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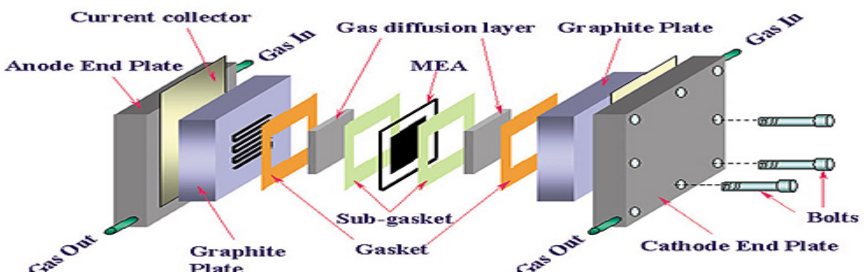
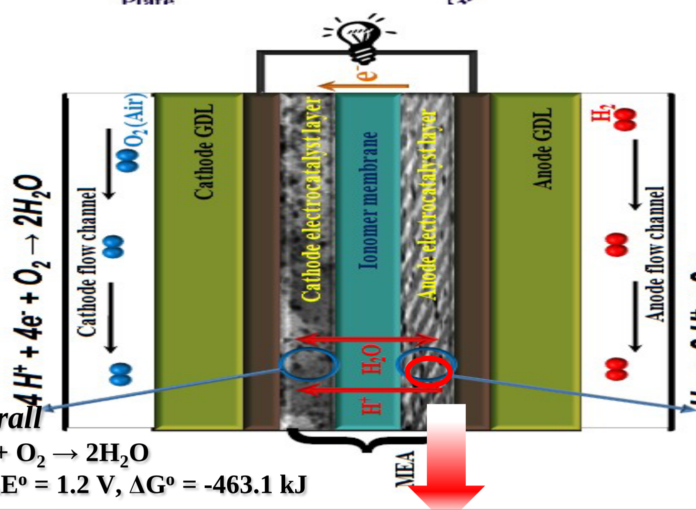
Phosphorus-doped ordered mesoporous carbon : effect of size on electrocatalytic activity towards oxygen reduction in alkaline conditions

Dae-Soo Yang, Jinsol Park, Min Young Song, Hyun-Yeol Park and Jong-Sung Yu*

Energy Materials Lab.,
Dept. of Advanced Materials Chemistry,
Korea University,
Sejong, Chungnam 339-700, Korea
E-mail : jsyu212@korea.ac.kr

Fuel Cell



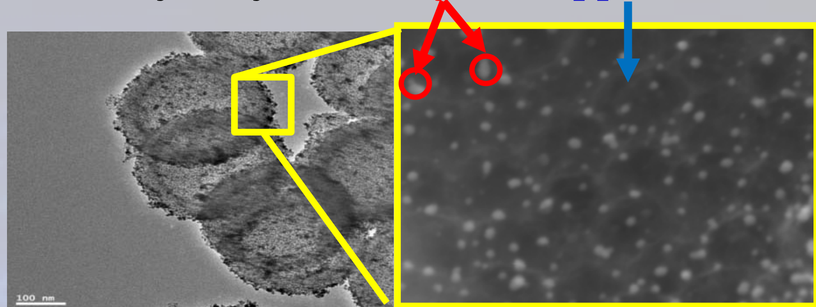


Overall

$2H_2 + O_2 \rightarrow 2H_2O$

$\Delta E^o = 1.2$ V, $\Delta G^o = -463.1$ kJ

Catalyst layer : catalyst + support



PAFC (Phosphoric acid FC)
- Electrolyte : H_3PO_4
- Operating temperature : 190~200℃

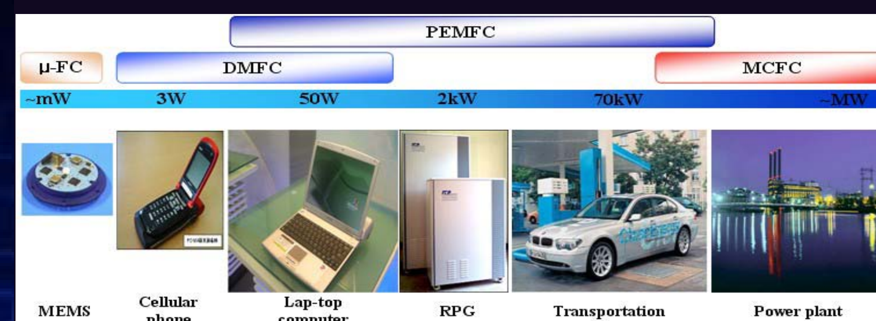
PEMFC (Proton exchange membrane FC)
- Electrolyte : Nafion
- Operating temperature : 25~80℃

DMFC(Direct methanol FC)
- Electrolyte : Nafion
- Operating temperature : 25~90℃

AFC (alkaline FC)
- Electrolyte : KOH
- Operating temperature : 80~90℃

MCFC (molten carbonate FC)
- Electrolyte : Li_2CO_3 or K_2CO_3
- Operating temperature : 650℃

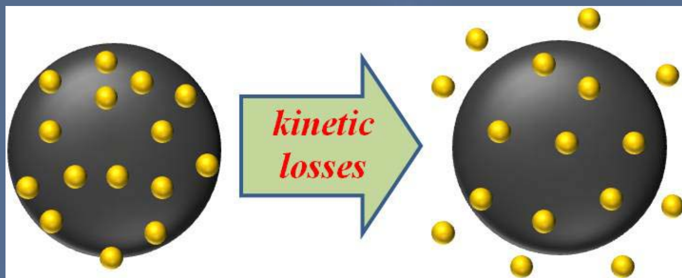
SOFC (Solid oxide FC)
- Electrolyte : ZrO_2
- Operating temperature : 600~1000℃

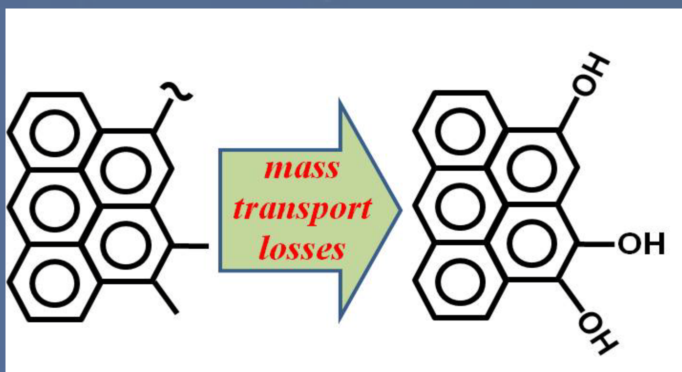


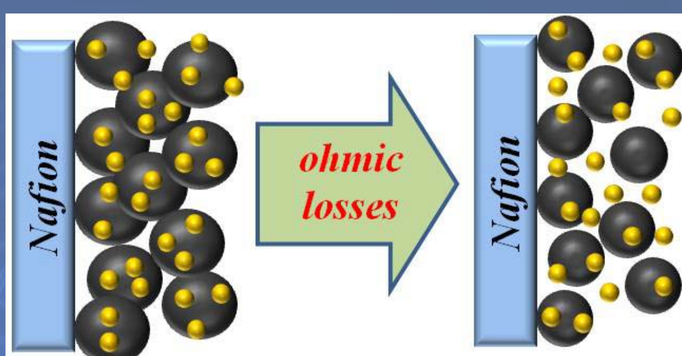
Introduction

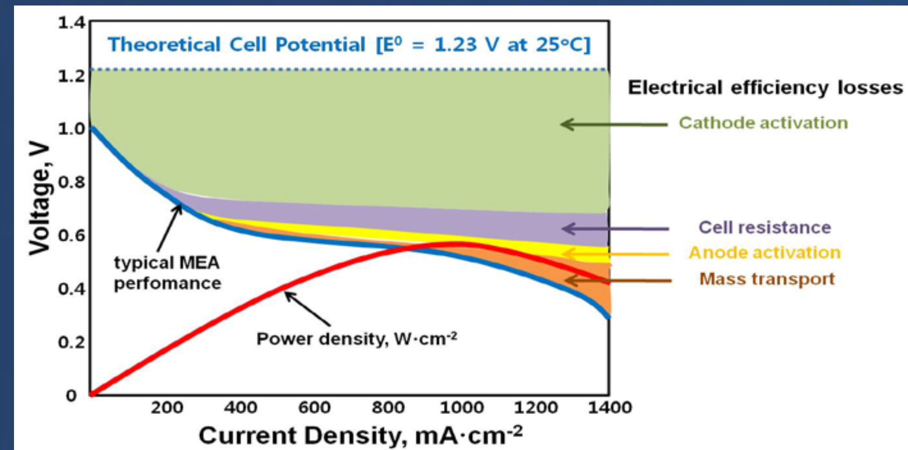
- **Fuel cells (FCs) are envisioned as one best possible solution due to their high energy density, high efficiency and negligible emission of harmful gases.**
- **The foremost limitations in low temperature FCs are the kinetically sluggish oxygen reduction reaction (ORR) at the cathode and corrosion of Pt catalysts.**
- Recently, PGM-free doped carbons have been reported as highly efficient and cheap ORR catalysts, particularly using nitrogen-doped carbon.
- In this work, metal-free P-doped ordered mesoporous carbon (POMC) nanorods were prepared using nanocasting method and studied as an electrocatalyst for ORR in alkaline conditions.
- Effect of POMCs with different rod length on ORR performance was also studied.

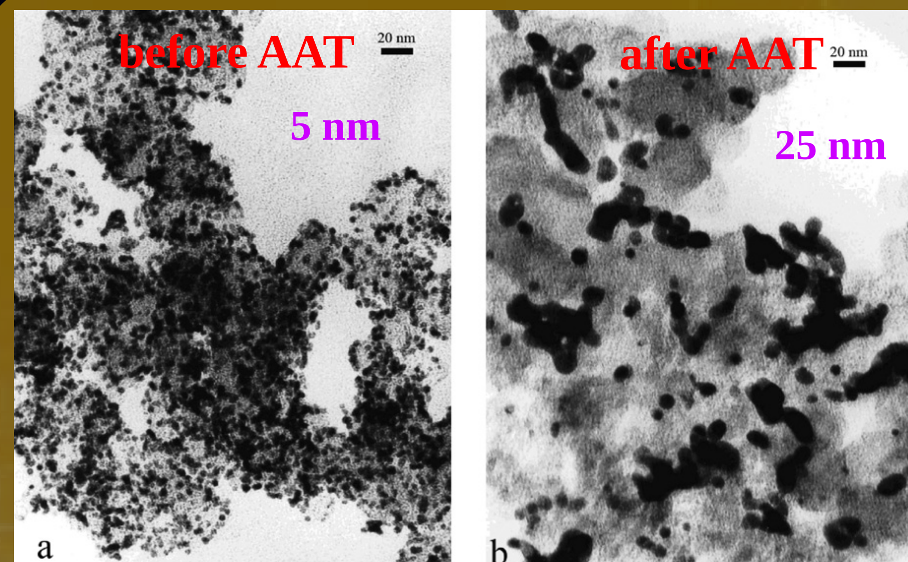
Catalyt corrosion











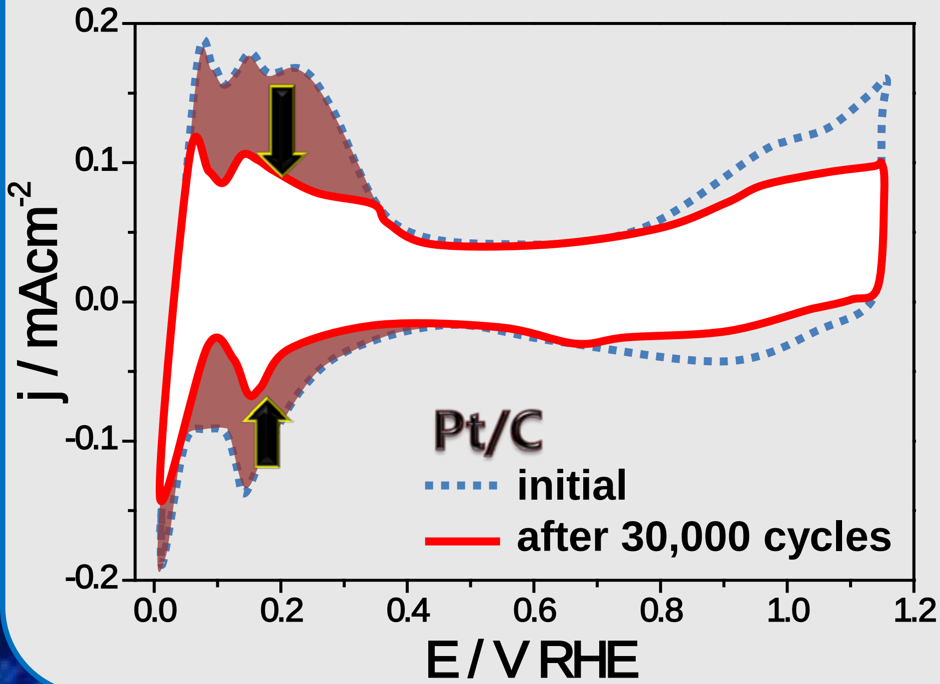
Pt/C : Accelerating aging test

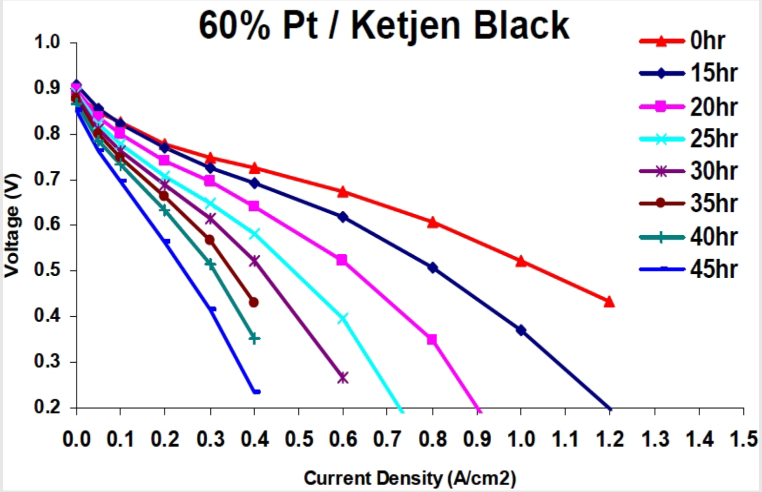
Journal of Power Sources *195 (2010) 4098–4103*

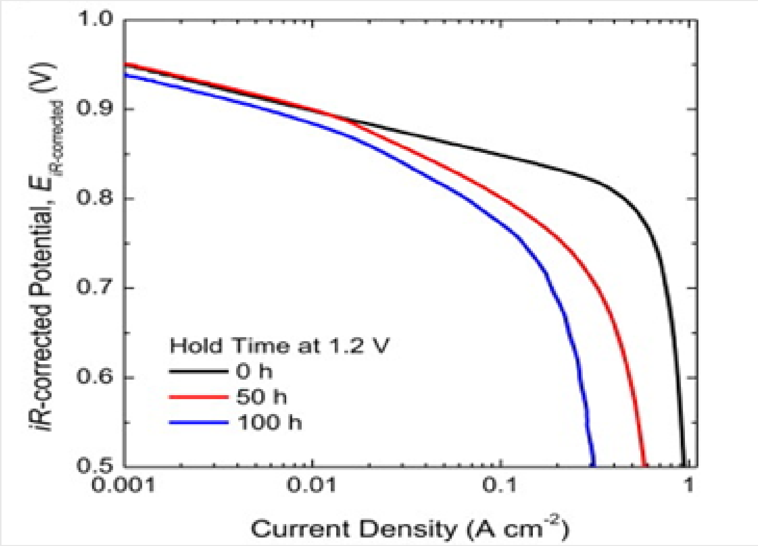
Catalyst/carbon corrosion

pure Pt

unstable !!







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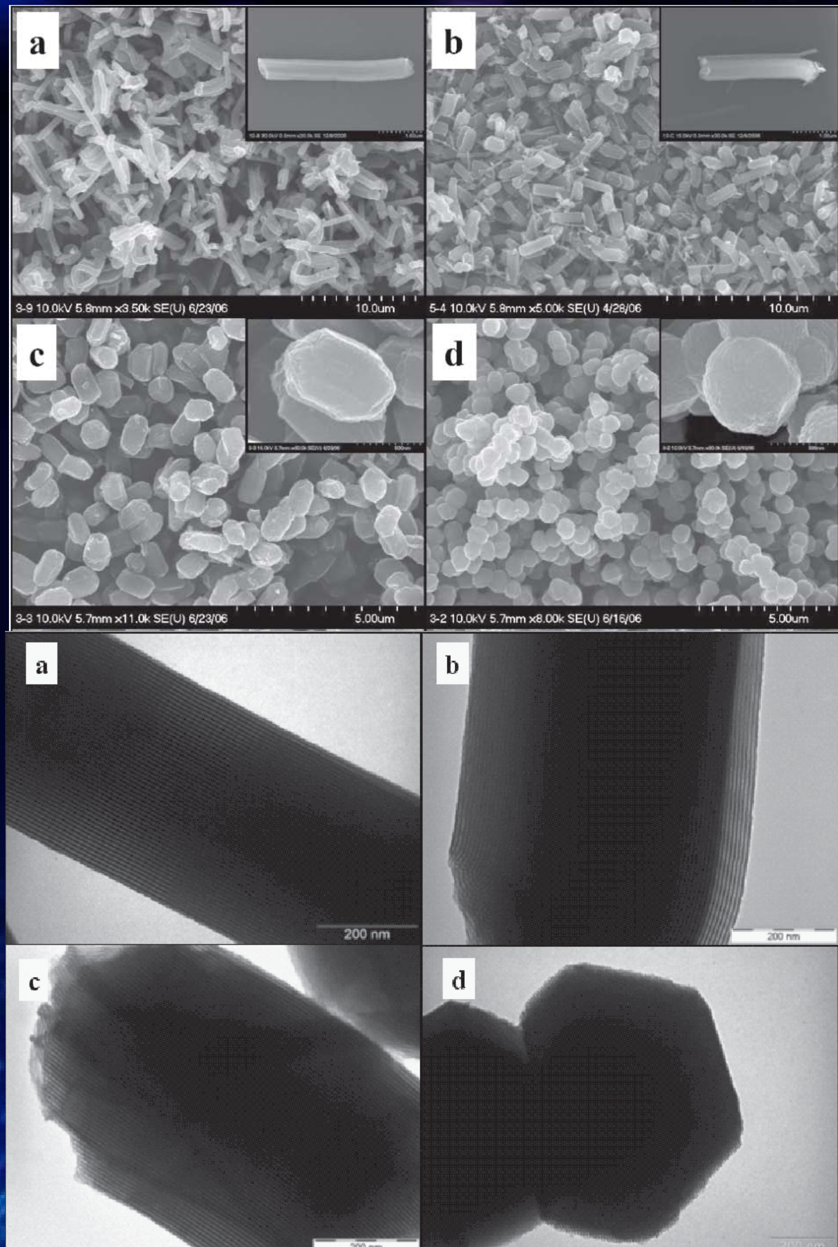
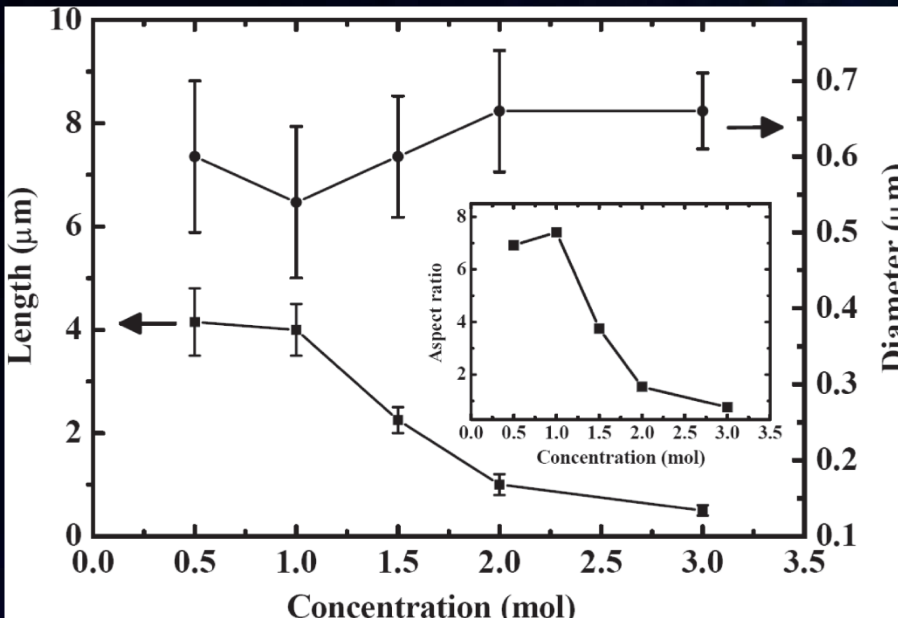
- The foremost limitations in low temperature FCs are the kinetically sluggish oxygen reduction reaction (ORR) at the cathode and corrosion of Pt catalysts.
- **Recently, PGM-free doped carbons have been reported as highly efficient and cheap ORR catalysts, particularly using nitrogen-doped carbon.**
- **In this work, metal-free P-doped ordered mesoporous carbon (POMC) nanorods were prepared using nanocasting method and studied as an electrocatalyst for ORR in alkaline conditions.**
- **Effect of POMCs with different rod length on ORR performance was also studied.**

Size-Tunable Synthesis of SBA-15 Silica with Rodlike Morphology using HCl



Sol-gel hydrothermal method

- Pluronics P123 ($PEO_{20}PPO_{70}PEO_{20}$) in deionized water and HCl with different HCl concentrations in the range of 0.1~5.0 M.
- TOES added.

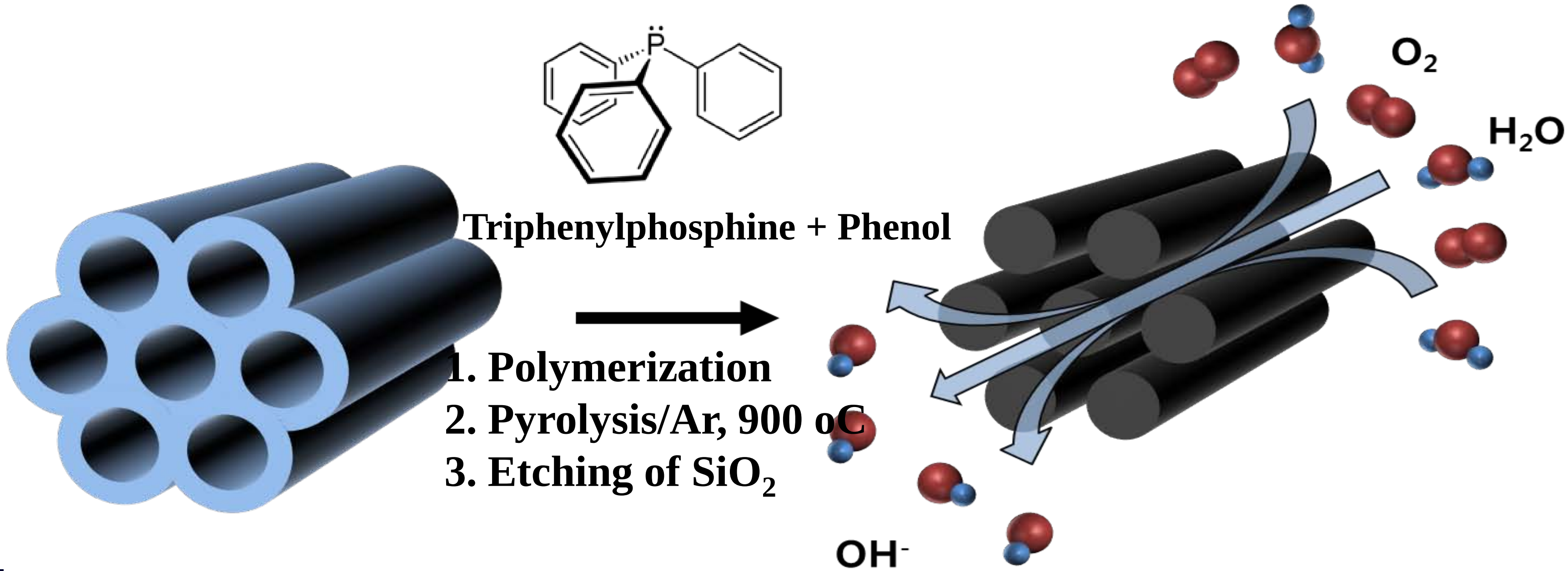


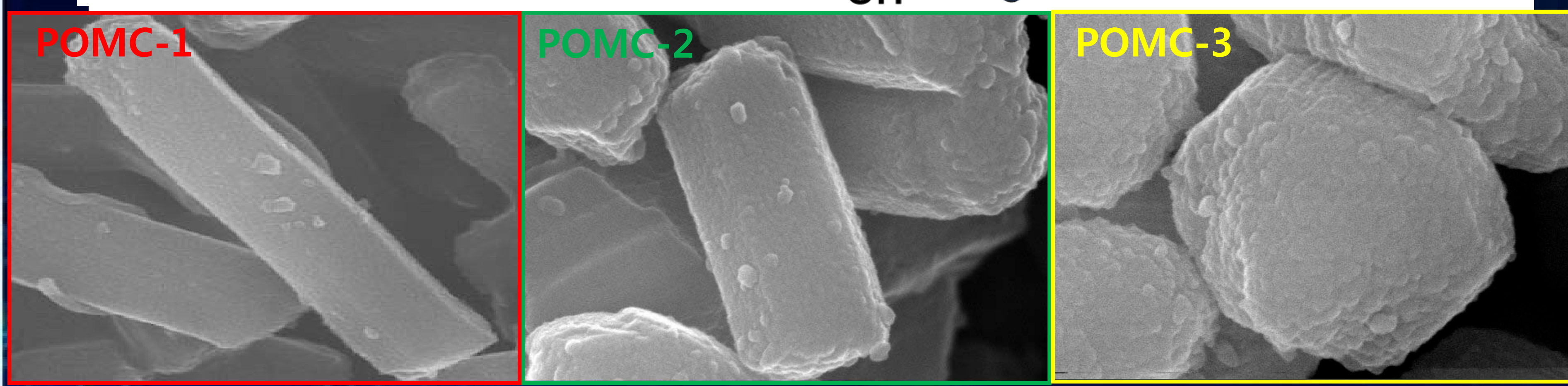
Effects of HCl concentration on length and diameter of SBA-15 particles. Inset represents the aspect ratios of the SBA-15 particles as a function of HCl concentration.

J. Nanosci. Nanotechnol. 9, 527–532, 2009

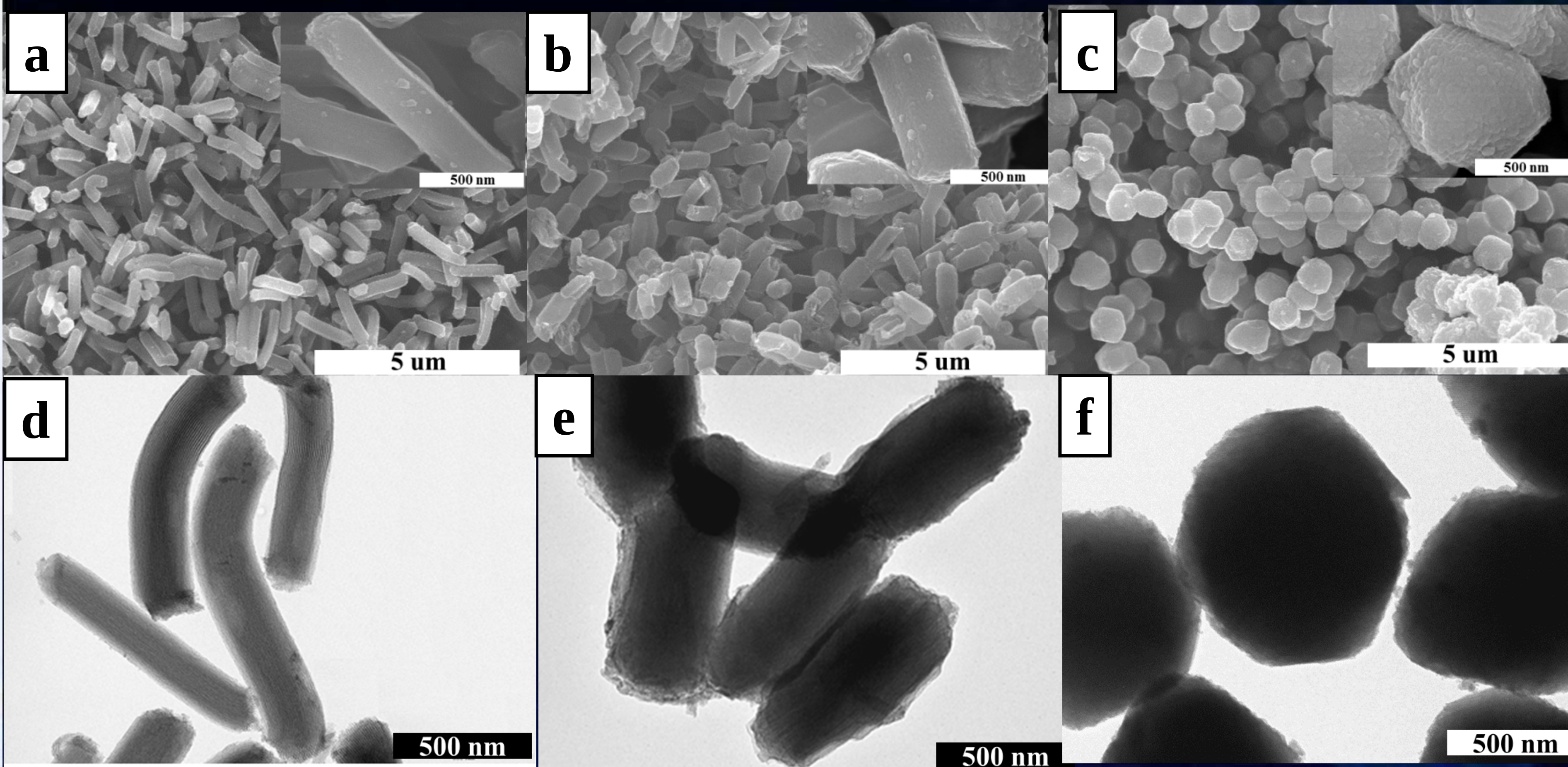
Phosphorus-doped ordered mesoporous carbons (POMC) with different rod lengths

Schematic illustration of POMC preparation





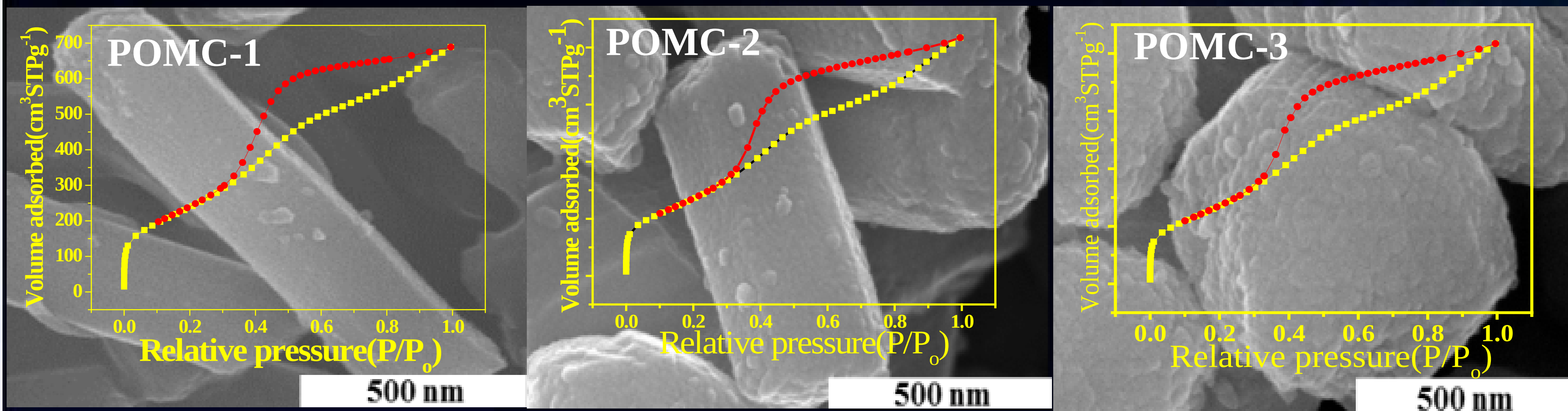
POMC with different rod lengths



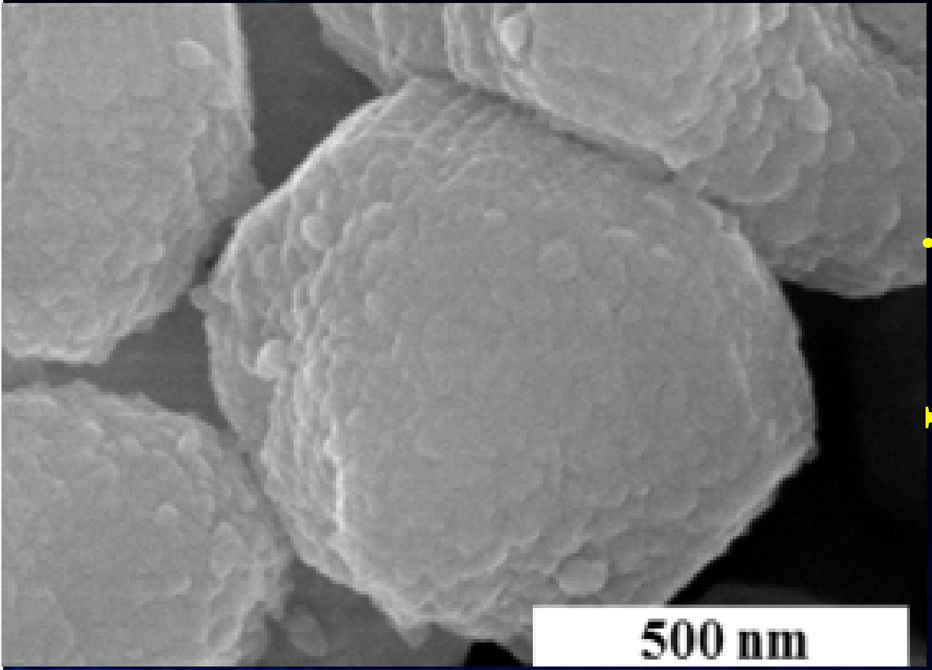
FE-SEM and TEM images of POMCs with different sizes: **(a, d) POMC-1, (b, e) POMC-2 and (c, f) POMC-3**. (length of 1.5, 1.0, and 0.7 μm and thickness of 0.2, 0.4, and 0.8 μm, respectively)

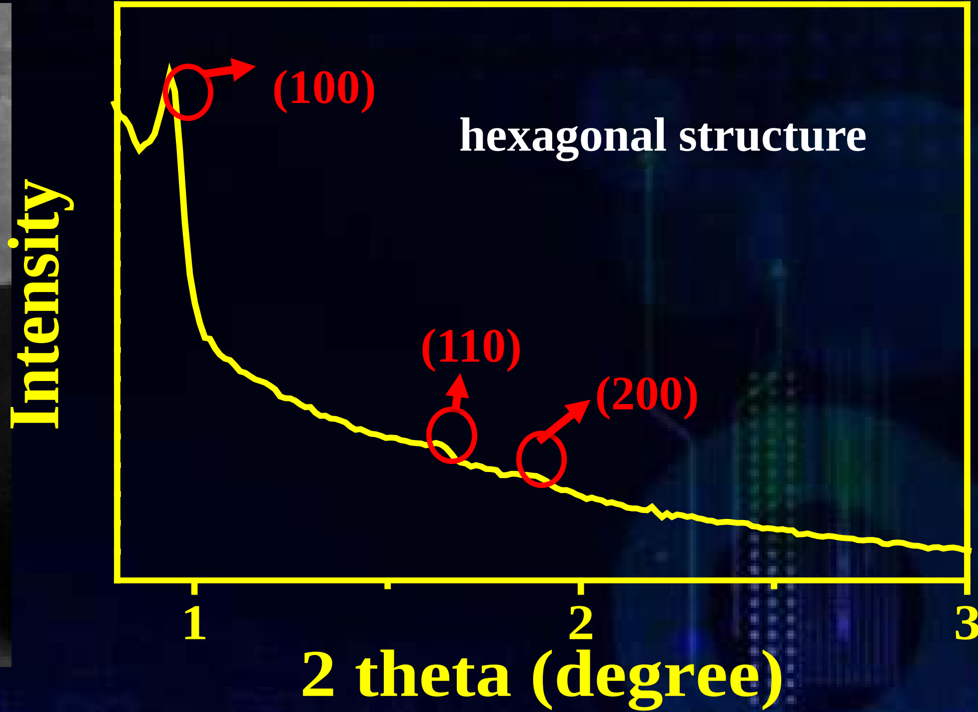
Surface properties of POMCs with different sizes

N_2 sorption isotherms with pore size distribution

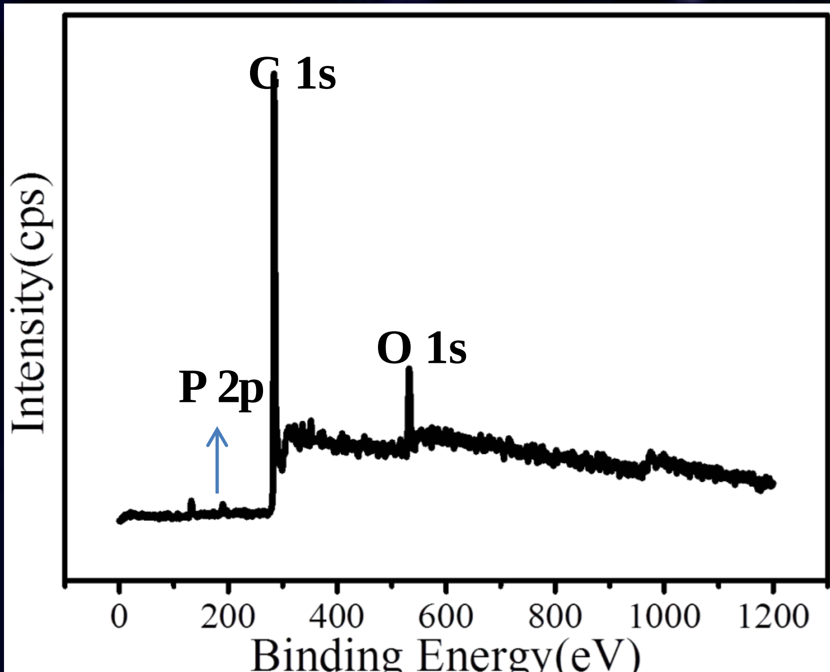


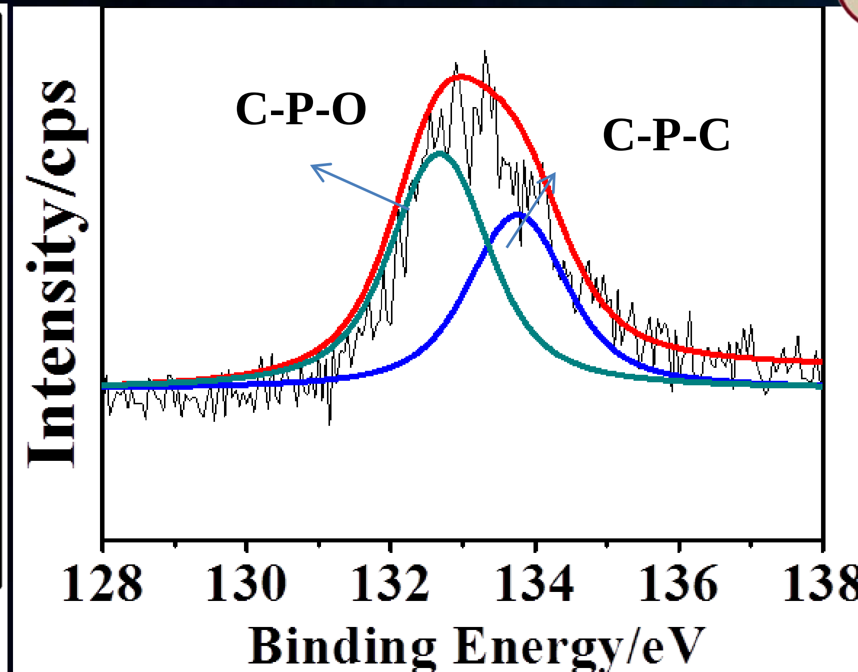
	S_{BET} (m^2g^{-1})	V_{micro} (cm^3g^{-1})	V_{meso} (cm^3g^{-1})	V_{total} (cm^3g^{-1})	Pore size (nm)	L - T (µm)	C : O : P atomic %
POMC-1	813.5	0.41	0.99	1.40	3.1	1.5 - 0.2	93.7 : 4.9 : 1.4
POMC-2	930.3	0.42	1.24	1.66	3.2	1.0 - 0.4	92.6 : 6.0: 1.4
POMC-3	1181.9	0.45	1.42	1.87	3.4	0.7 - 0.8	93.5 : 5.1; 1.4





SEM image and small angle XRD of POMC-3



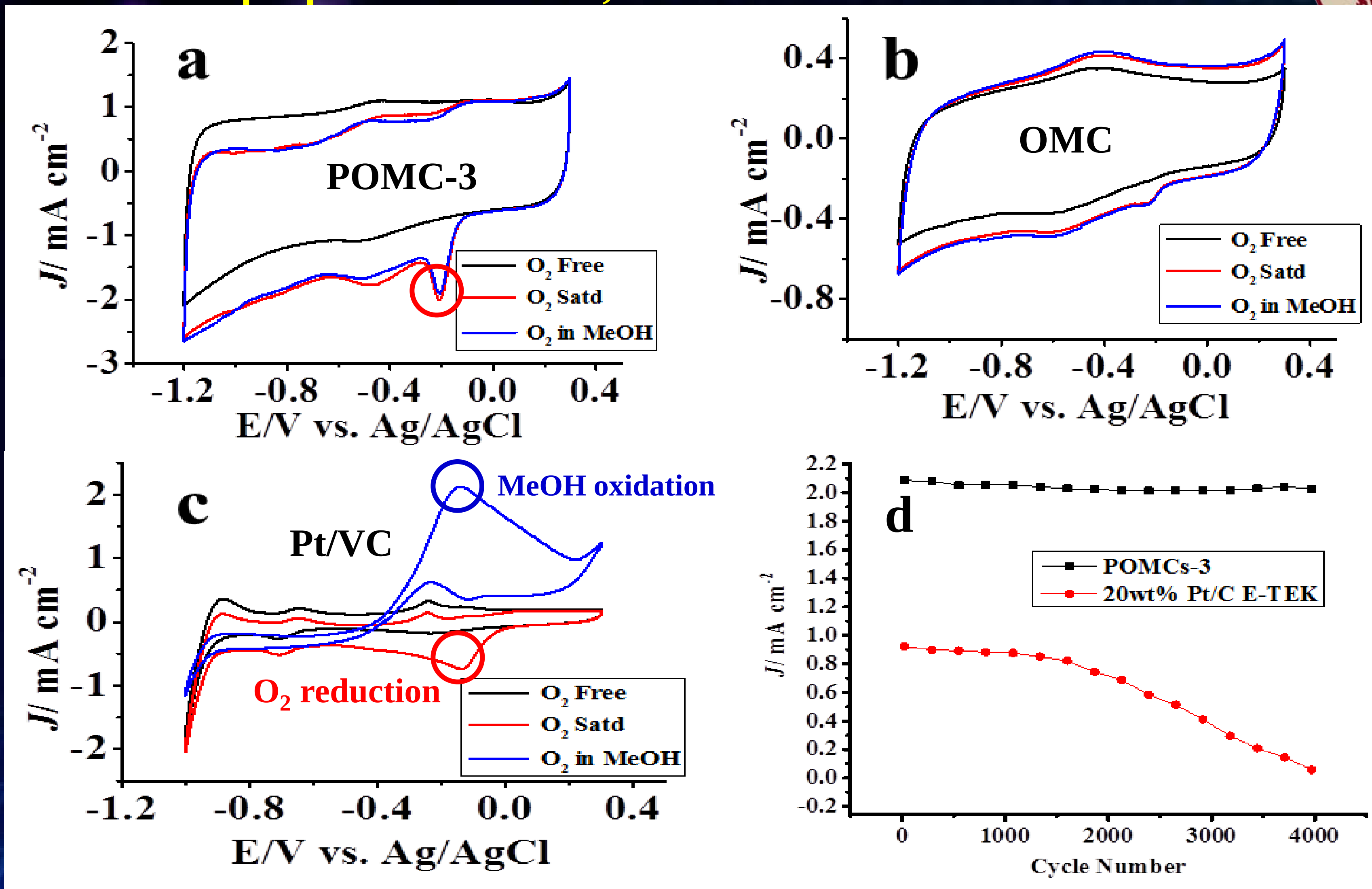


HR-XPS of P 2p spectrum of POMC-3

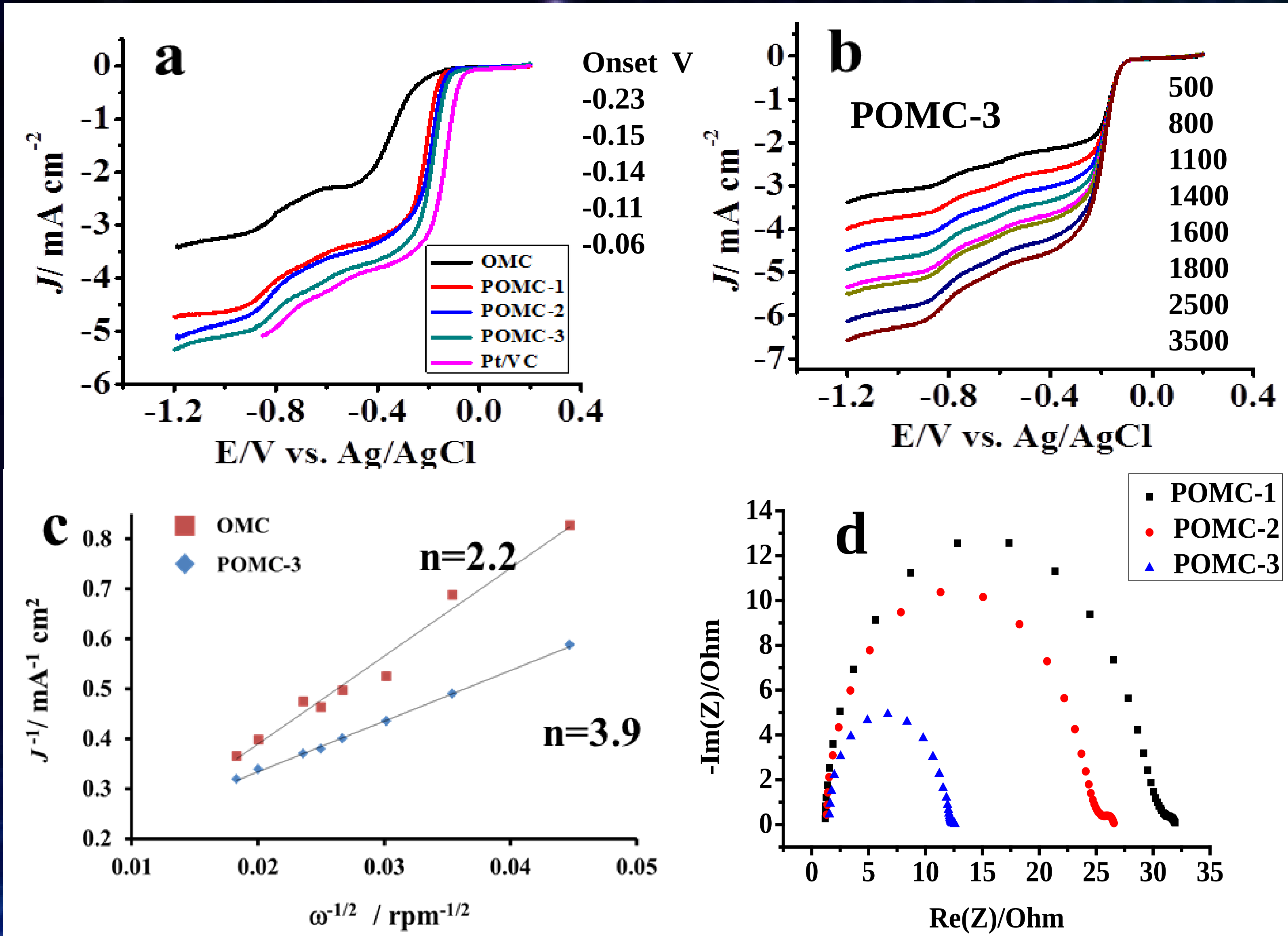
The physical parameters and electrochemical properties of POMCs with different sizes.

Sample name	S_{BET} (m^2g^{-1})	V_{micro} (cm^3g^{-1})	V_{meso} (cm^3g^{-1})	V_{total} (cm^3g^{-1})	Pore size (nm)	Electron-transferred number (*n*)	Onset potential (V vs Ag/AgCl)	P content (atomic. %)	R_{ct}/Ω
OMC	1120	0.44	1.39	1.83	3.3	2.4	-0.23	-	-
POMC-1	814	0.41	0.99	1.40	3.1	3.4	-0.15	1.39	29.7
POMC-2	930	0.42	1.24	1.66	3.2	3.6	-0.14	1.43	24.1
POMC-3	1182	0.45	1.42	1.87	3.4	3.9	-0.11	1.36	10.5
Pt/VC	261	0.01	0.39	0.40	-	4.0	-0.06	-	-

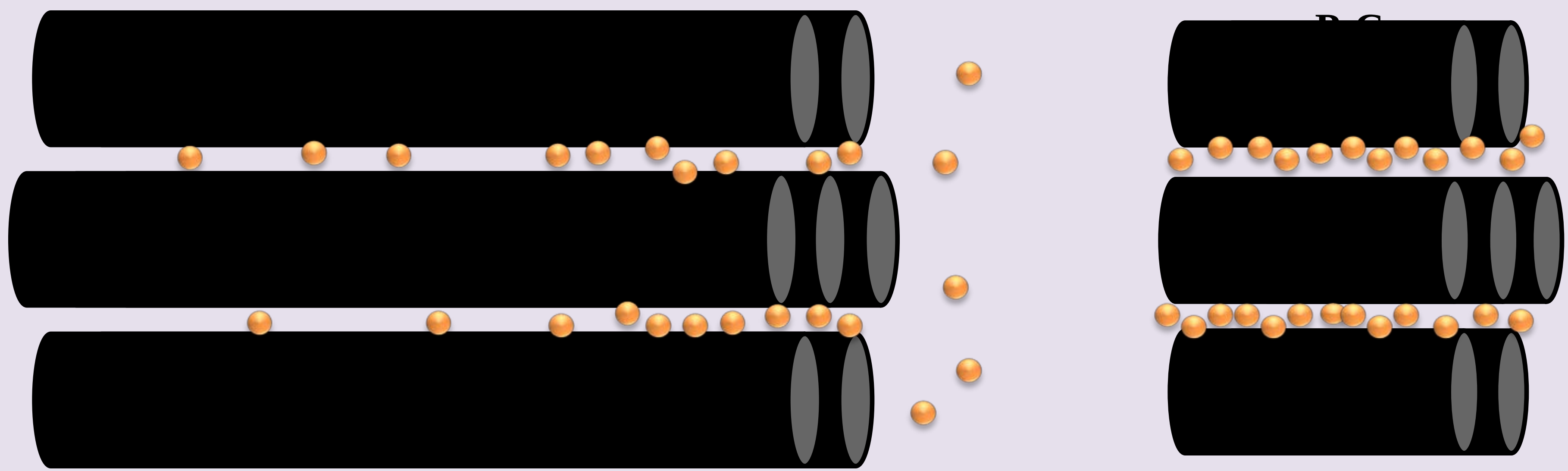
Electrochemical properties of OMC, POMC and Pt/C



CVs for POMC-3 (a), undoped OMC (b), and commercial Pt (20 wt%)/VC catalysts (c) at different conditions. ORR peak max currents for POMC-3 and commercial 20 wt% Pt/VC catalysts during the repeated potential cycling (d).



The LSV curves at 1600 rpm (a), LSV curves for POMC-3 at different rotation speeds (b), Koutecky–Levich plots of POMC-3 at different electrode potentials (c). Electrochemical impedance spectroscopic (EIS) Nyquist plots measured (d) for the three different POMCs



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Pt/VC	261	0.01	0.39	0.40	-	4.0	-0.06	-	-

Conclusions

1. We have demonstrated the fabrication of a novel P-doped OMC cathode by a simple, cost-effective, and readily reproducible approach.
2. The resulting metal-free POMC catalysts exhibited outstanding electrocatalytic activity, long-term stability, and excellent resistance to alcohol crossover effects for ORR.
3. The effect of rod length of the prepared POMC on catalytic ORR performance was also investigated, showing increase in activity with decrease in rod length of POMC, probably due to increased surface area and decreased resistance of shorter rod.
4. Overall, with proper optimization on P-loading amount and distribution, which are now in progress, the future replacement of expensive Pt/VC catalyst can be achieved by more stable and effective P-doped carbon for practical applications of fuel cells.

Future Work : metal-free N, P and S doped carbons

SBA-15 silica with different aspect-ratios

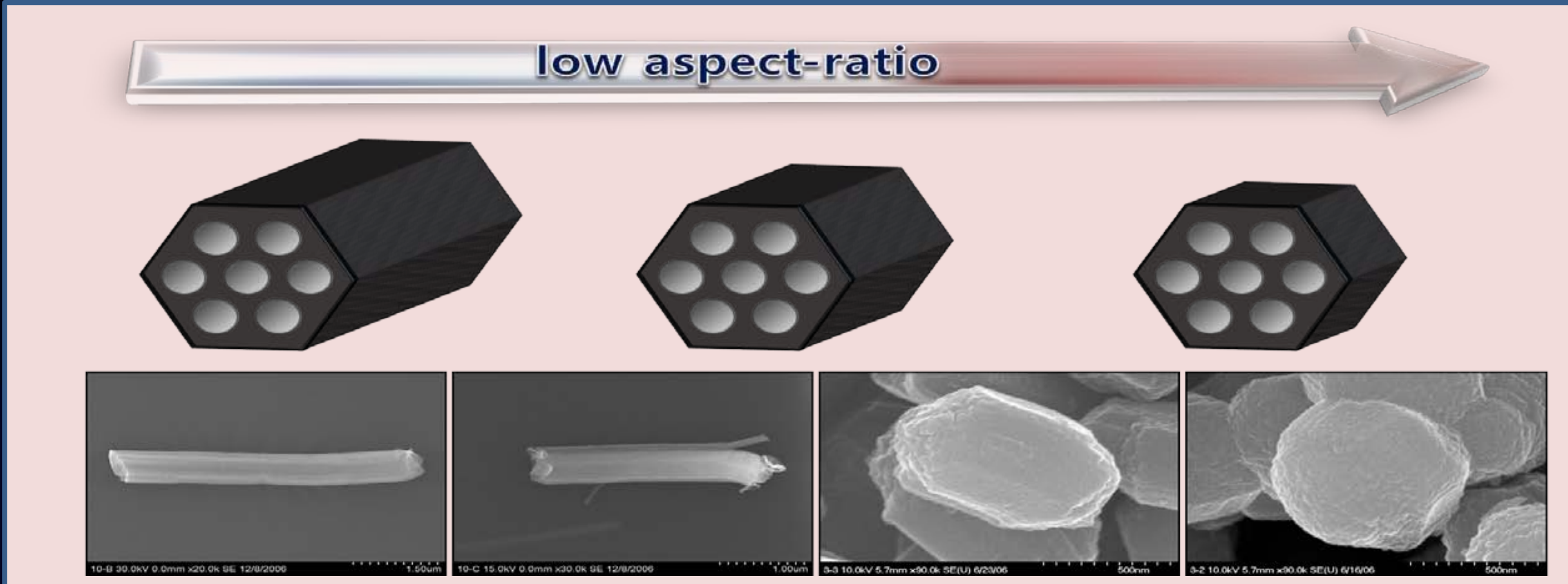
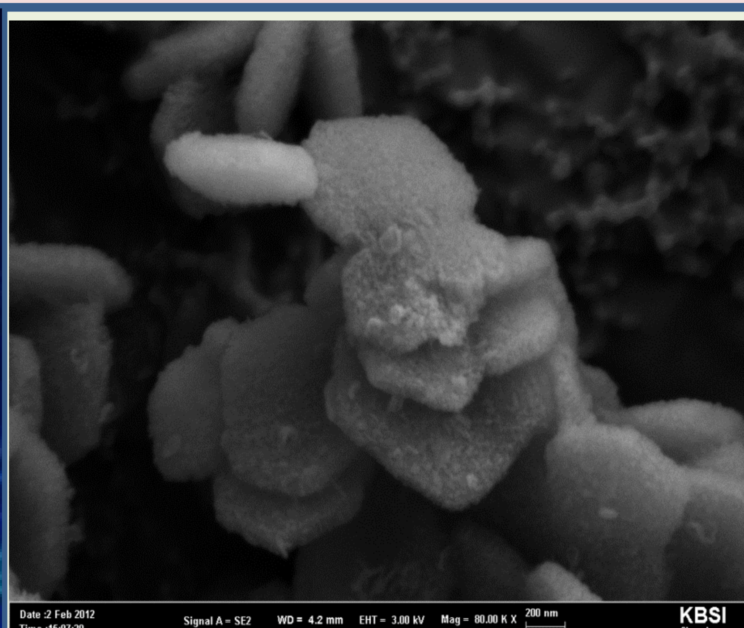
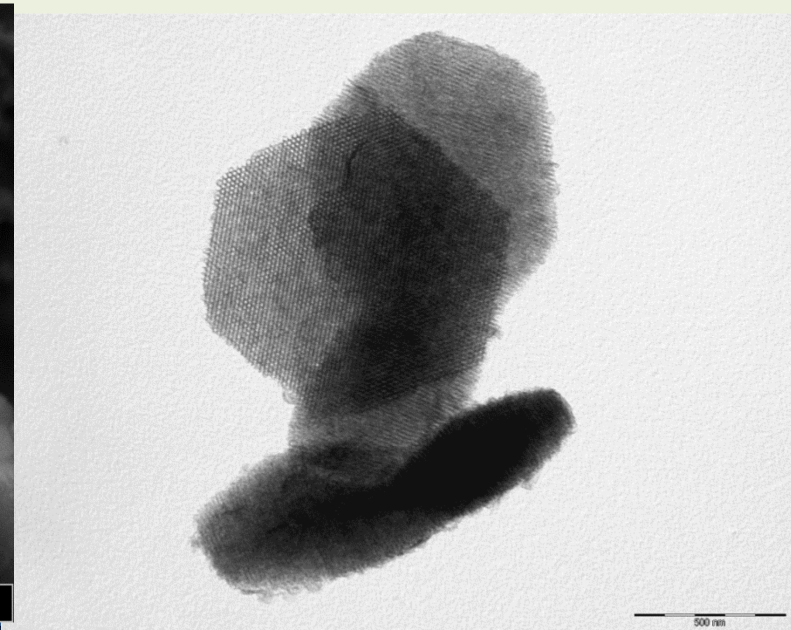


Plate-like SBA-15





Synthesis of plate-like CMK-3 and CMK-5 carbons

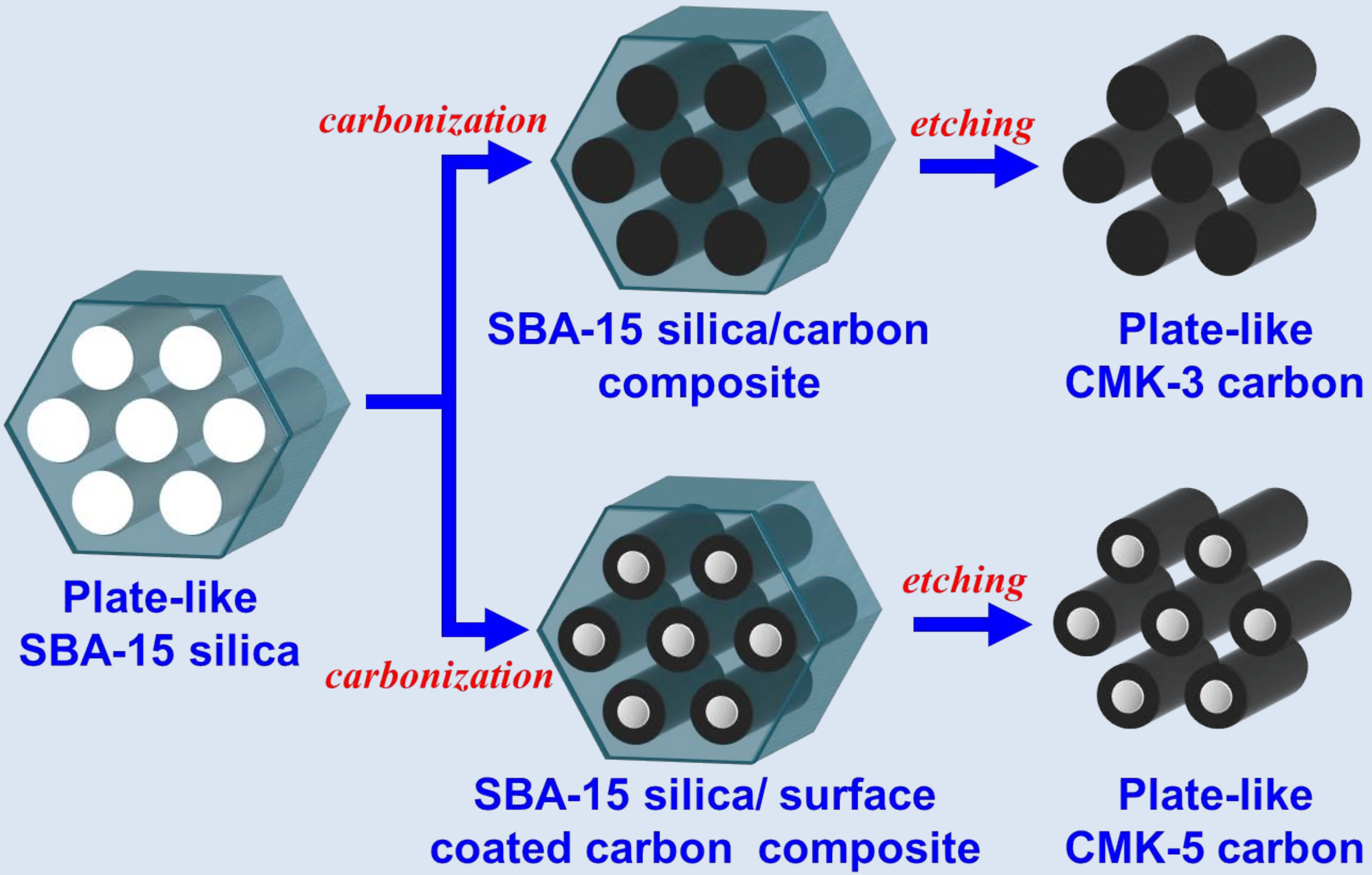
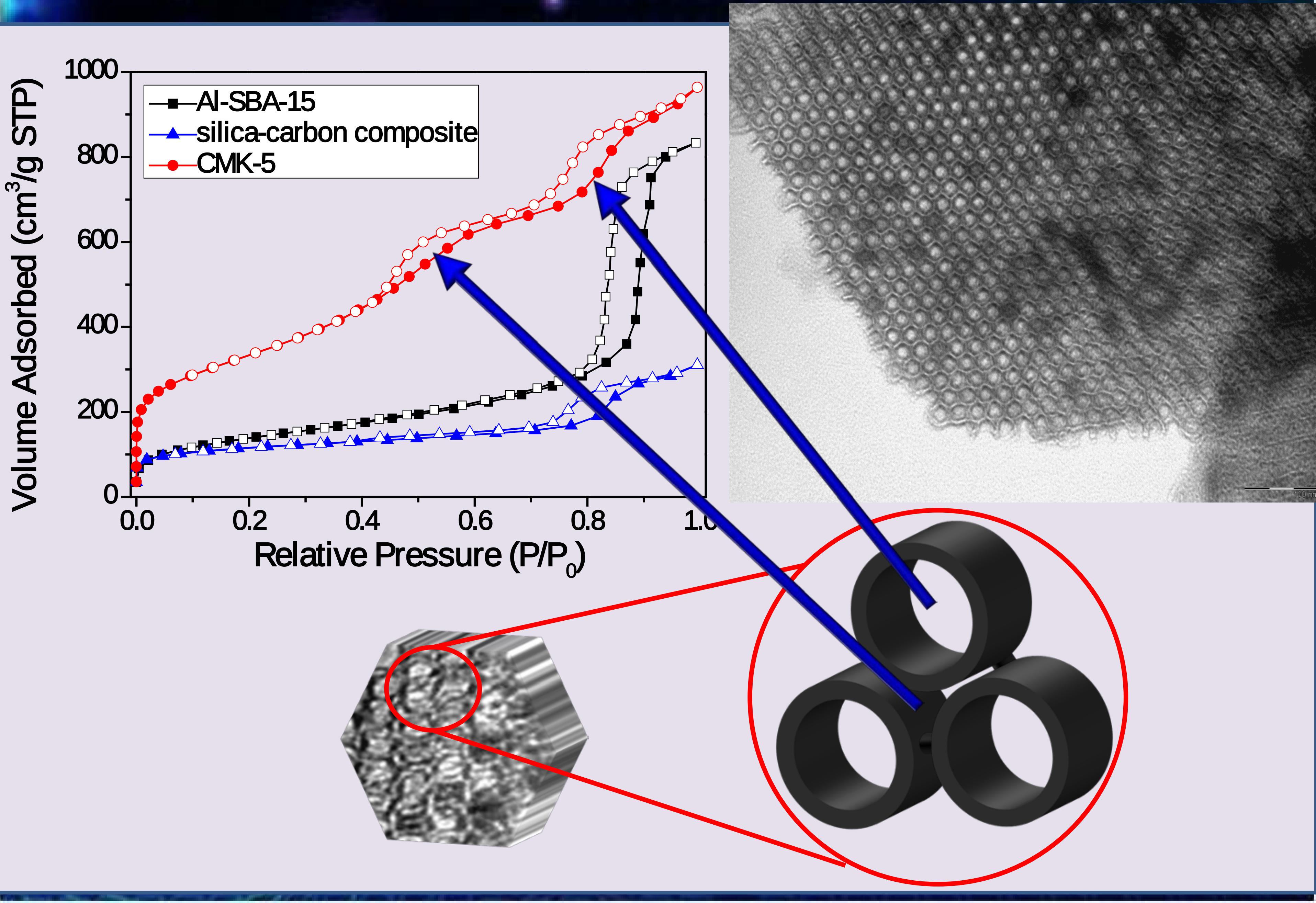
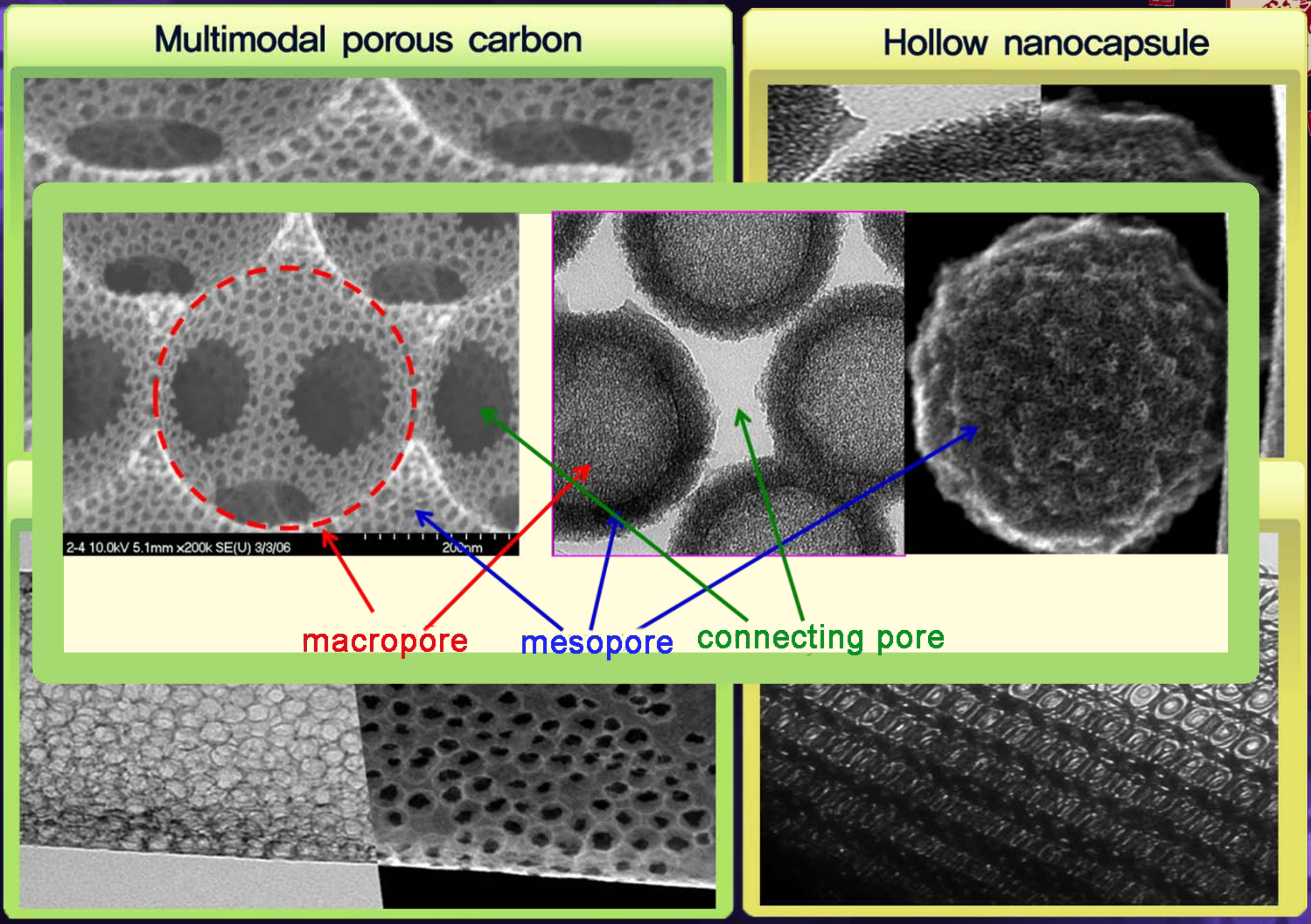


Plate-like CMK-5 carbon



◆ Hierarchical nanostructured carbon



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Seon Young Kwon, Hyuck Soo Choi
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Brain Korea 21
WORLD CLASS UNIVERSITY WCU

Thank you