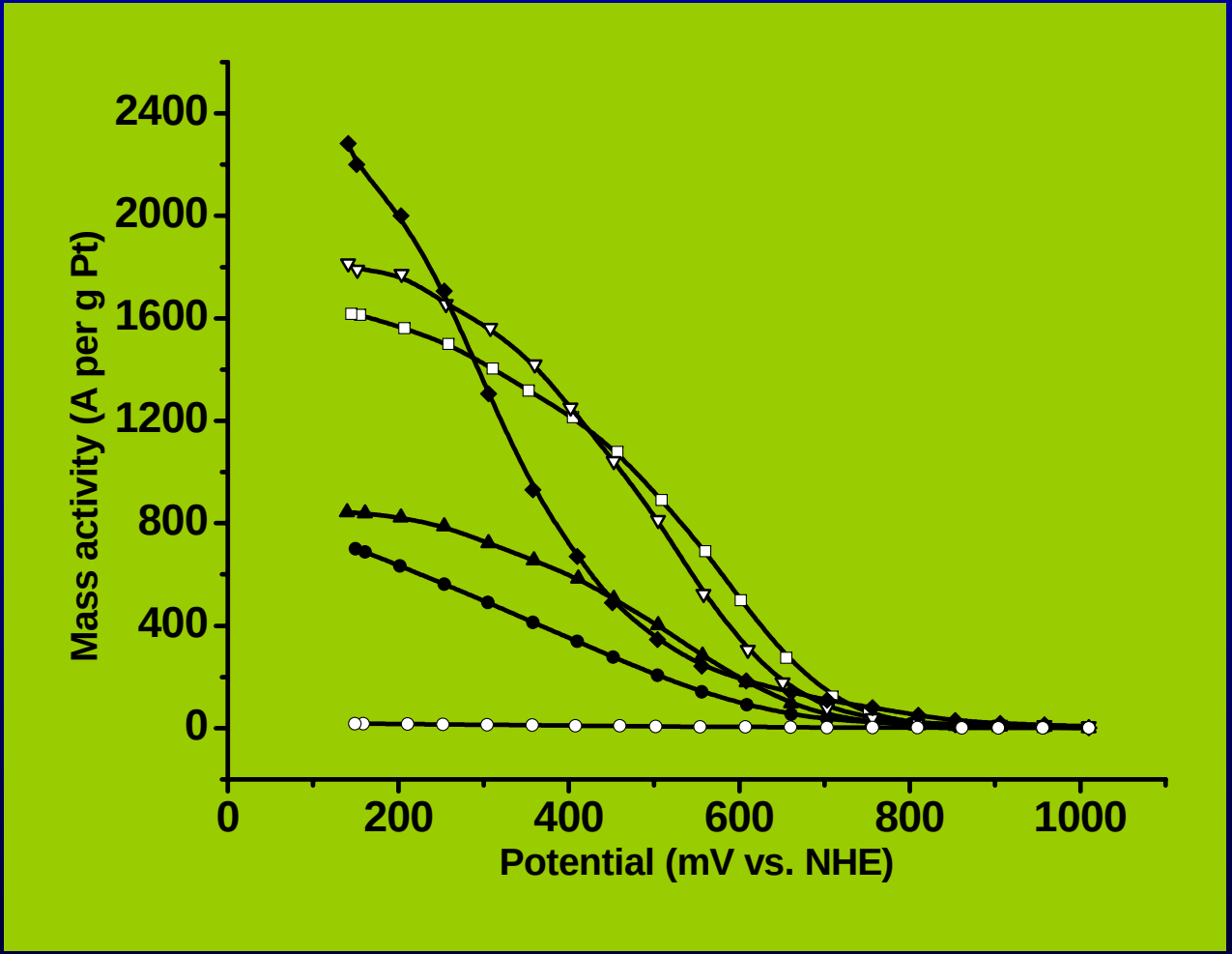
Electrochimica Acta 36, 973 (1991)
J. Electrochem. Soc. 137, 845 (1990)

- ✓ Studded Pt nano particles
- ✓ Micro pores only for oxygen diffusion





Oxygen electroreduction



Electrocatalytic mass activity for oxygen reduction with Pt-carbon nanocomposite (12 wt% Pt) (▽), Pt-carbon nanocomposite arrays (24 wt% Pt) (□), Pt/CMK-3 (24 wt% Pt) (▲), Pt/Vulcan XC-72 (24 wt% Pt) (●) and Pt-carbon nanocomposite arrays (8.5 wt% Pt) (◆) and Pt/CMK-3 (○) after treatment with bromide solution.

Oxygen electroreduction mass activity

Samples (Pt content, wt%)	Mass activity (A/g Pt) 0.96 V	0.76 V	Structural parameters* Pair	CN	*R* (Å)	σ^2 (nm)	χ^2 (%)
PtCN arrays (24)	5.9	56.5	Pt-C Pt-Pt	2.73±0.03 4.31±0.05	2.041±0.0008 2.735±0.0006	48.9±1.6 73.5±0.9	13.8
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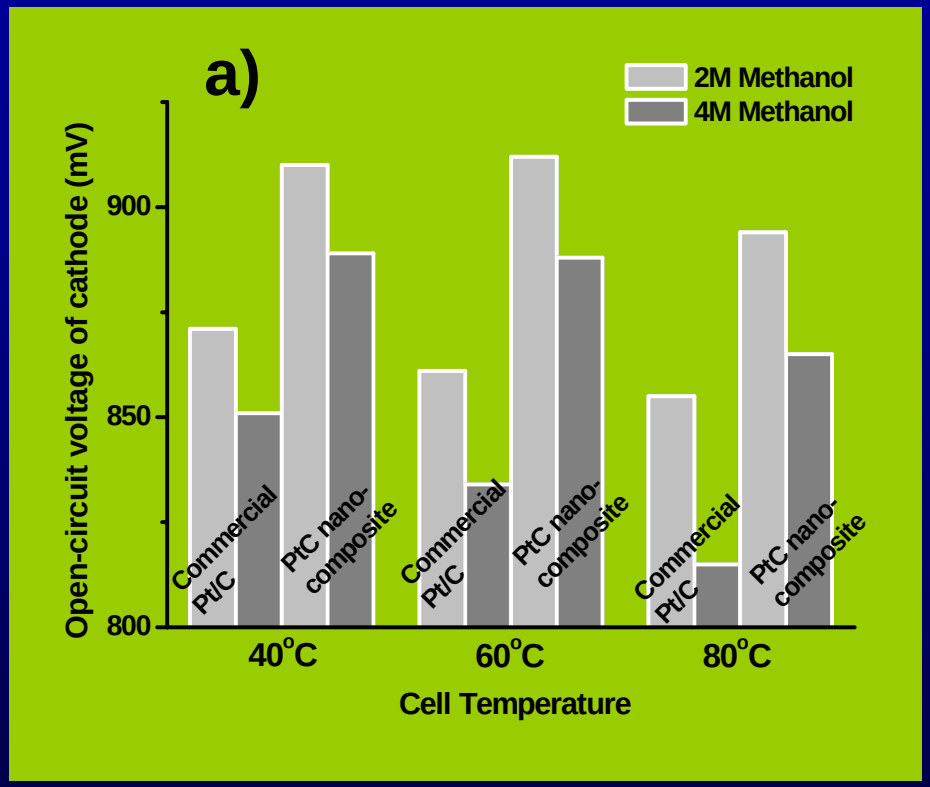
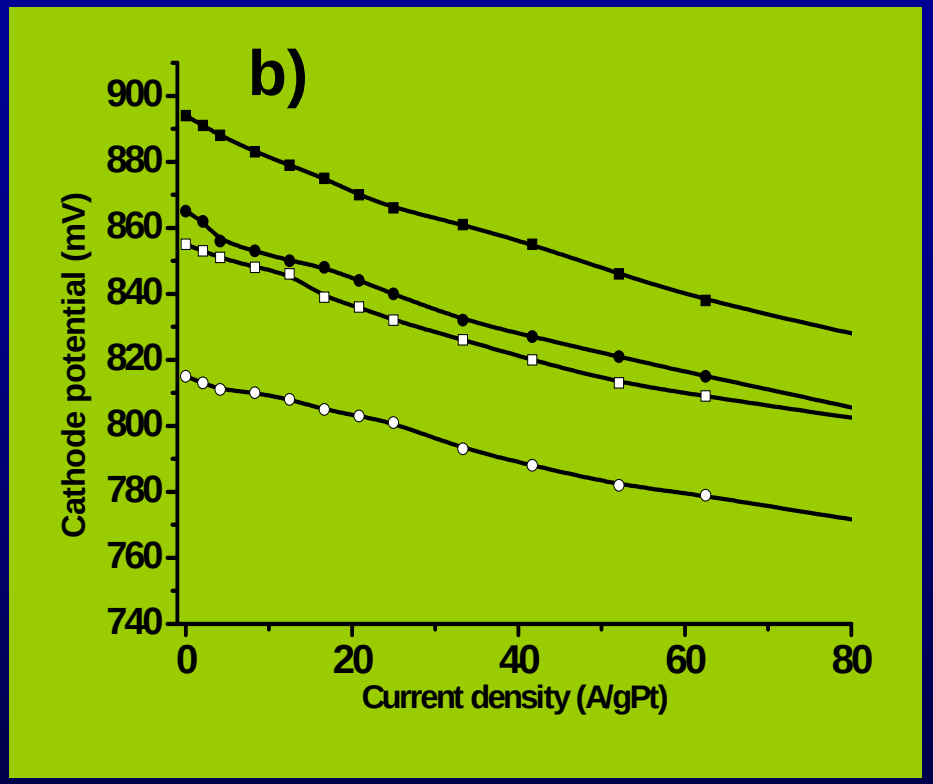
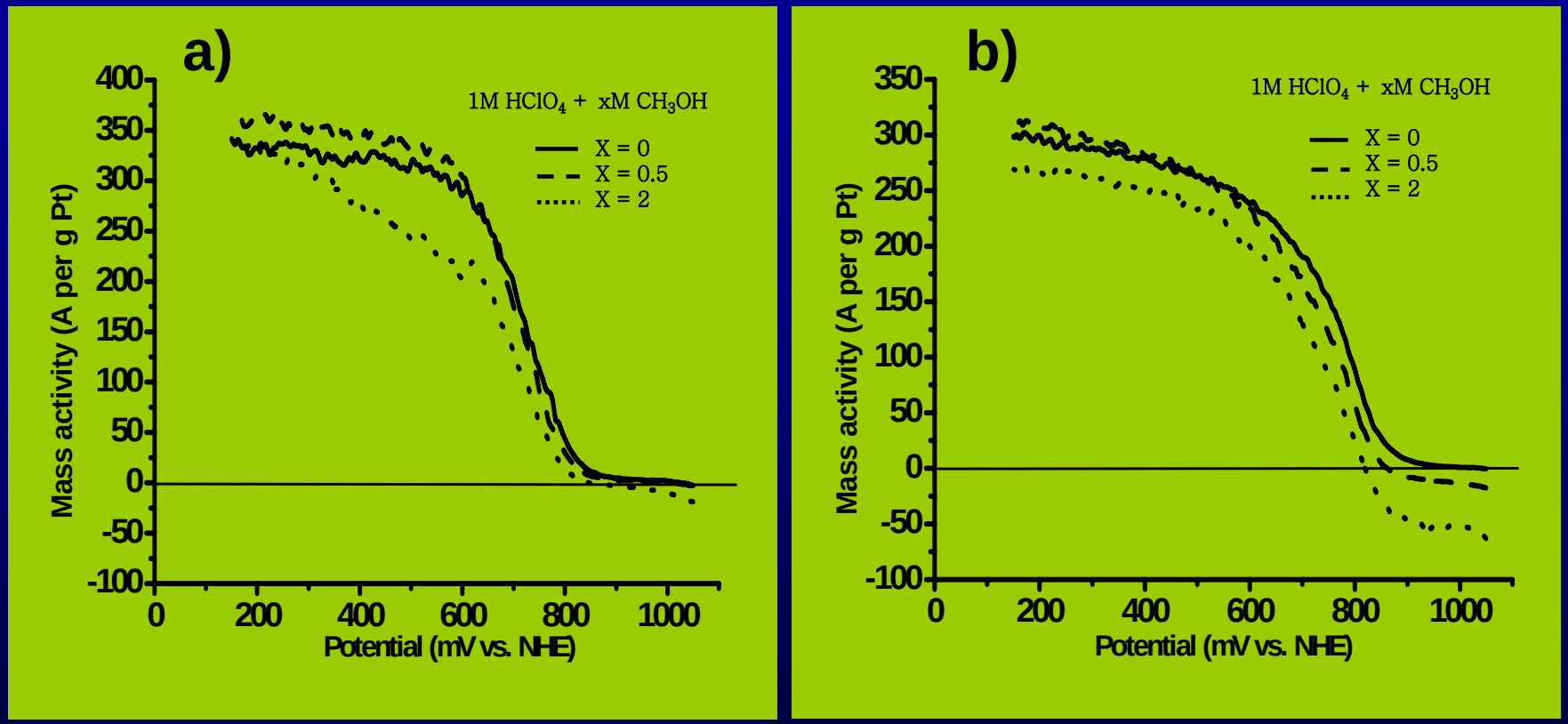
Methanol-tolerant PtC nano composite (I)





Open-circuit voltages of cathode (a) at various cell temperature and methanol concentration at anode and polarization curves of cathode (b) for DMFC at 80°C using commercial 20 wt% Pt/C (EC-20-PTC, empty) and 24% PtC nano composite (filled) with 2M (squares) and 4M (circles) methanol solution.

Methanol-tolerant PtC nano composite (II)



Electrocatalytic mass activity of 12 wt% PtC nano composite (a) and commercial 20 wt% Pt/C (Electrochem, Inc., EC-20-PTC) (b) for the oxygen reduction in oxygen-saturated 1M $HClO_4$ with xM CH_3OH (x = 0, 0.5 and 2).

Conclusions

- ✓ New mesoporous PtC nanocomposite
- ✓ Highly microporous PtC nanocomposite
- ✓ Electrocatalytic active Pt in micropores
- ✓ Ultrafine Pt clusters with narrow size distribution
- ✓ Methanol-tolerant PtC nanocomposite