Multiscale Porous Carbon Materials for Energy Storage

Chengdu Liang

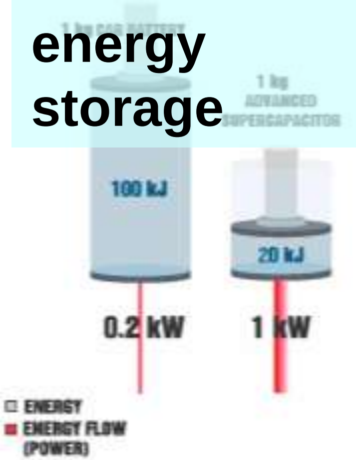
CNMS User Meeting

Sept. 2010

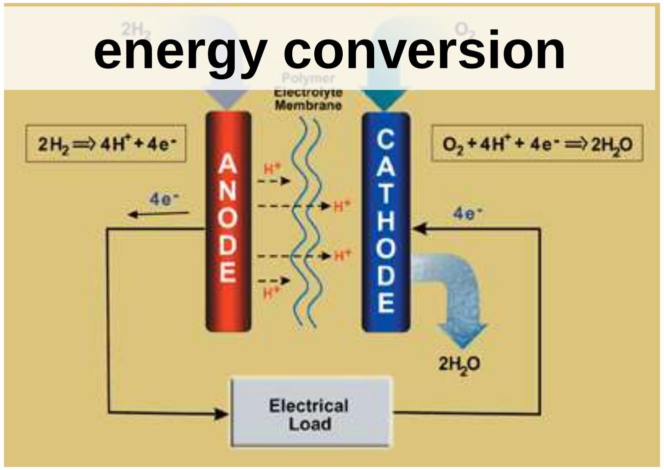
Oak Ridge National Laboratory

Porous Carbon is Important for Energy Applications

energy storage



energy conversion



porous carbon

- Batteries
- Capacitors

Fuel cells

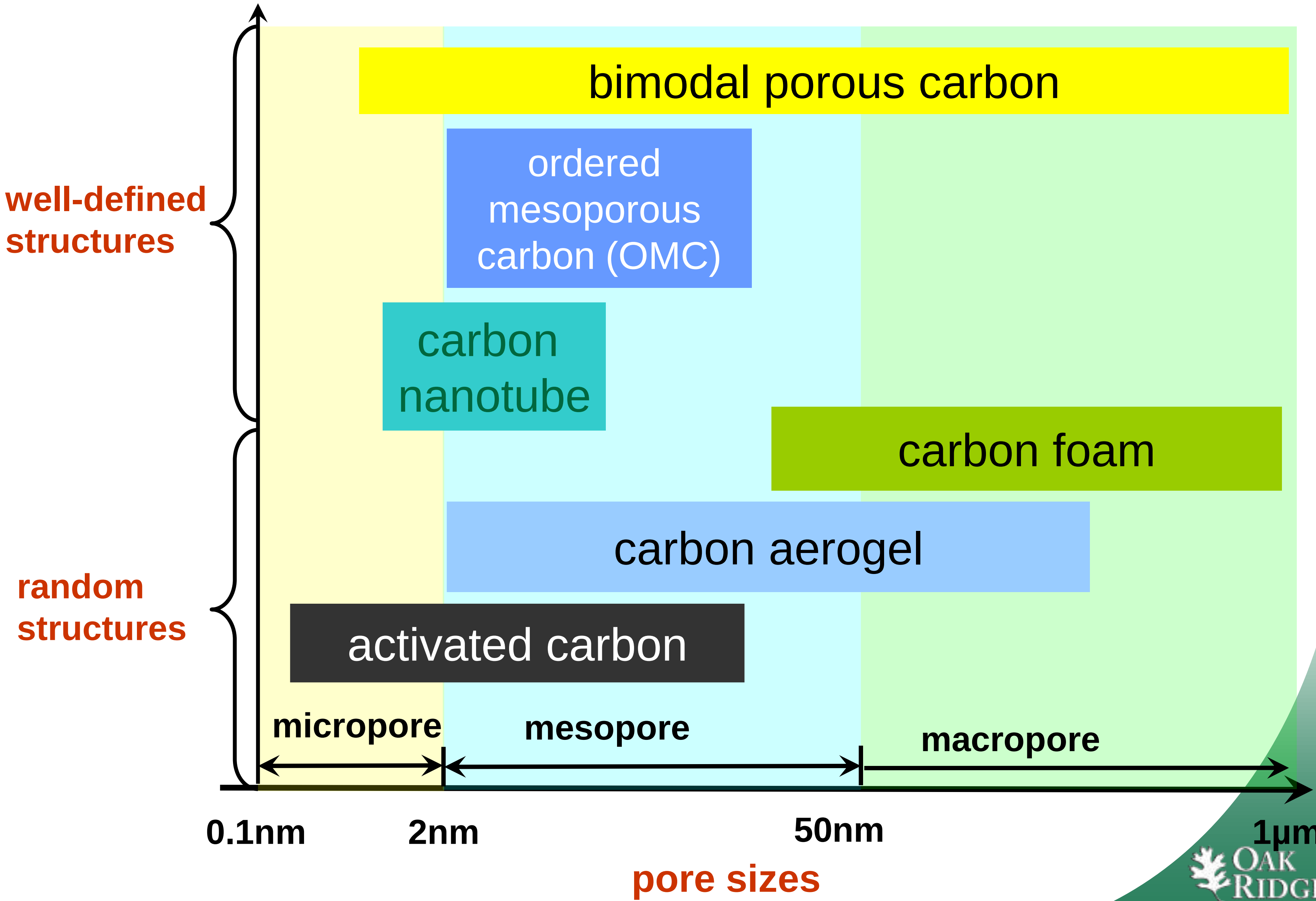
Goal: Tailed mesoporous carbon for energy applications

Outline

- Synthesis of mesoporous carbon materials
  - Soft templates for ordered nanostructures
  - Bimodal macro-mesoporous carbons
  - Bimodal meso-microporous carbons
- Manipulation of physiochemical and interfacial properties
  - Chemical modification of carbon surfaces
- Porous carbon for energy storage
  - Li-S batteries
  - Supercapacitors
- Conclusions and perspectives

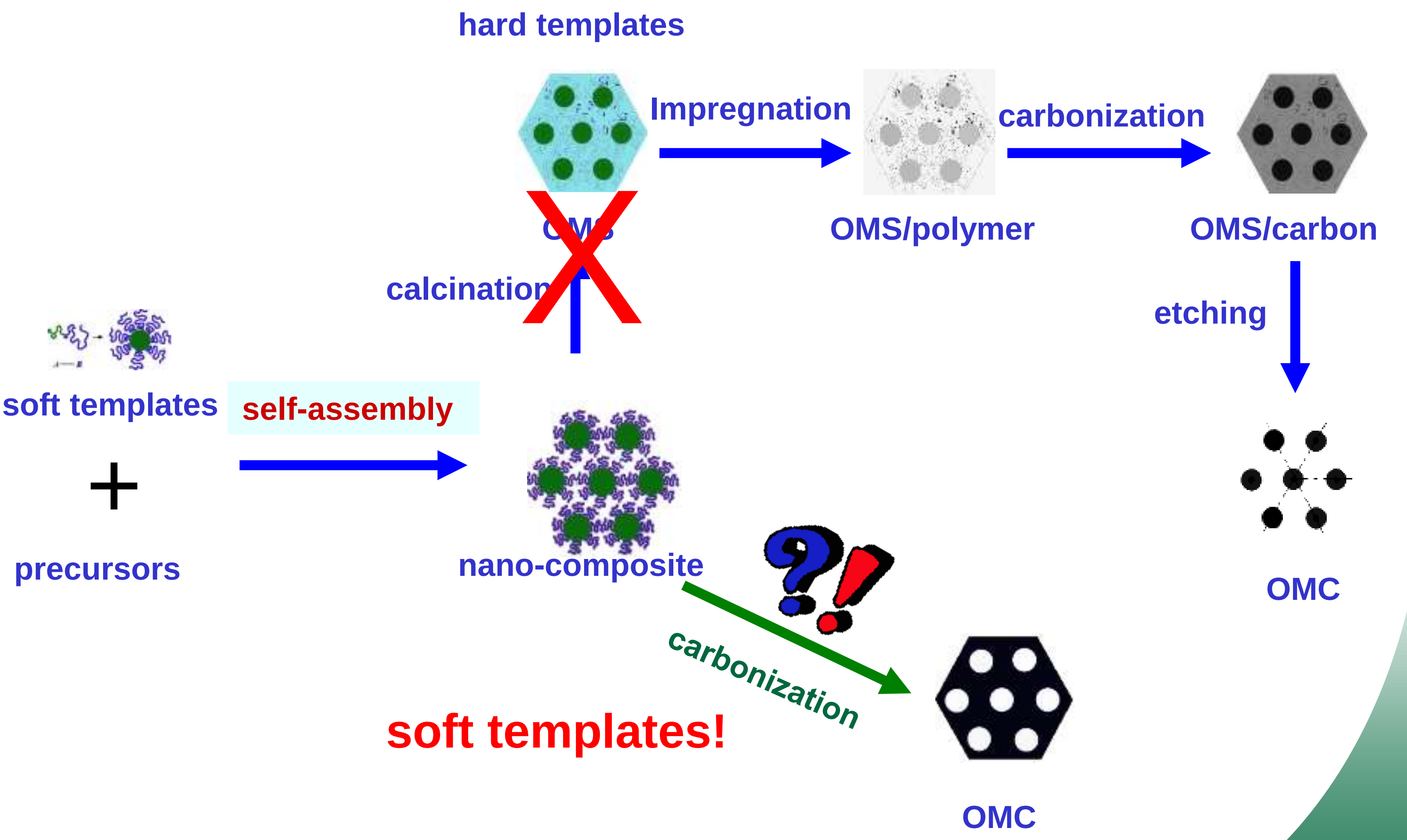
OAK RIDGE National Laboratory

Background of Porous Carbon Materials



OAK RIDGE National Laboratory

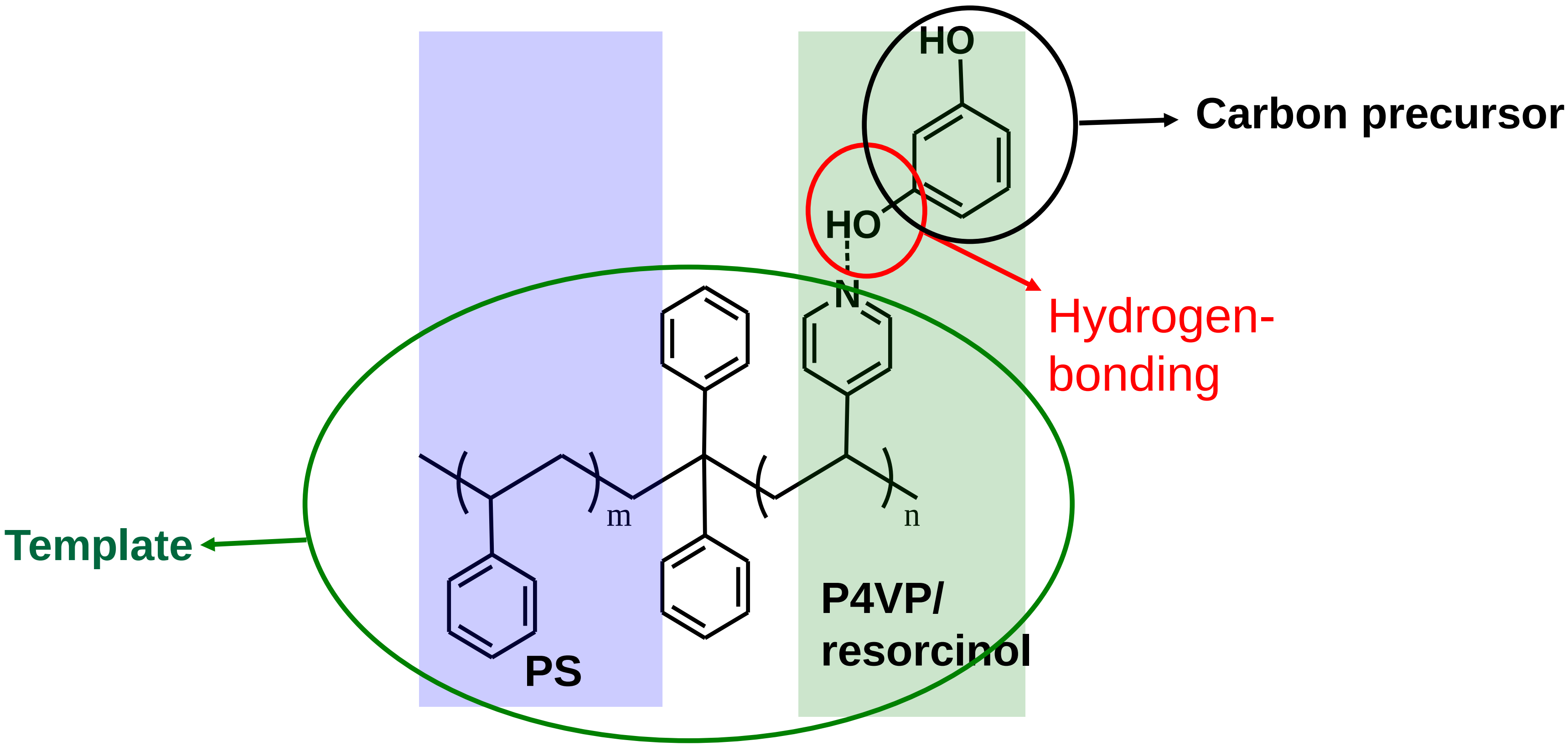
Synthesis of OMCs via Soft Templates



Kresge CT, Leonowicz, Roth WJ, Vartuli JC, Beck JS, *Nature* **1992**, 359, 10834.

Zhao DY, Feng JL, Huo QS, Melosh N, Fredrickson GH, Chmelka BF, Stucky GD, *Science*, **1998**, *227*, 548.

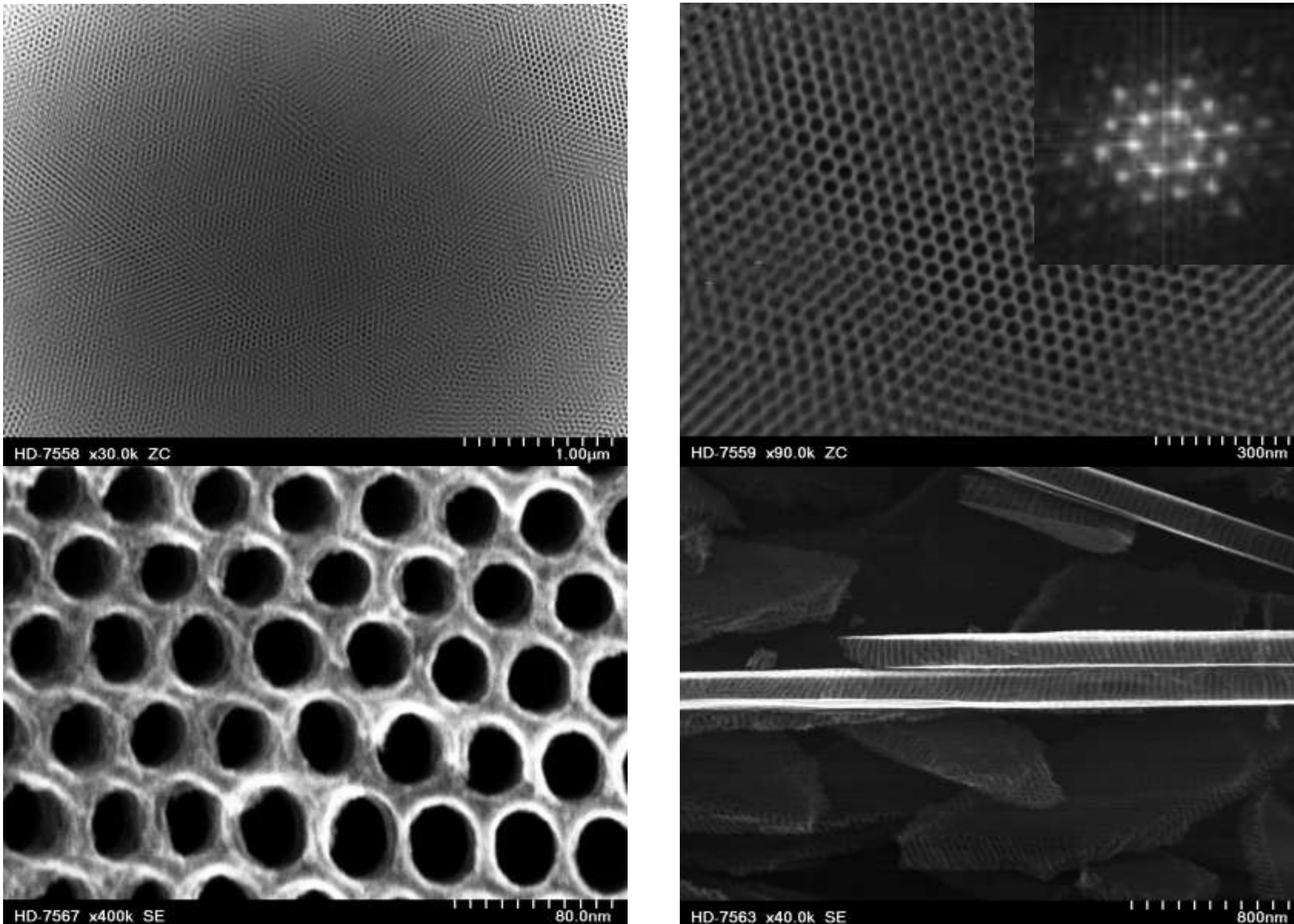
Synthesis of OMC(I): Hydrogen-bonding Directed Self-Assembly of PS-b-P4VP/Resorcinol Blends



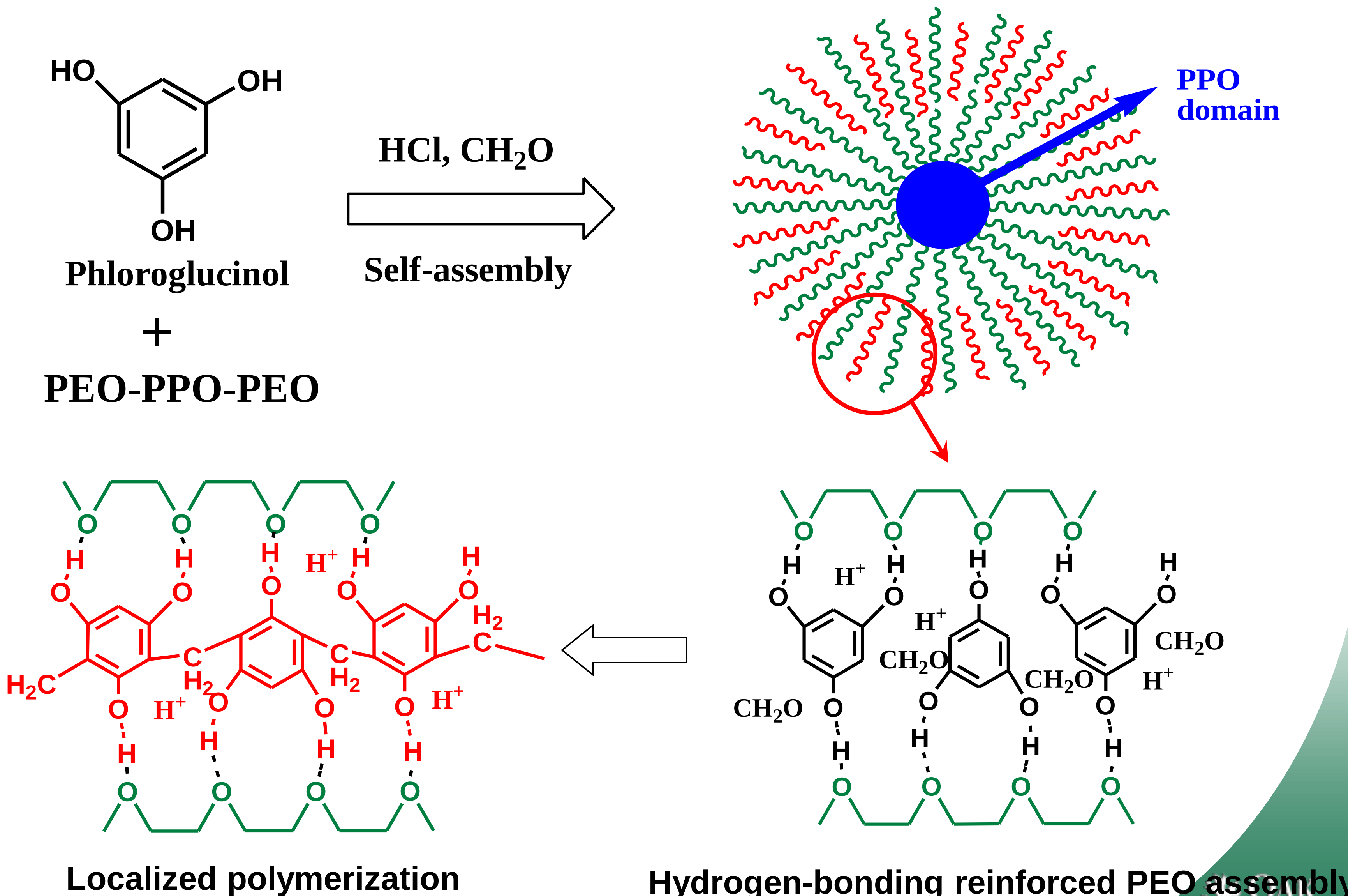
Microphase separation with Hydrogen-bonding associated small molecules

Liang, C. D.; Hong, K. L.; Guiochon, G. A.; Mays, J. W.; Dai, S., *Angew. Chem.-Int. Edit.* **2004,** *43*, 5785;
Dai, S.; Liang, C. US patent 2006 057051

Highly Ordered Mesoporous Carbon Film

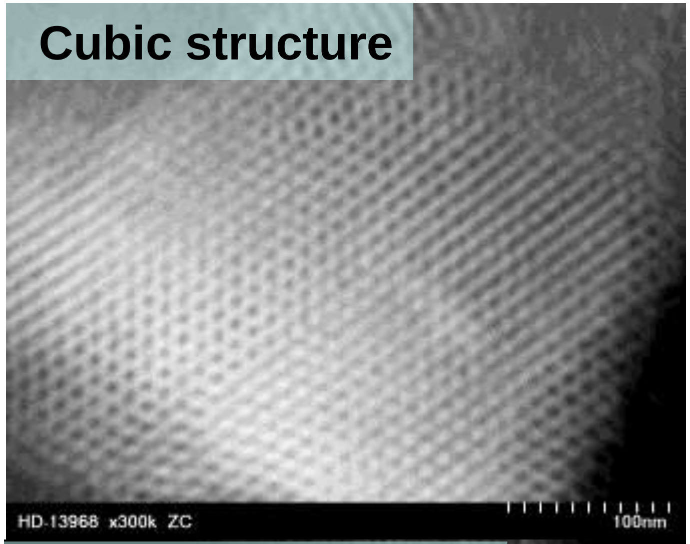


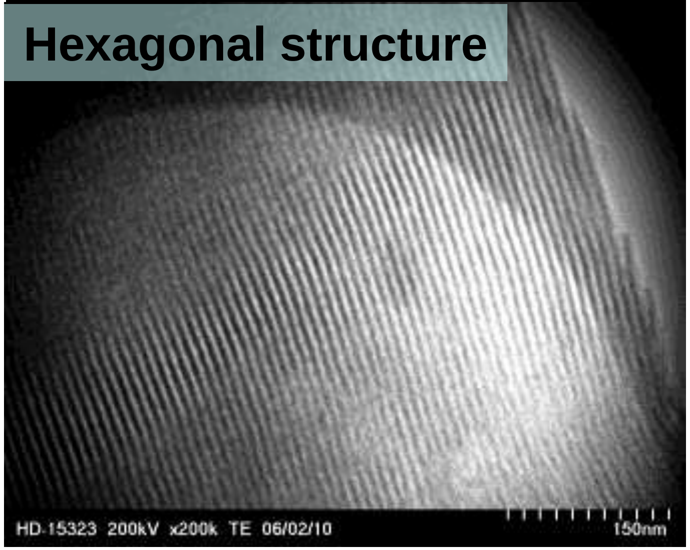
Synthesis of OMCs(II): One-Pot Synthesis of OMCs via Enhanced Hydrogen-bonding

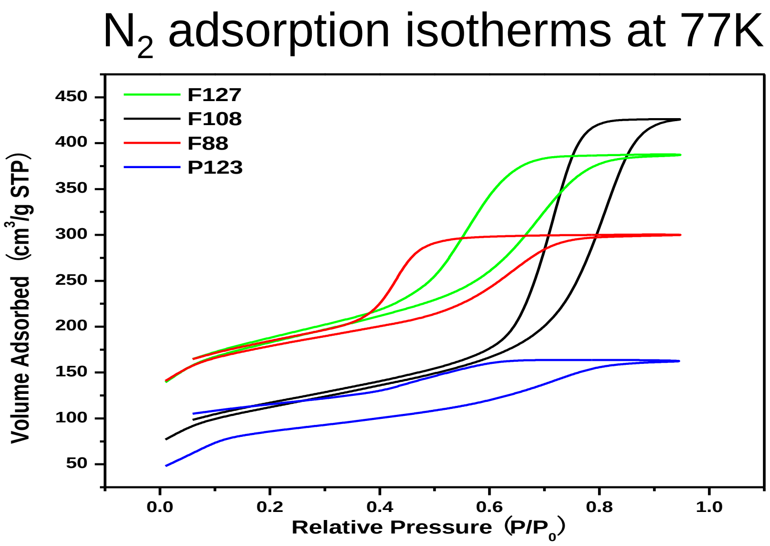


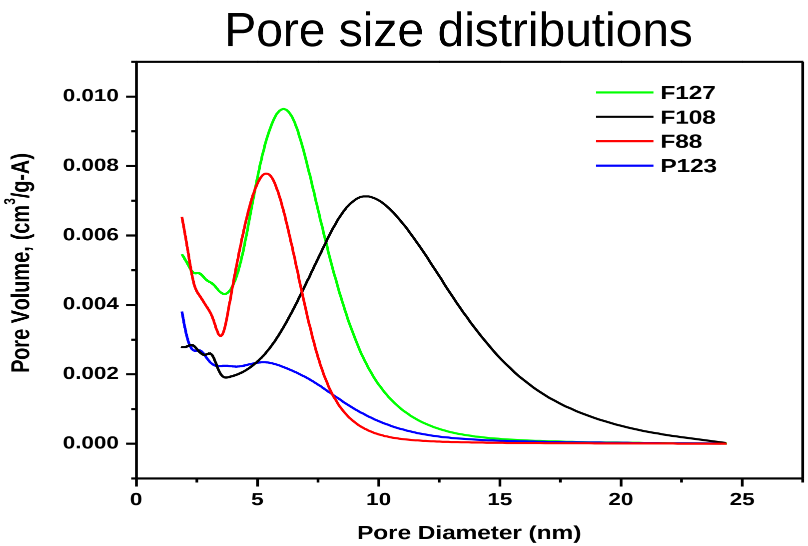
Liang, C. D.; Dai, S., *J. Am. Chem. Soc.* **2006,** *128*, 5316

Tunable Porous Structure





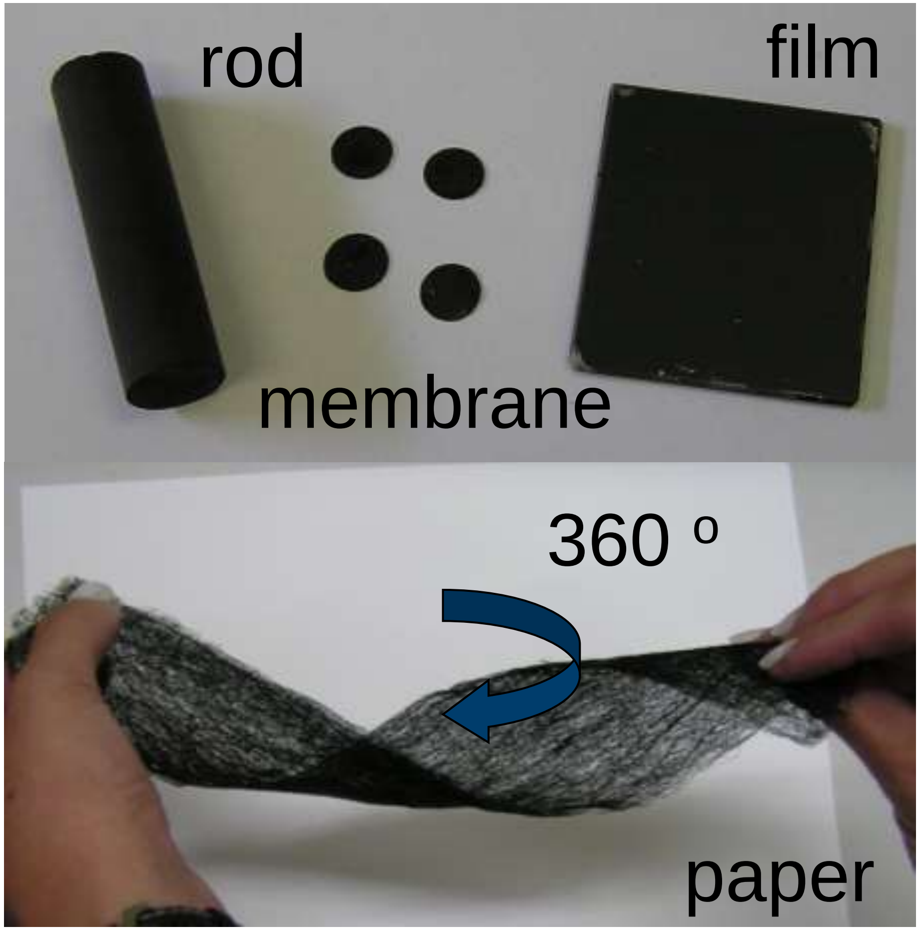




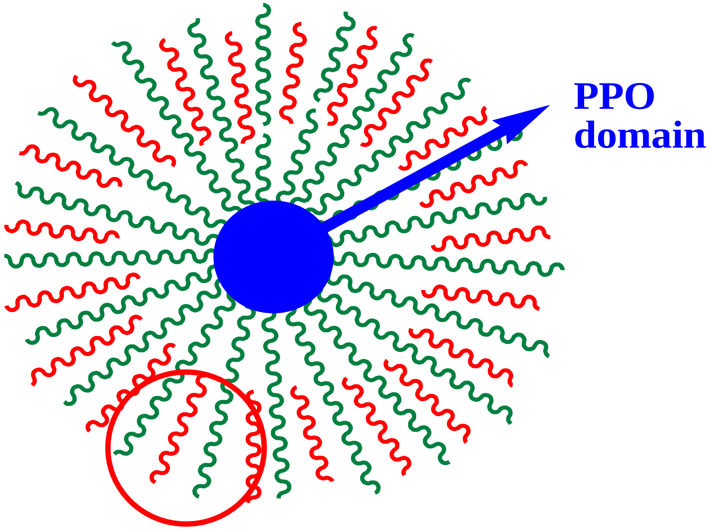
The templates determine the size and structure of mesoporous carbon

Oak Ridge National Laboratory

Various forms of OMCs



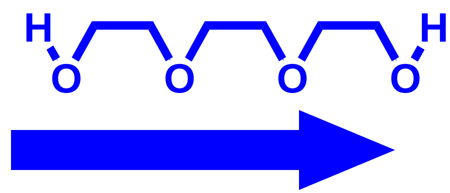
Synthesis of Bimodal Macro-MesoPorous Carbons by Dual Phase Separation



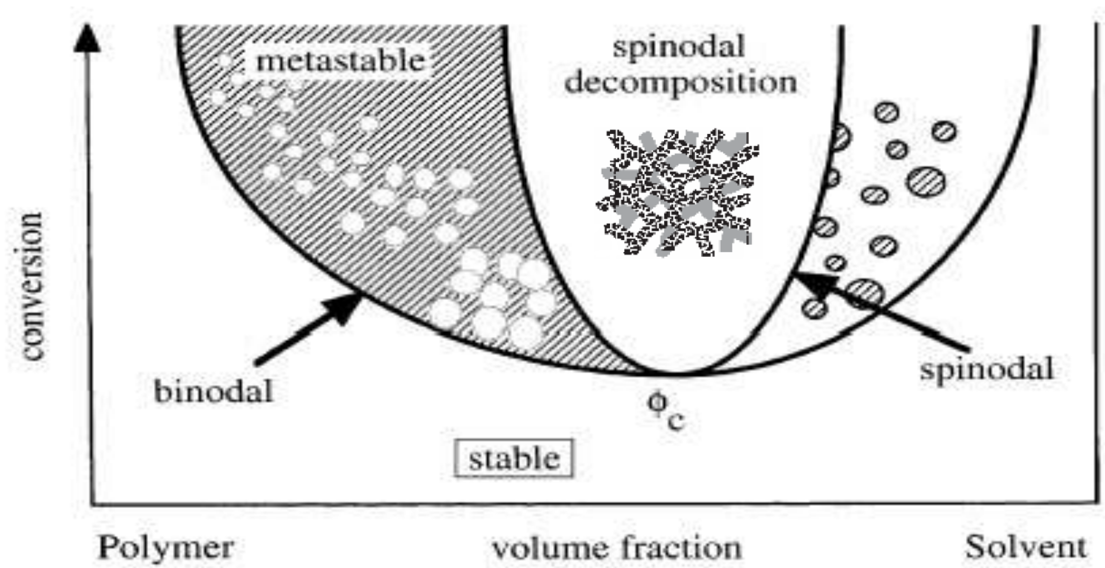
PEO + PF

1st PS: microphase separation

TEG



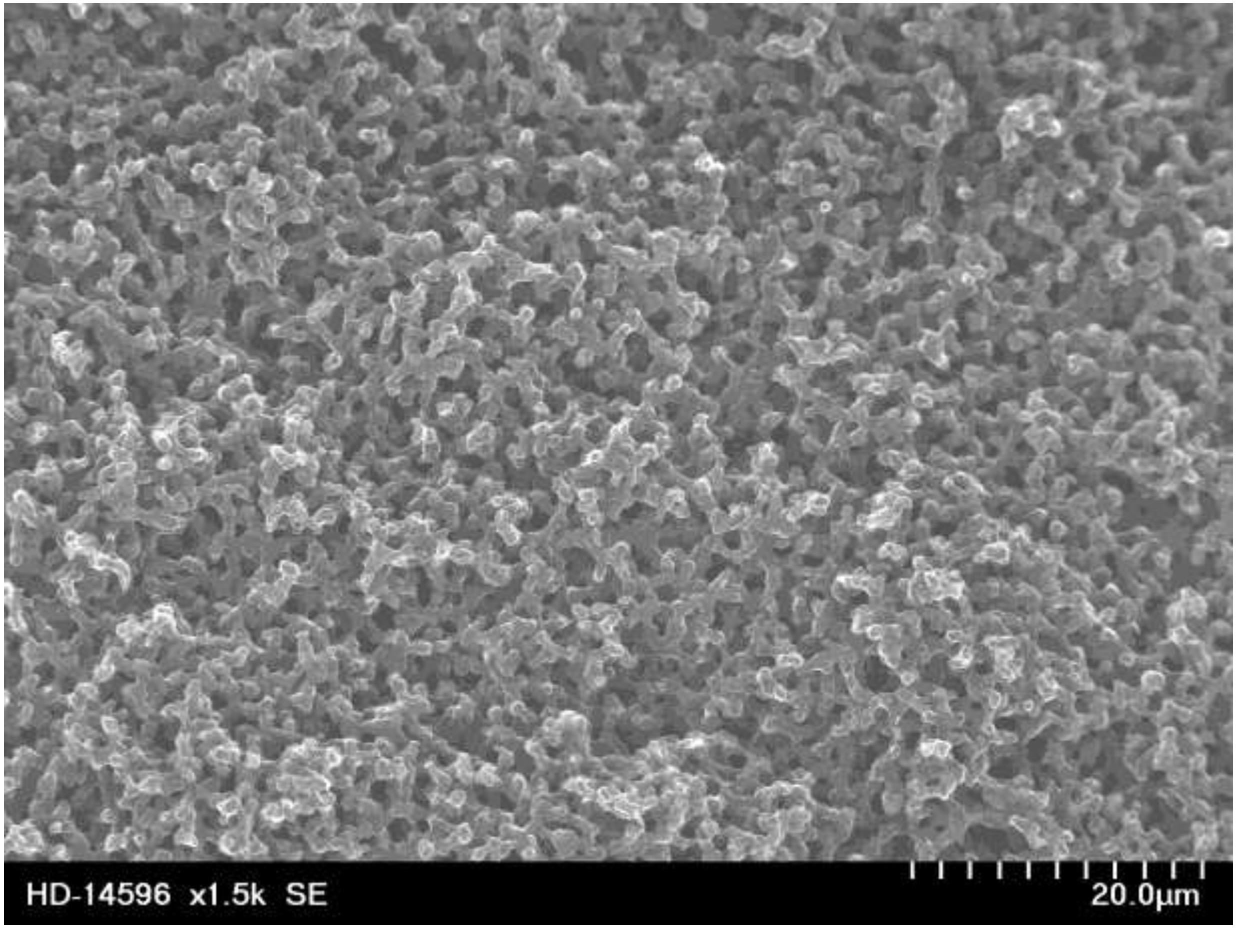
2nd PS: spinodal decomposition



I. W. Hamley, *Introduction to Soft Matter*, John Wiley & Sons: New York, 2000

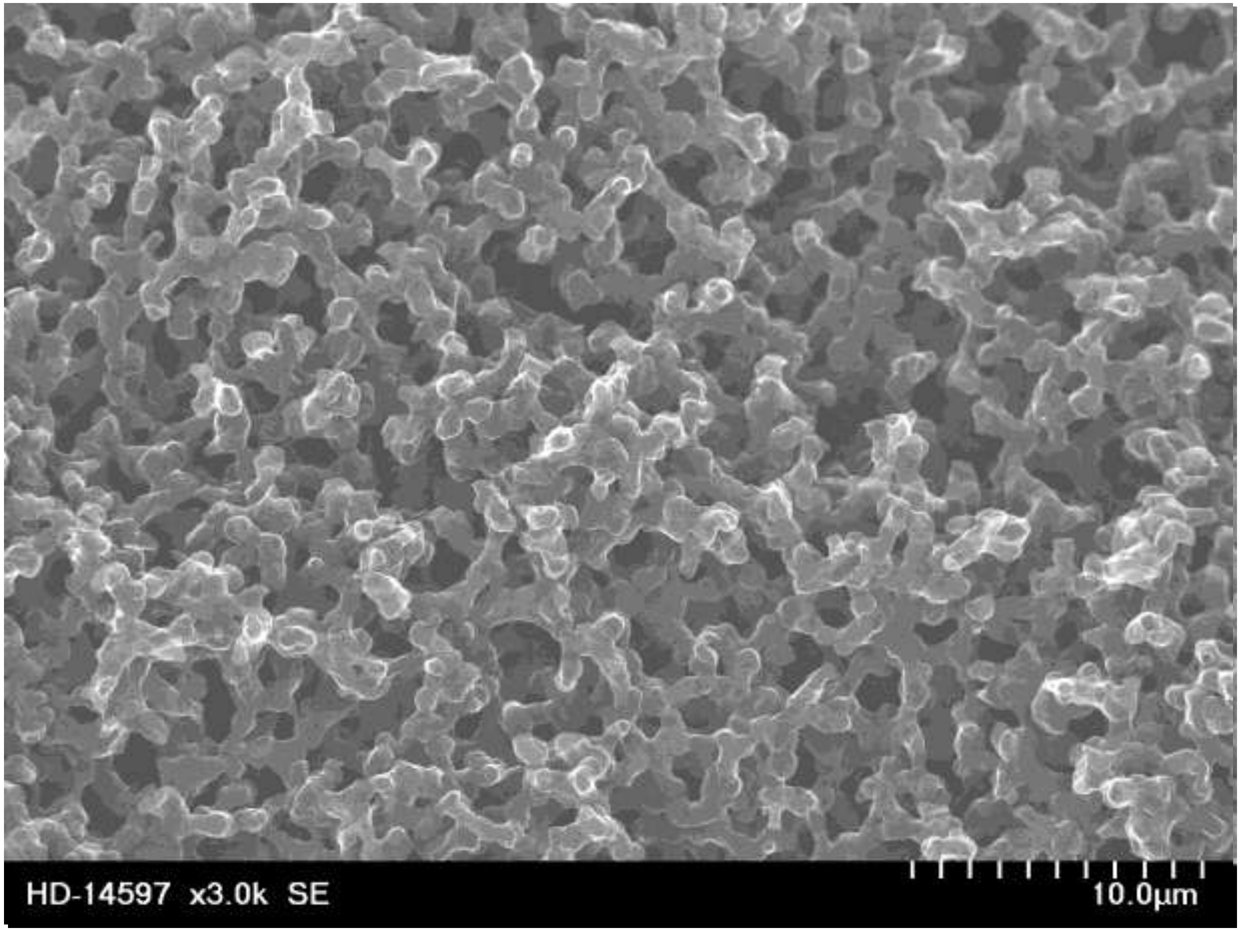
Oak Ridge National Laboratory

“Pore-in-Pore”



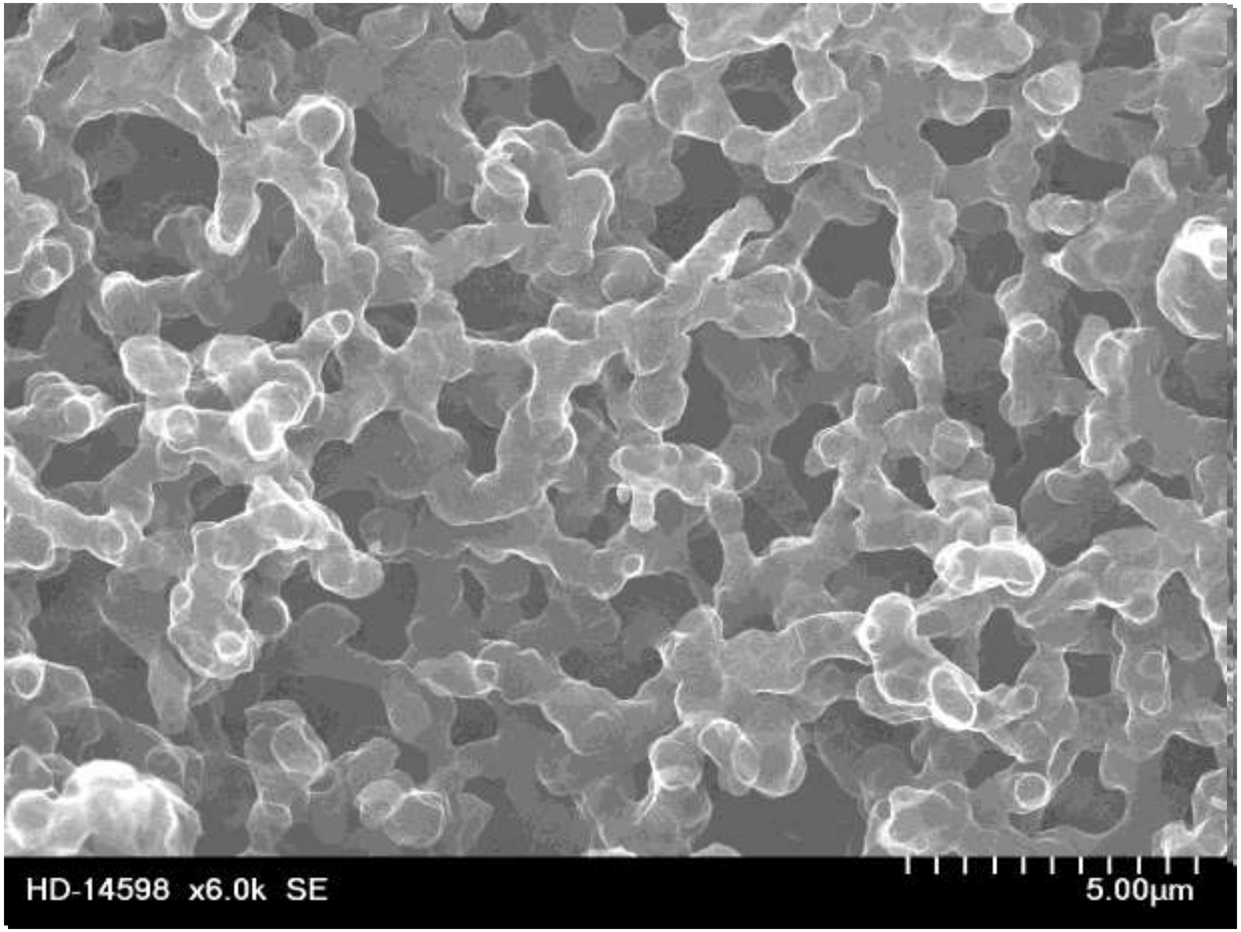
Liang and Dai, *Chemistry of Materials*, 2009, 2125

“Pore-in-Pore”



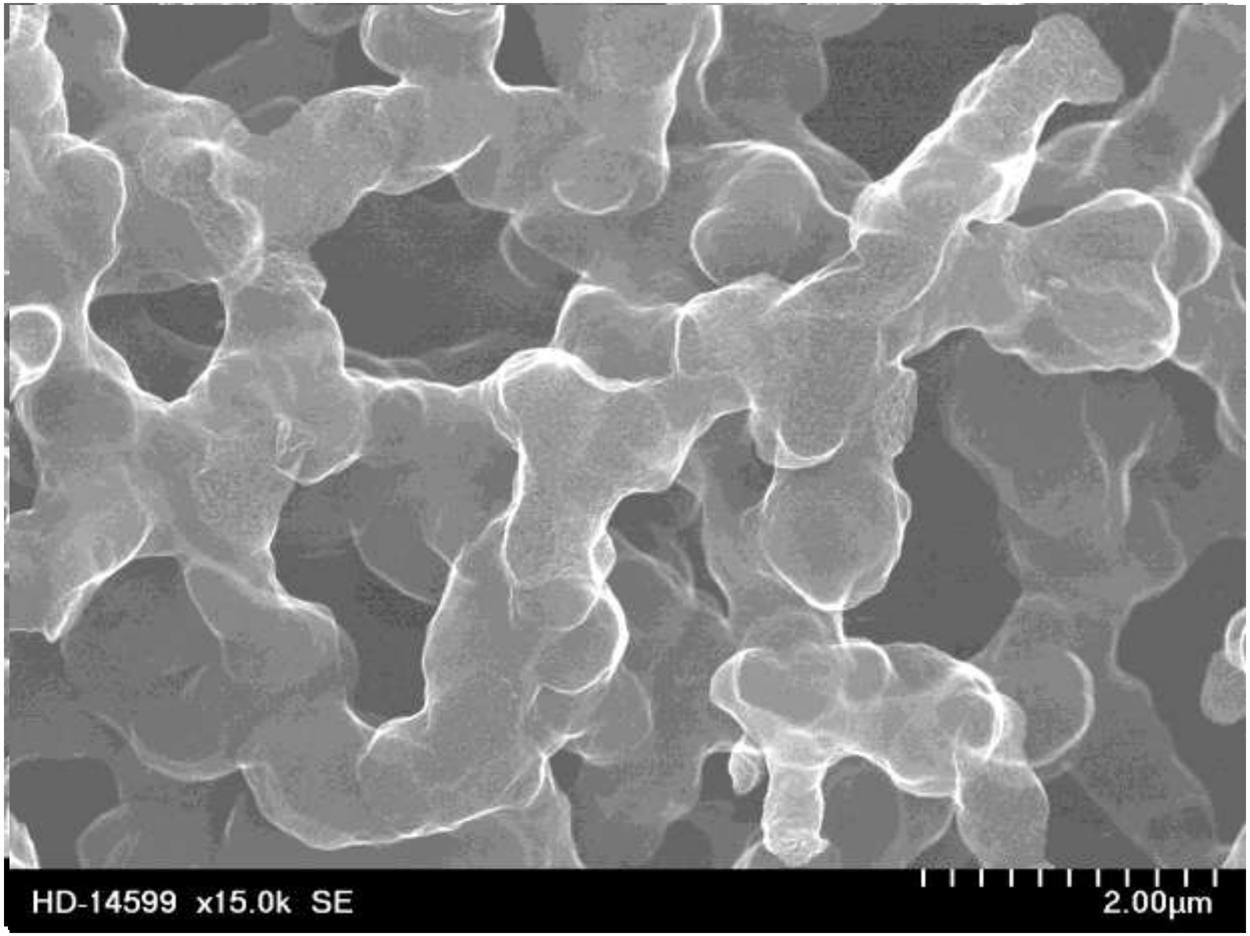
Liang and Dai, *Chemistry of Materials*, 2009, 2125

"Pore-in-Pore"



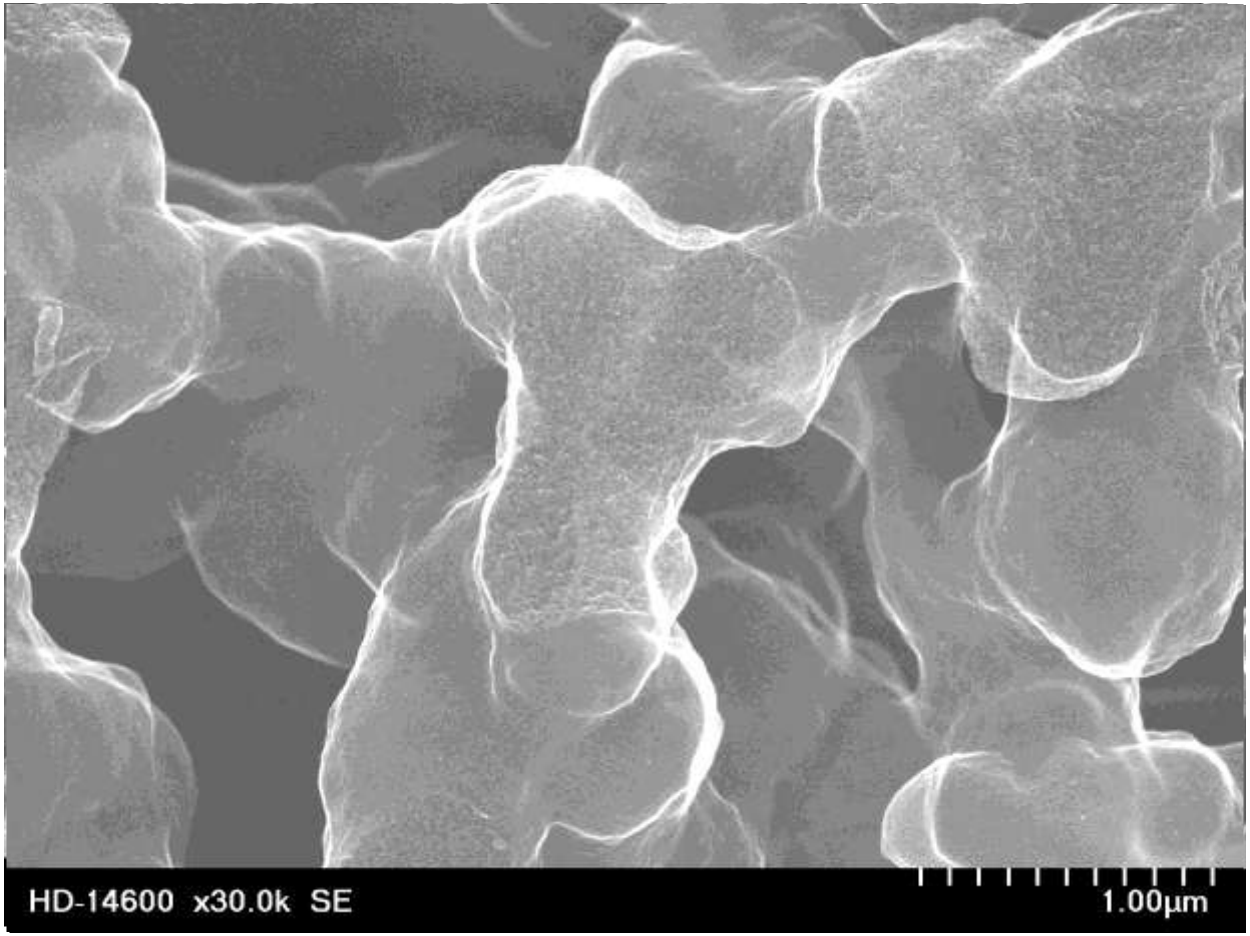
Liang and Dai, *Chemistry of Materials*, 2009, 2125

“Pore-in-Pore”



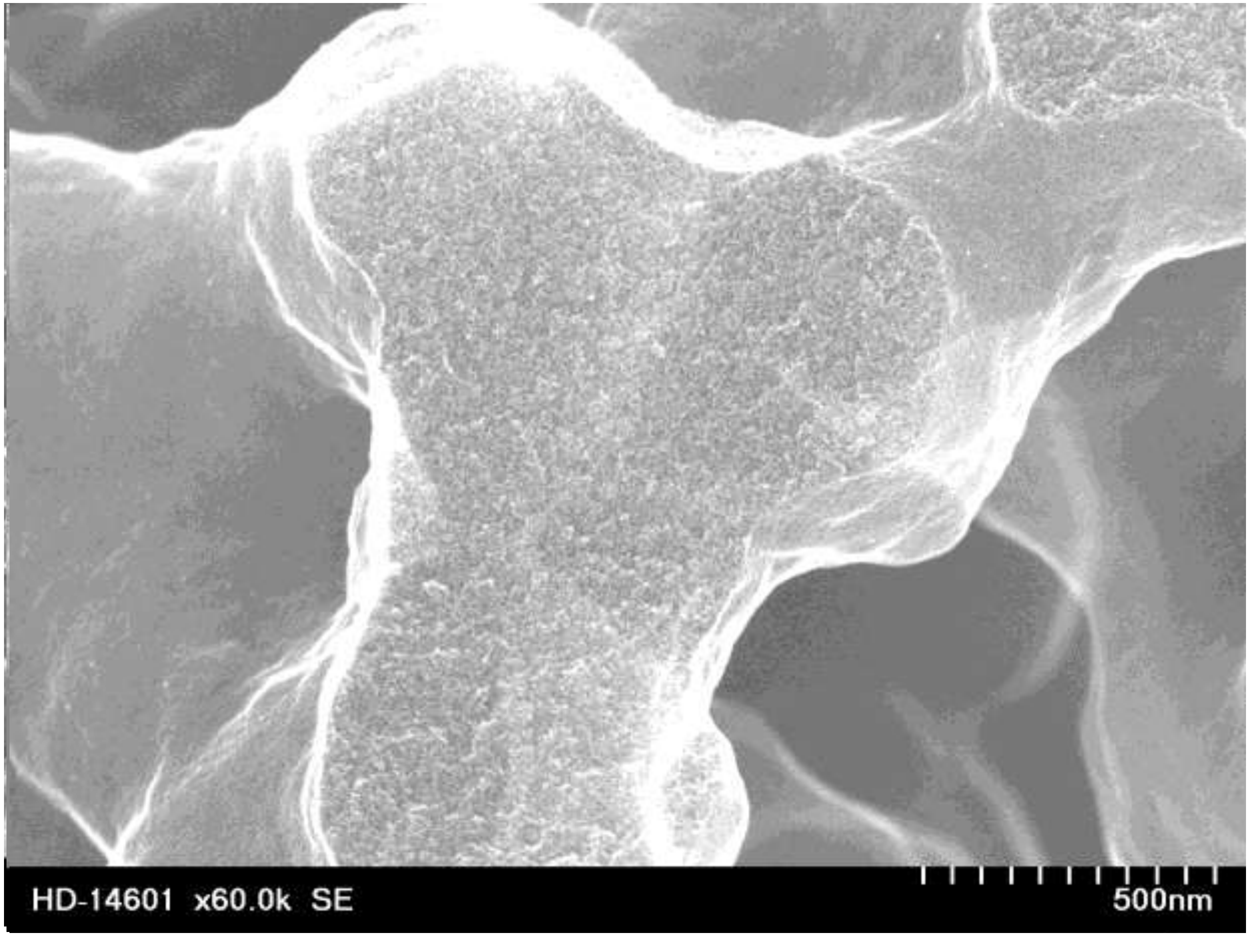
Liang and Dai, *Chemistry of Materials*, 2009, 2125

"Pore-in-Pore"



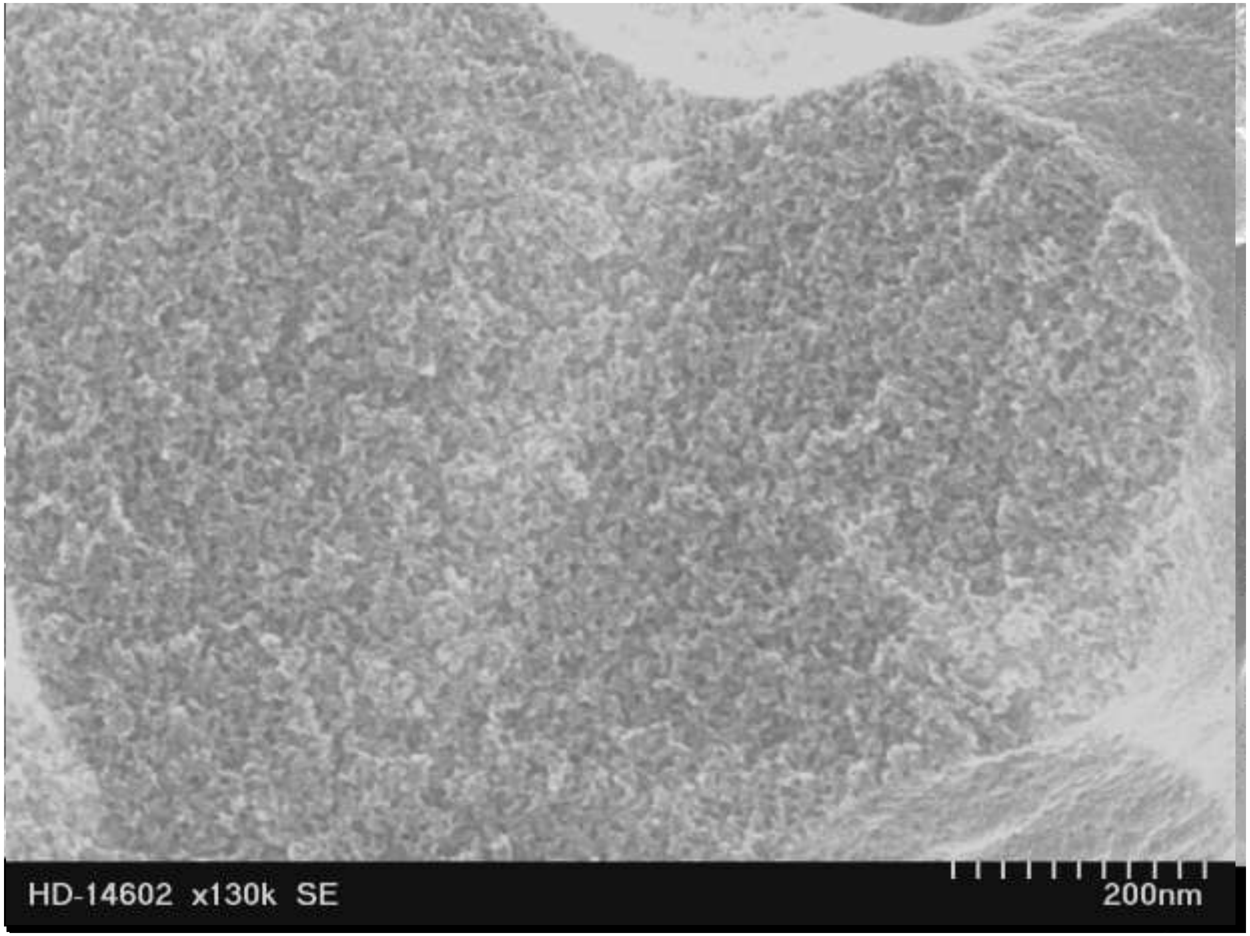
Liang and Dai, *Chemistry of Materials*, 2009, 2125

"Pore-in-Pore"



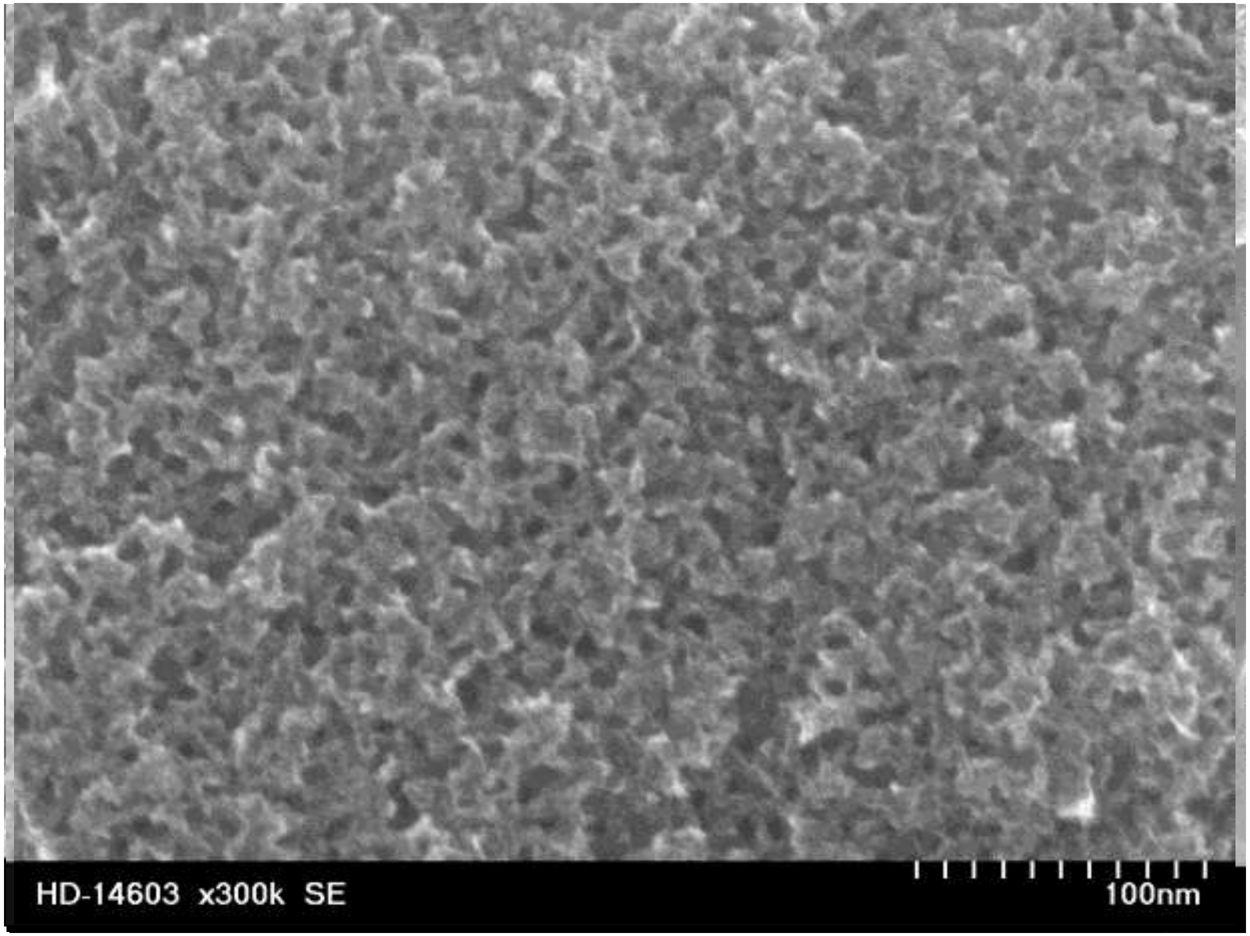
Liang and Dai, *Chemistry of Materials*, 2009, 2125

“Pore-in-Pore”



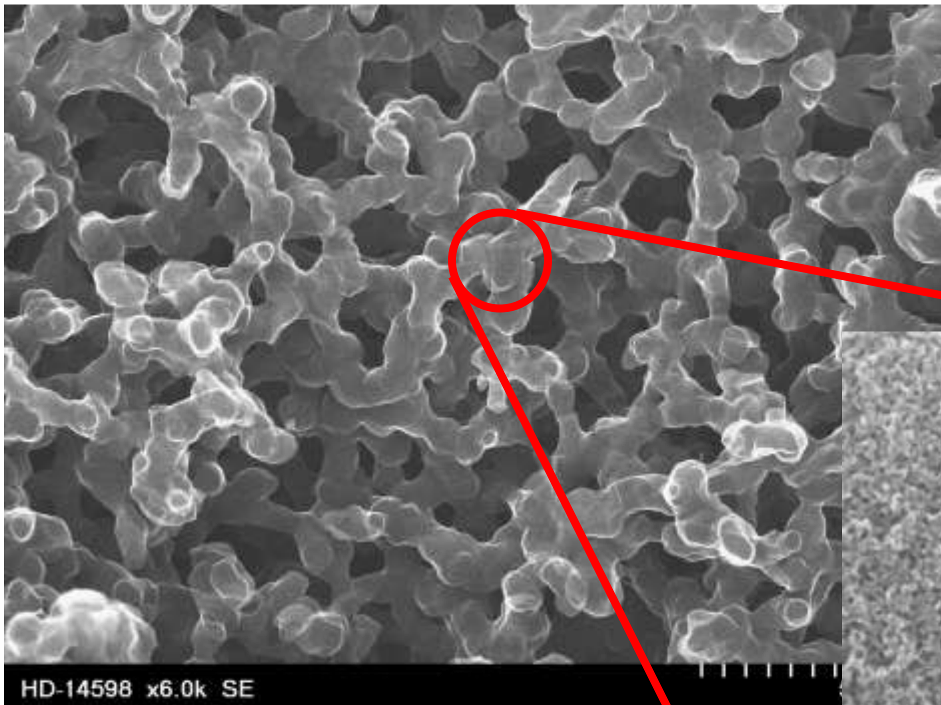
Liang and Dai, *Chemistry of Materials*, 2009, 2125

"Pore-in-Pore"



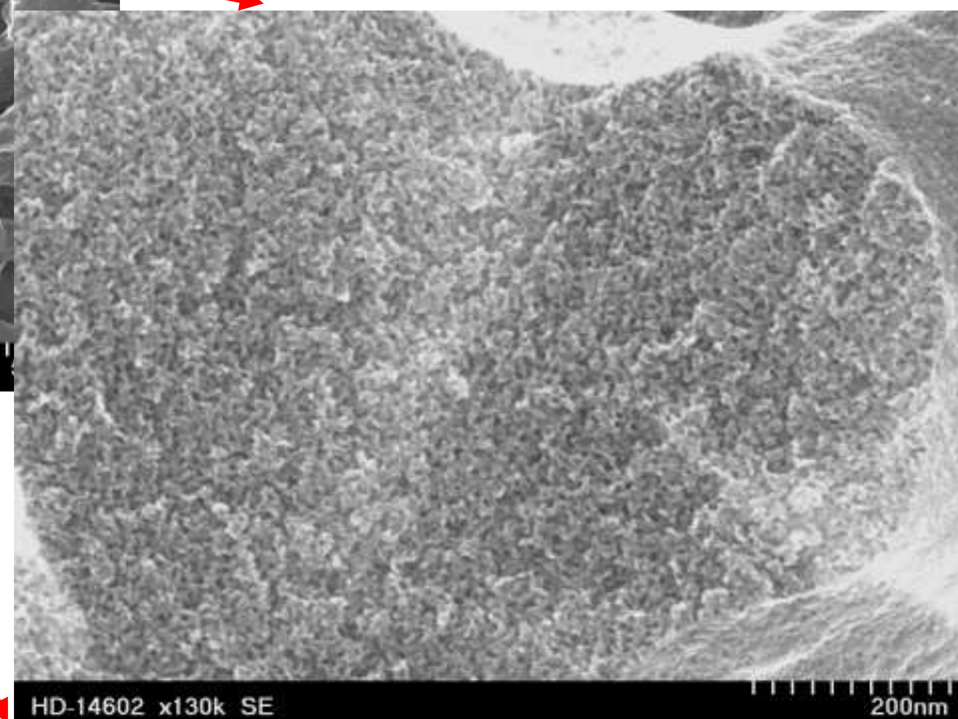
Liang and Dai, *Chemistry of Materials*, 2009, 2125

“Pore-in-Pore”



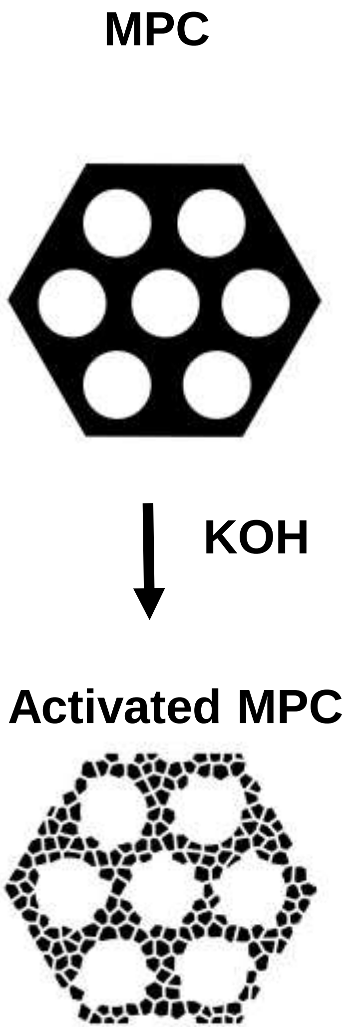
Macropores resulting from spinodal decomposition

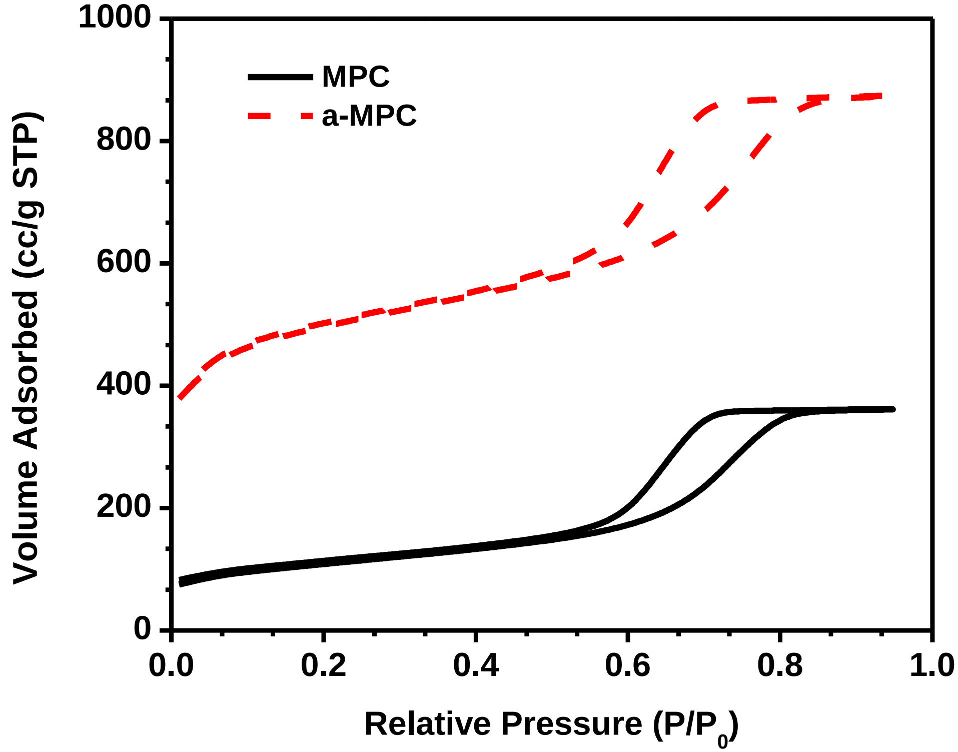
Mesopores resulting from microphase separation



Liang and Dai, *Chemistry of Materials*, 2009, 2125

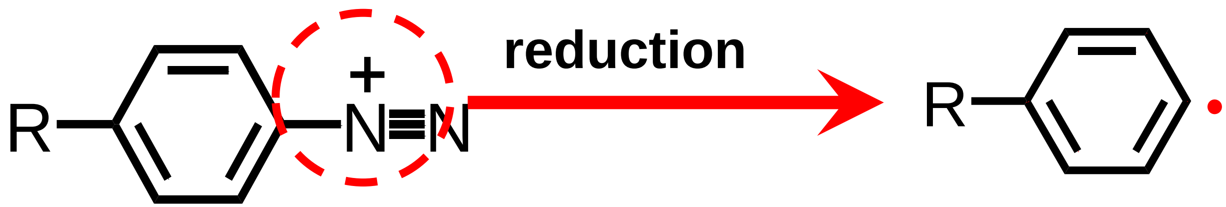
Synthesis of Bimodal Meso-MicroPorous Carbons by Activation



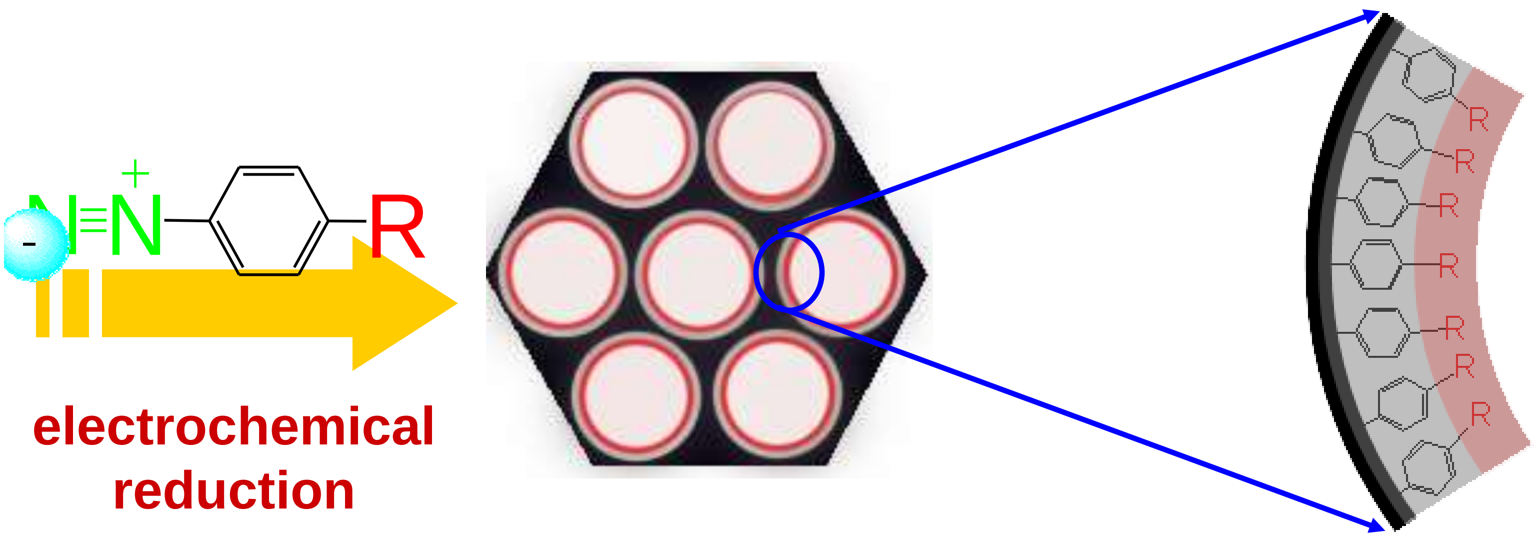


The mesopores unchanged after activation.

Diazonium Chemistry Enables Covalent Modification of OMCs



Delamar M.; Hitmi R.; Pinson J.; Saveant J.M. *J. Am. Chem. Soc.* **1992**, 114, 5883

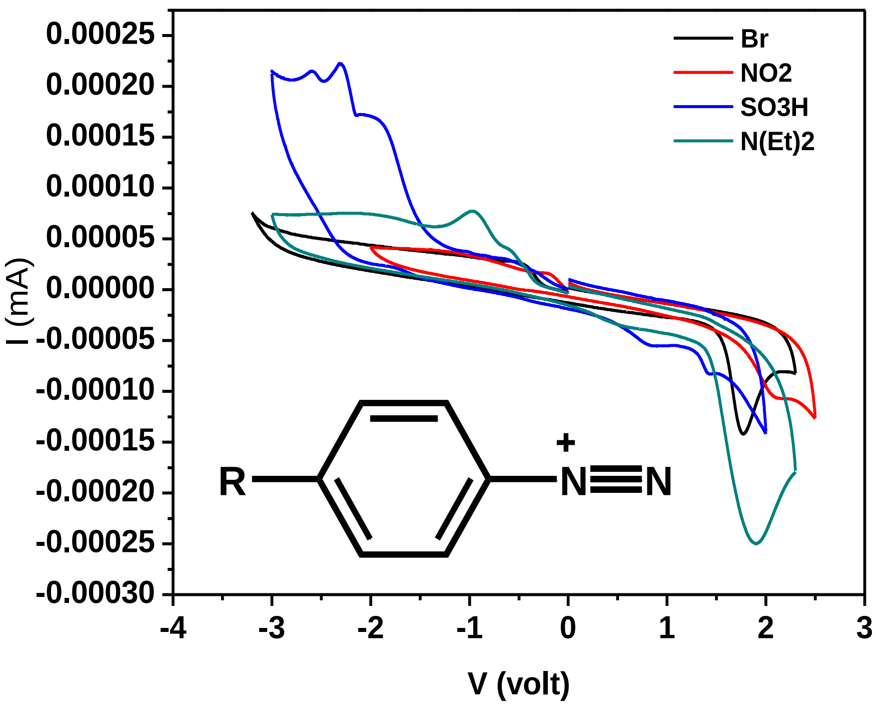


Liang, C. D.; Huang, J. F.; Li, Z. J.; Luo, H. M.; Dai, S., *Eur. J. Org. Chem.* **2006**, 3, 586

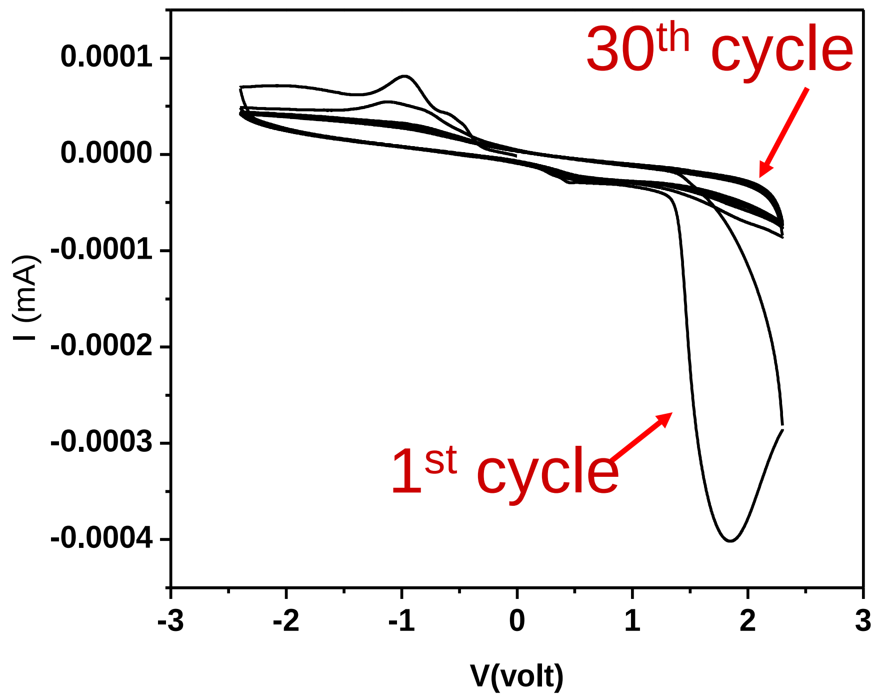
OAK RIDGE National Laboratory

Electrochemical Modification: Simple, Easy Approach to Functionalized OMCs

cyclovoltammograms



R= Br, NO_2, SO_3H, $N(Et)_2$



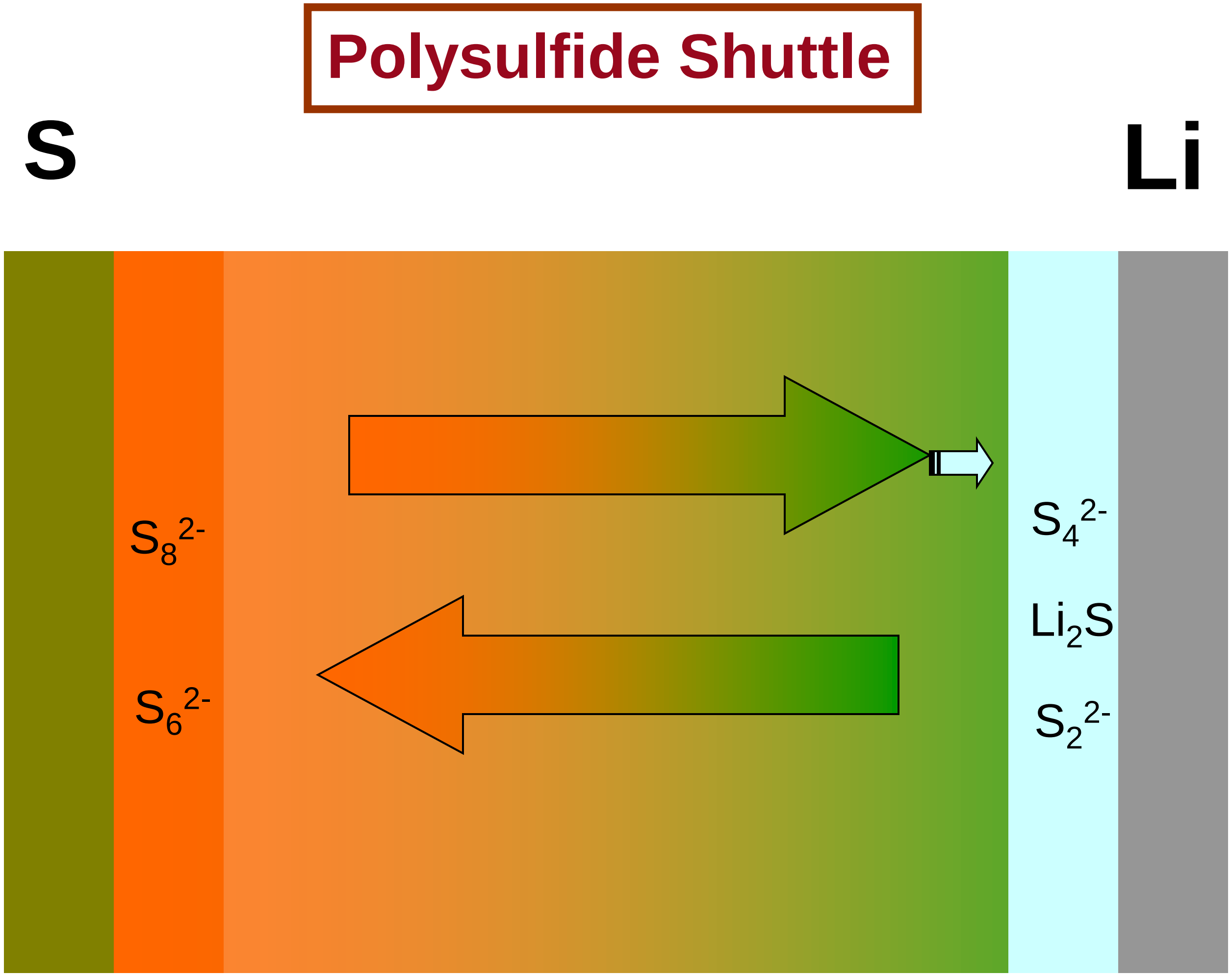
30 cycles in R, $N(Et)_2$

Application 1

High-Energy Li-S Batteries

- Retain sulfur at the cathode
- High utilization of active materials
- Long cycle-life

Why Li/S can't cycle long?



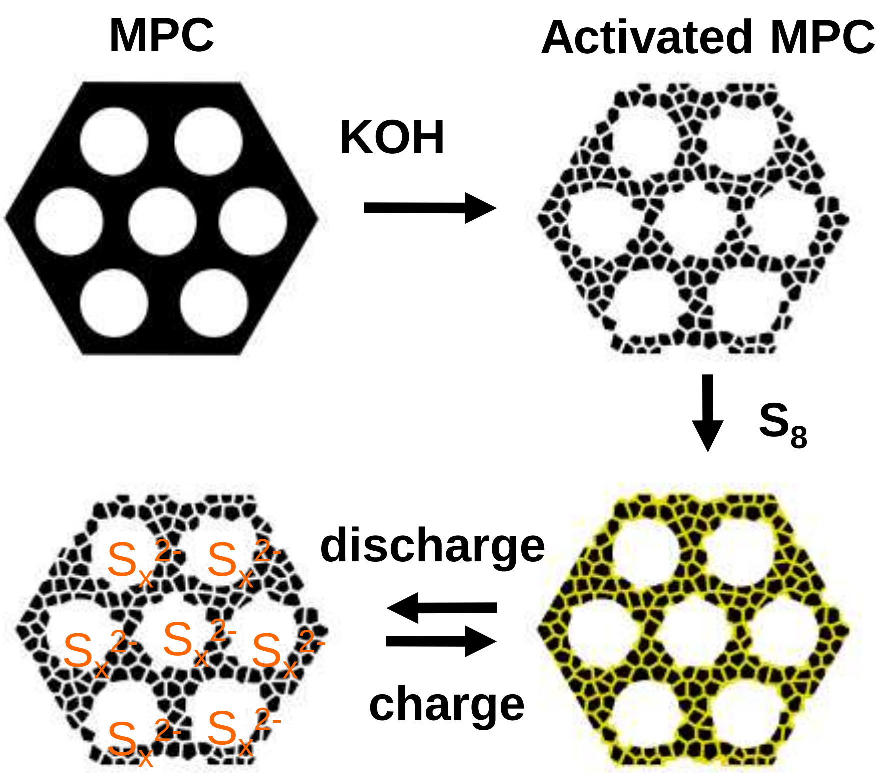
•Self-discharge
•Capacity fading
•Cell resistance increase
•Poor cyclability

•Passivate Li anode
•Decrease the diffusivity of ions
  •Gel electrolytes
  •Solid electrolytes
•Physically absorb S
  •High surface area carbons
  •Conducting polymers
•Chemically immobilize S
  •S-polymers
  •S-salts

1) Cheon, S. E.; Choi, S. S.; Han, J. S.; Choi, Y. S.; Jung, B. H.; Lim, H. S. *Journal of the Electrochemical Society* 2004, *151*, A2067-A2073. 2)Mikhaylik, Y. V.; Akridge, J. R. *Journal of the Electrochemical Society* 2004, *151*, A1969-A1976.

Retain S at Cathode

- **S/C composites by using bimodal porous carbon**
  - **Physical confinement of S in < 2nm pores**
  - **Electronic contact of S**
  - **Adsorption of polysulfides**

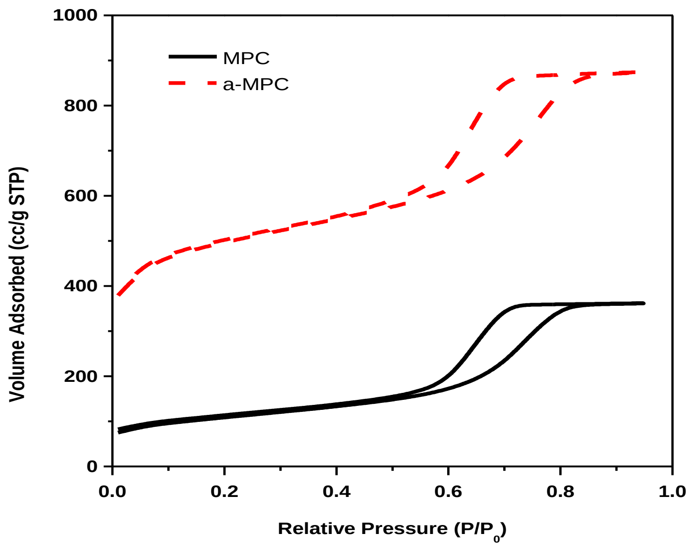


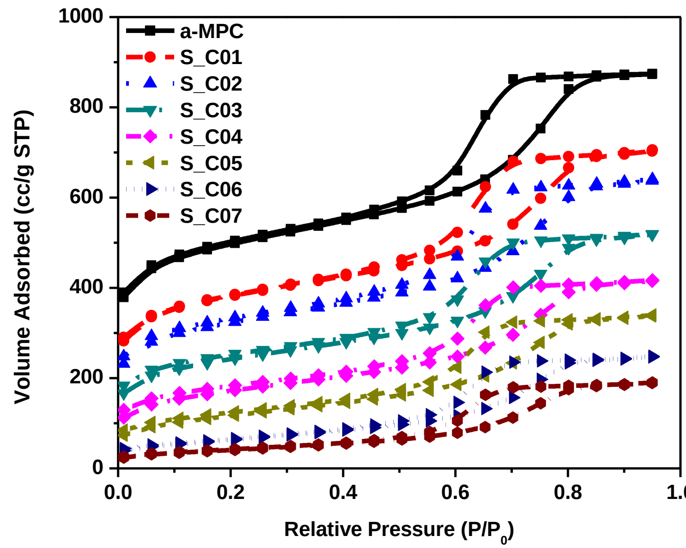
Micropores (<2nm): host site for S
Mesopores (2-50 nm): path for Li^+ transport

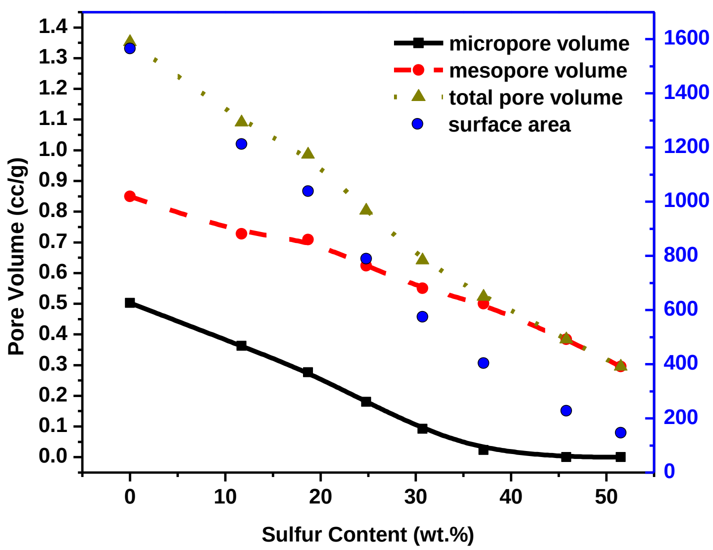
Liang, Dudney, and Howe, *Chemistry of Materials* 2009, 4724

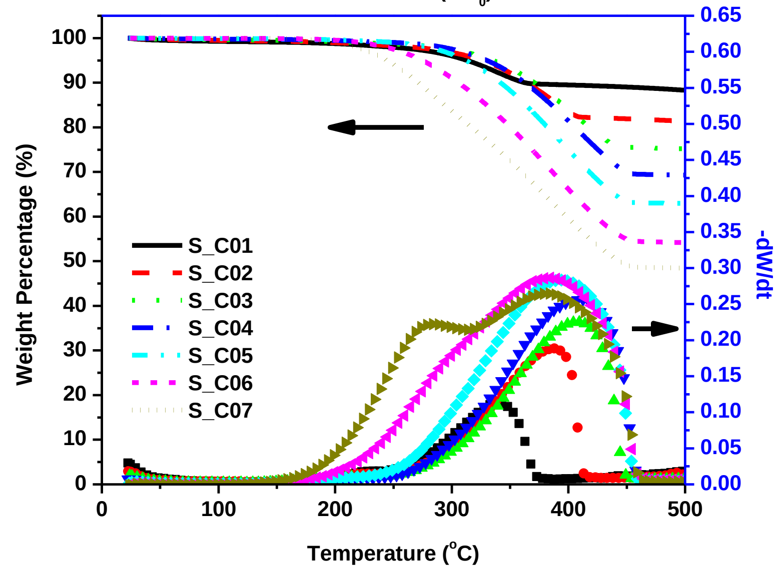
OAK RIDGE National Laboratory

Sulfur Infiltration in Micropores



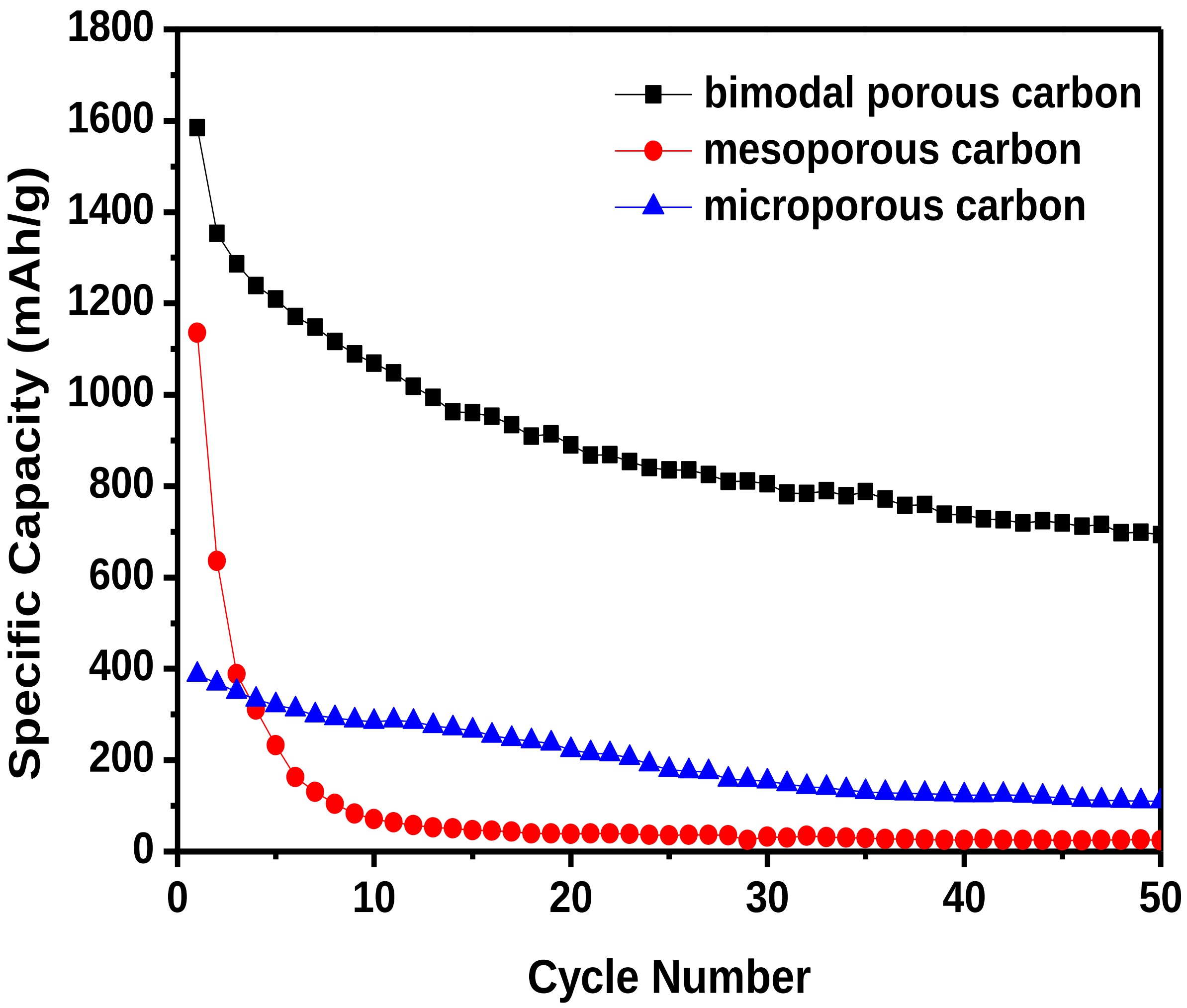






OAK RIDGE
National Laboratory

Nanostructure of S/C Composites Is Key to Retaining S at Cathode



Nano-engineered S/C composites improve the retention of S at the cathode

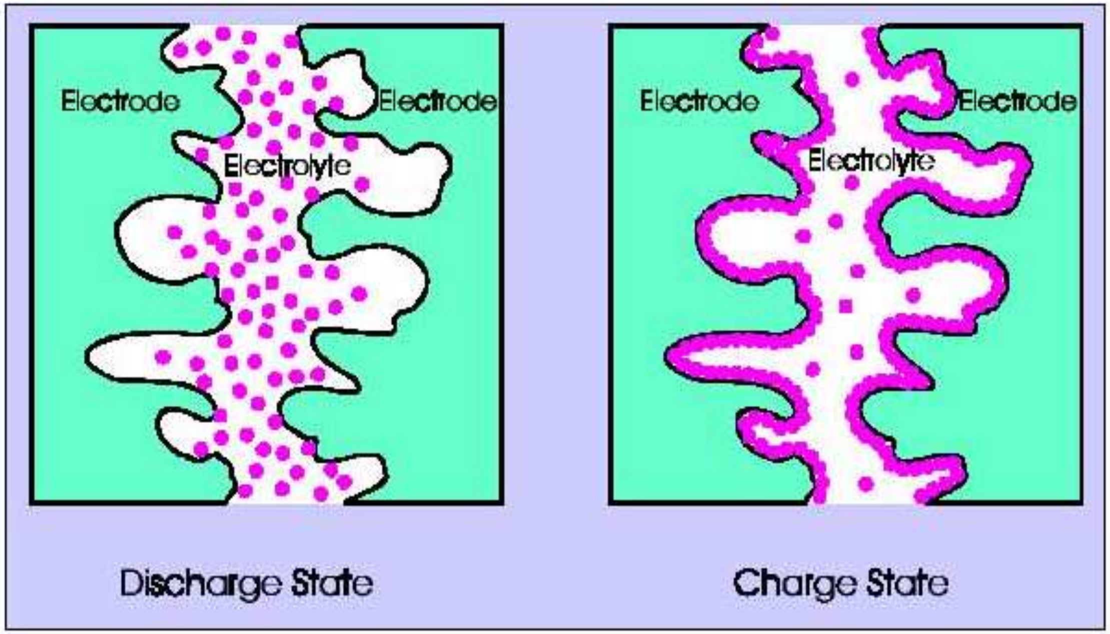
Application 2
Supercapacitors

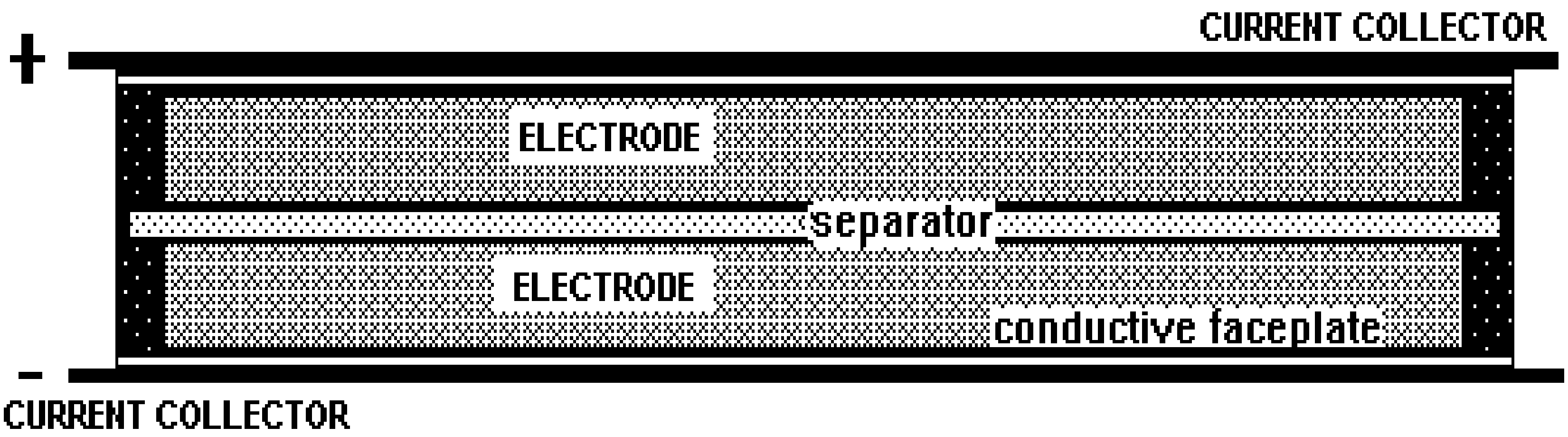
- **Major applications in**
  - **Transportation (hybrids, fuel cells)**
    - **Power boost**
  - **Power quality**
    - **High-power capability for grid "defibrillators"**
  - **Defense**
    - **Weapons, vehicles, portable power systems**
- **Needs:**
  - **Electrode materials with**
    - **High accessible surface area**
    - **High conductivity**
  - **Compatibility of electrodes with electrolyte**
    - **low degradation at higher cell voltages**

HEMTT-LHS hybrid truck

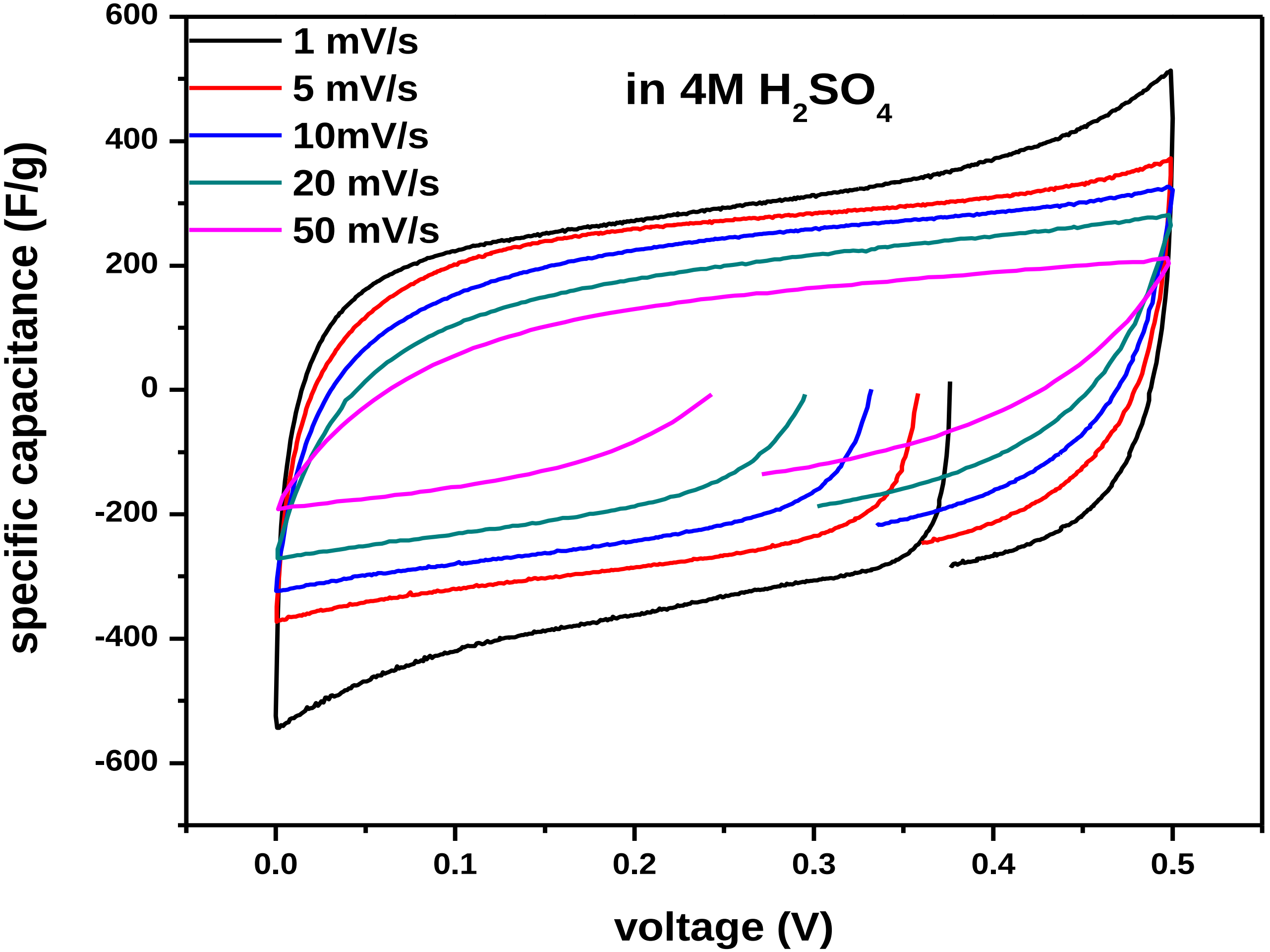
Oak Ridge National Laboratory

Mesoporous carbons are Key to Improved Energy Storage



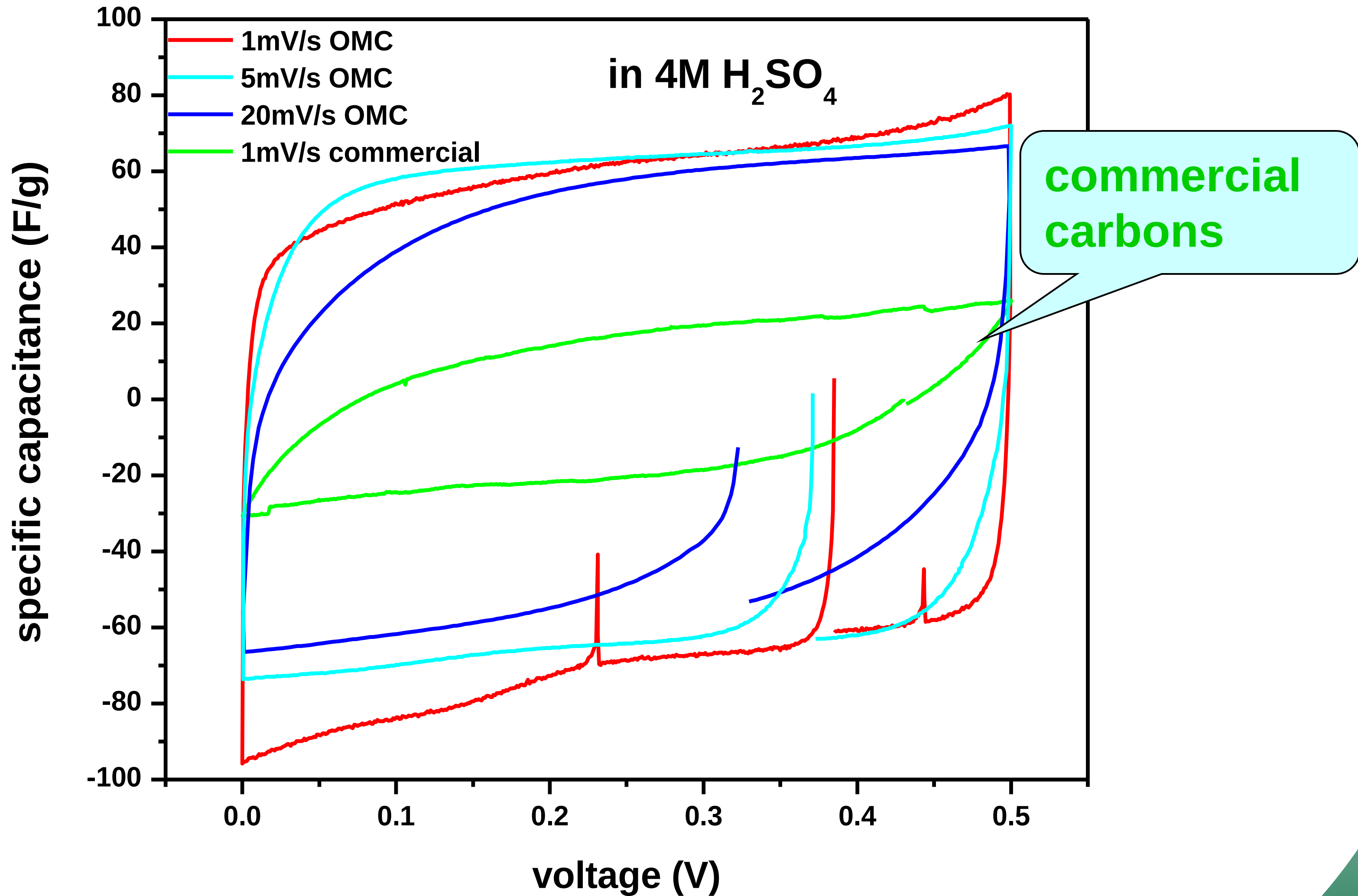


850°C-Treated OMC Has High Specific Capacitance but Slow Response



Micropore: slow response

Comparison of the 1600 °C Treated OMCs with Commercial Carbons

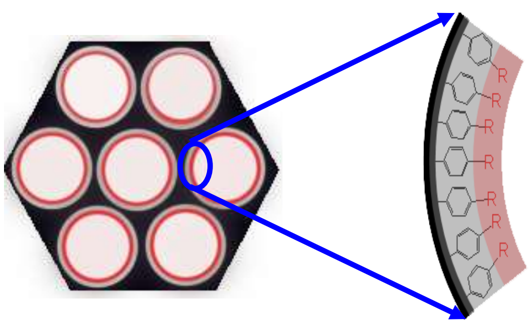


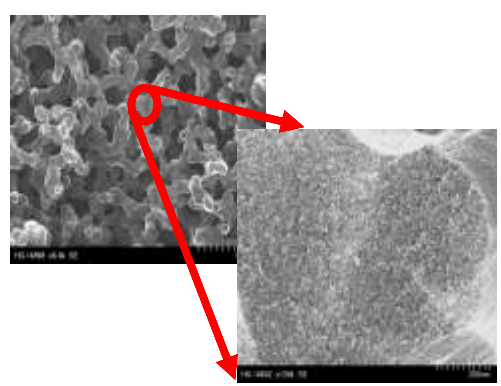
1600 ºC treated OMCs: fast response, high capacitance, low resistance

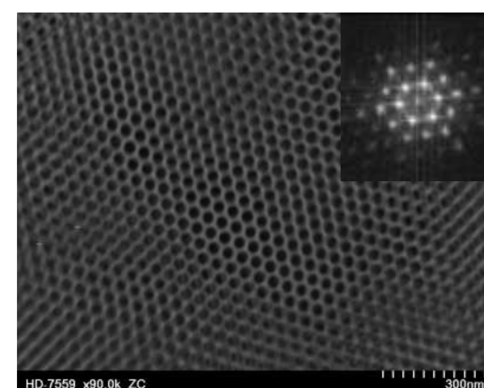
OAK RIDGE National Laboratory

Conclusions

- Soft-templating methodologies have been developed for synthesis of OMCs
  - Adjustable pore sizes and morphologies of carbons through direct block copolymer templates.
  - Bimodal porous structures through dual phase separation or activation.
- Chemistries of OMCs can be fine tuned
  - Surface modification through diazonium chemistry.
- OMCs have a great potential in energy storage
  - Li-S batteries
  - Supercapacitors







Acknowledgement

- **People**
  - Members of Multiscale Functionalities Group
  - Kunlun Hong
  - Jingfang Huang
  - Sam Park
  - Nancy Dudney
  - Jane Howe

- **Funding**
  - DOE BES programs: battery and user facilities
  - ORNL LDRD supercapacitor program
  - ORNL SEED high-power batteries
  - Honeywell Inc. supercap.

Oak Ridge National Laboratory