Synthesizing functional materials for energy research

Sheng Dai

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Oak Ridge, TN 37831,USA

Dec. 12, 2023
(BESAC Meeting)

Academy Family

Past:

Abney, Carter W.; Bagri, Prashant; Bai, Yin; Baker, Gary A.; Baker, Shirla; Bao, Lili; Bauer, J. Chris; Bell, Jason R.; Binder, Andrew; Bouvy, Claire; Brooks, Rachel; Brown, Suree S.; Burleigh, Mark C. (deceased); Cai, Yinchun Chai, Songhai; Che, Siyi; Chen, Banglin; Chen, Gang; Chen, Hao; Chen, Nanqing; Cleemann, Lars N.; Cui, Guo-Kai; Dahaudt, Jeremy; Das, Sadananda; Ding, Shunmin; Dolzhnikov, Dmitriy; Fang, Youxing; Fleshman, Allison; Formo, Eric; Fulvio, Pasquale F.; Gao, Haijun; Gao, Yuanyiu; Gorka, Joanna; Guan, Hongyu; Guo, Bingkun; Guo, Wei; Hillesheim, Patrick C.; Hou, Chia Hung; Hou, Xisen; Huang, Kuan; Huang, Jingfang; Im, Hee-Jung; Jafta, Charl J.; Jiang, De-en; Jiang, Xueguang; Jiang, Wei; Jie, Kecheng; Jin, Xianbo; Jin, Tian; Ju, Yuhong; Kesanli, Banu; Kong, Liyun; Lee, Byunghwan; Lee, Je Seung; Leng, Yan; Li, Haiying; Li, Ling; Li, Meijun; Li, Meiying; Li, Mingtao; Li, Peipei; Li, Zuojiang; Liang, Chengdu; Liao, Chen; Liu, Fujiang; Liu, Jisheng; Liu, Miaomiao; Liu, Rui; Liu, Xiaofei; Liu Zigang; Lu, Hanfeng; Lu, Ziyang; Lukoosi, Michelle; Lyu, Hailong; Ma, Guicen; Ma, Zhen; Martin, Halie; Mayes, Richard T.; Mehio, Nada; Makote, R. D.; Mote, KC M.; Nelson, Kimberly M.; Neti, Venkata S.; Okejiri, Francis; Oyola, Yatsandra; Pan, Zhengwei; Peng, Honggeng; Powell, Jonathan; Qiao, Zhen-An; Schott, Jennifer A.; Shan, Weida; Shen, Yinlin; Shin, Y. S.; Stankovich, Joseph J.; Sun, Xiaoqi; Sun, Yifan; Surwade, Sumedh P.; Tao Duan-Jian; Tao, Ronnie; Teague, Craig; Tian, Chengcheng; Tian, Hongwei; Tian, Tao; Wan, Shun; Wang, Congmin; Wang, Gang; Wang, Li; Wang, Xiqing; Wang, Zongyu; Williams, Neil J.; Wu, Peiwen; Xia, Jiexiang; Xiao, Weimin, Xing, Huabin; Xu, Haidi; Xu, Wei; Xu, Wu; Xue, Zimin; Yan Wenfu; Ying, Hongfeng; Yu, Bo; Yuan, C.Y.; Yue, Yanfeng; Zhan, Wangcheng; Zhang, Chenxi; Zhang, Jianan; Zhang, Jingshui; Zhang, Pengfei; Zhang, Zhongtao; Zhang, Zihao, Zhao, Junmei; Zhou, Shenghu; Zhu, Haoguo; Zhu, Huiyuang; Zhu, Qing; Zhu, Wenshuai; Zhu Xiang

Current:

Adigun, Femi; Bridges, Craig; Do-Thanh, Chi-Linh; Fan, Juntian; Fletcher, Nathaniel; Gaugler II, James A.; Halstenberg, Phillip W.; Ivanov, Aleksandr; Kim, Ellie; Li, Meijia; Mahurin, Shannon M.; Maltsev, Dmitry; Moitra, Deb; Popovs, Ilja; Prasad Thapaliya, Bishnu; Siniard, Kevin; Sun, Xiao-Guang; Wang, Tao; Yang, Zhenzhen

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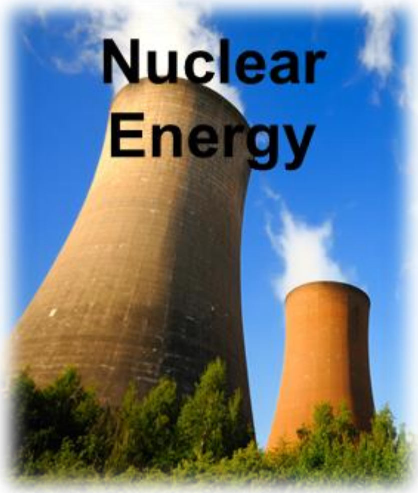
- Energy Frontier Research Center (EFRC) -U.S. Department of Energy, Office of Science

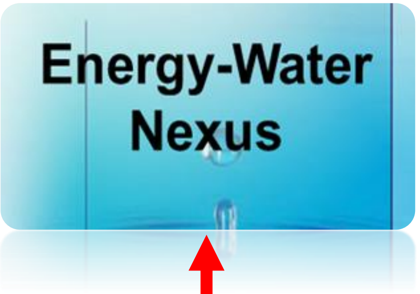
Outline

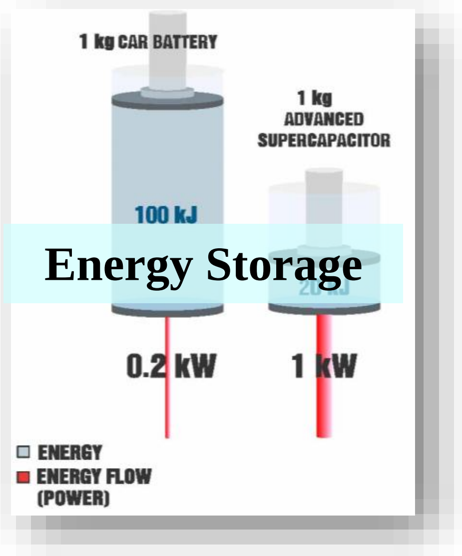
- Mesoporous Carbon Materials
- Emerging Porous Liquids
- Synthesis of Graphite

Mesoporous Carbon Materials

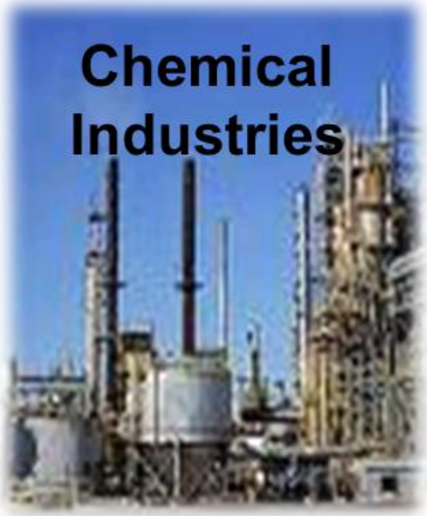
Importance of Porous Carbons

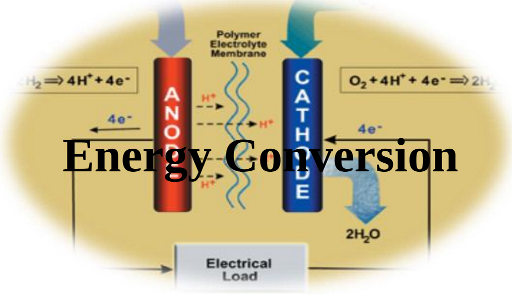






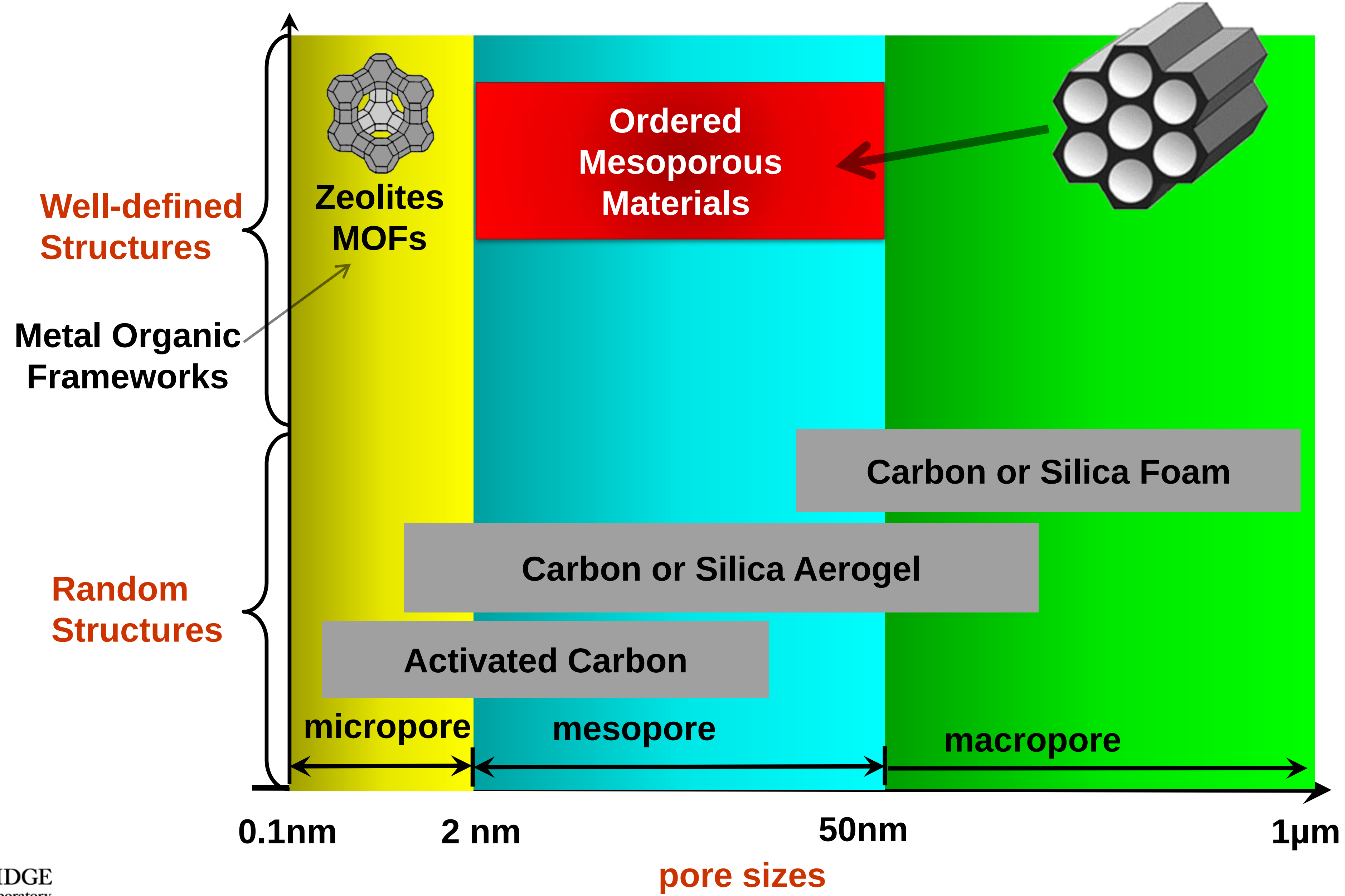
Porous Carbons





Goal: synthesis of mesoporous carbons for energy-related applications

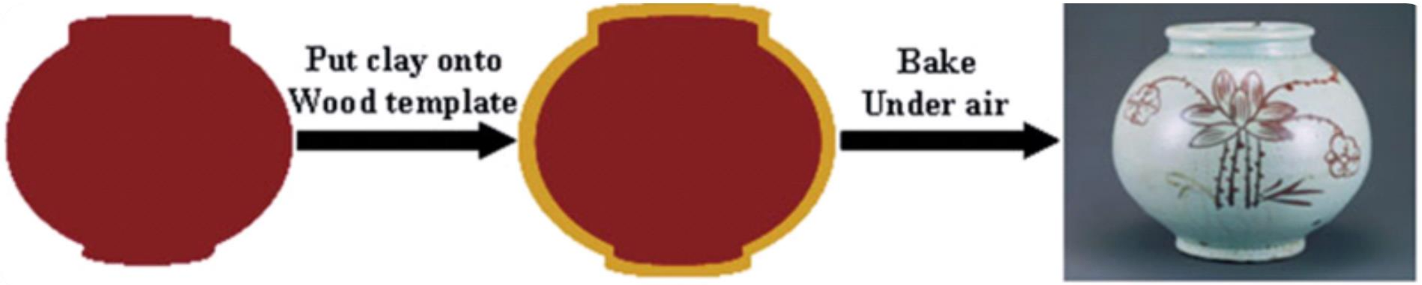
Classification of Solid Porous Materials



Self-Assembly Synthesis of Ordered Mesoporous Carbon (OMCs) via Soft Templates

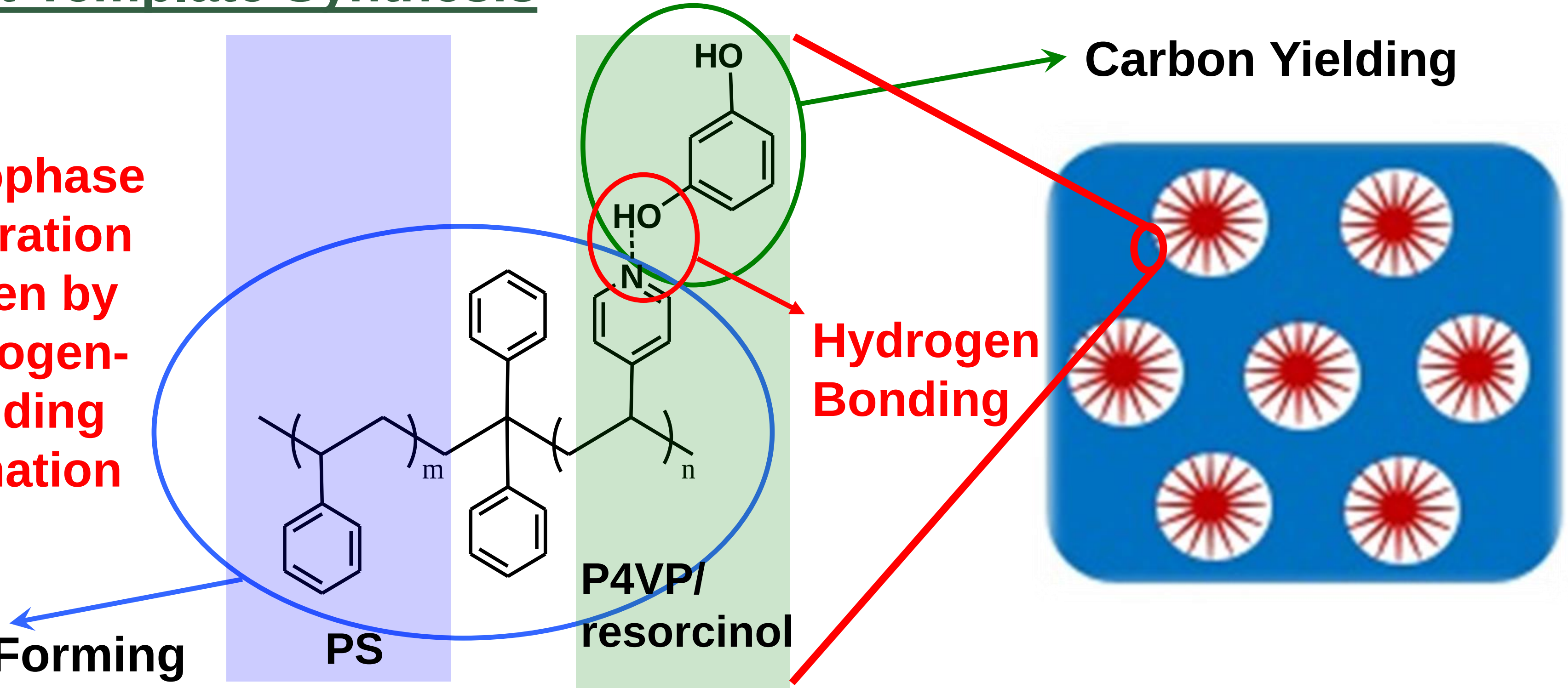
Hard-Template Synthesis

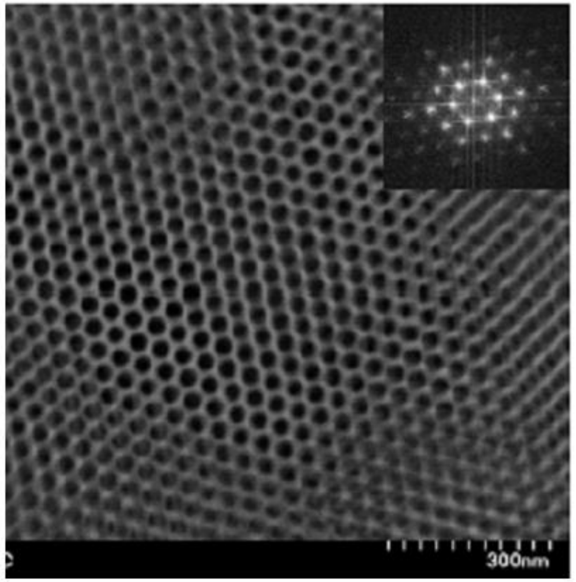
J. Lee, J. Y. Kim, and T. H. Hyeon, *Adv. Mater*. **2006**, *18*, 2073–2094



Soft-Template Synthesis

Microphase separation driven by hydrogen-bonding formation

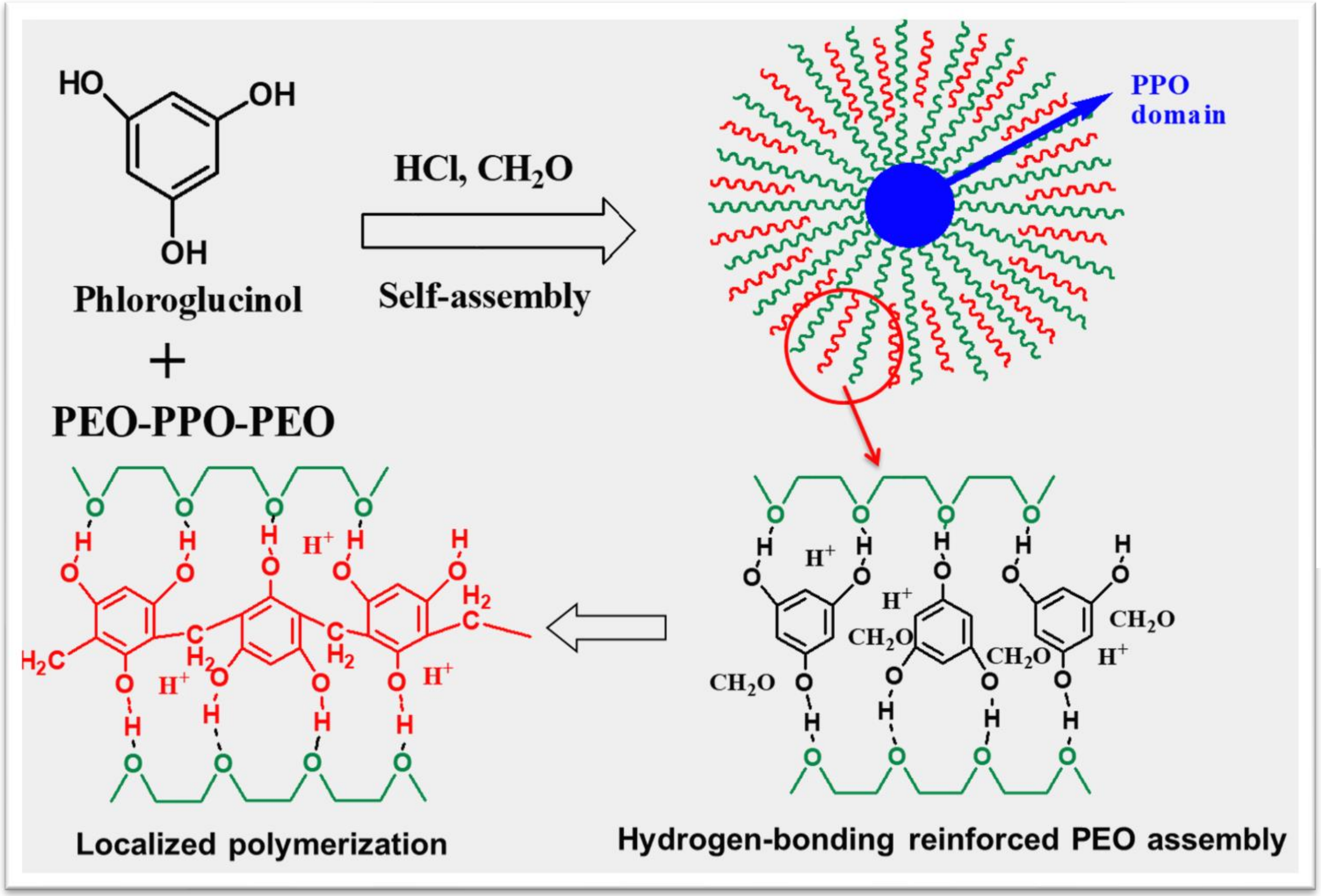


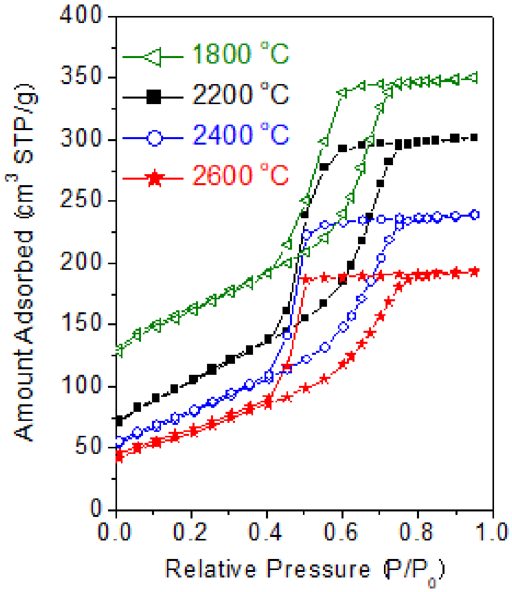


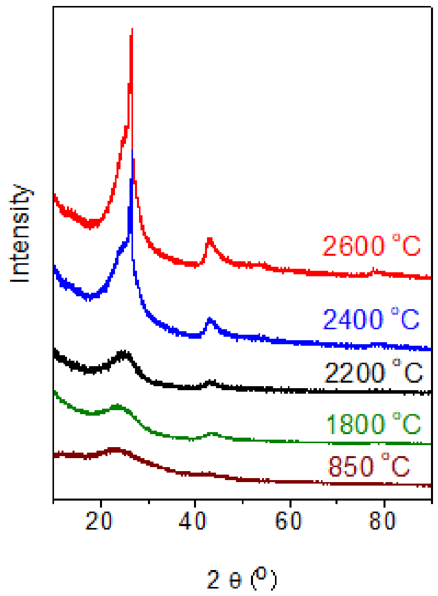
SEM Image

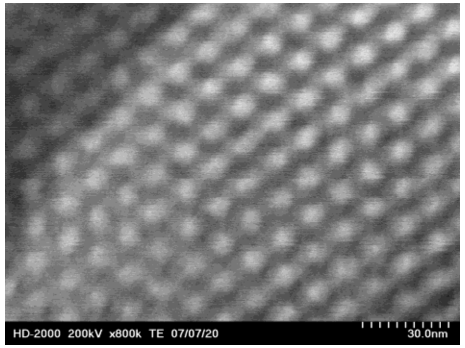
Liang, Dai, *et al.*, *Angew. Chem.-Int. Edit.* **2004,** *43,* 5785

Synthesis of Ordered Mesoporous Carbons (OMCs): One-Pot Synthesis of OMCs via Enhanced Hydrogen-bonding









Conductivity of mesoporous sheets:

4 Ω·cm (850°C) →

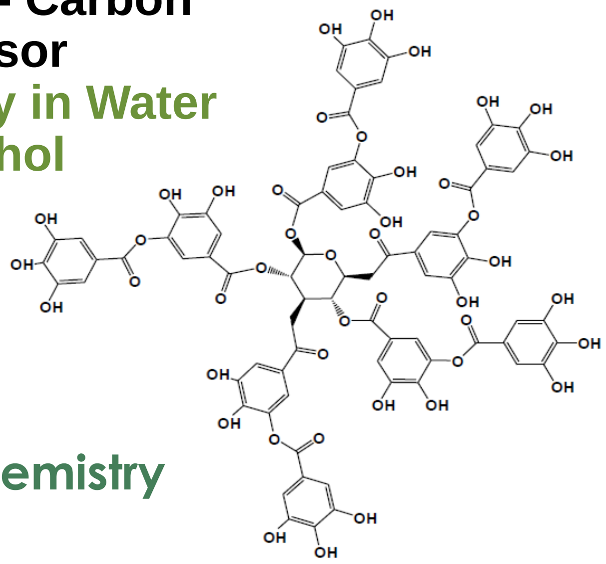
3 mΩ·cm (2400°C)

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

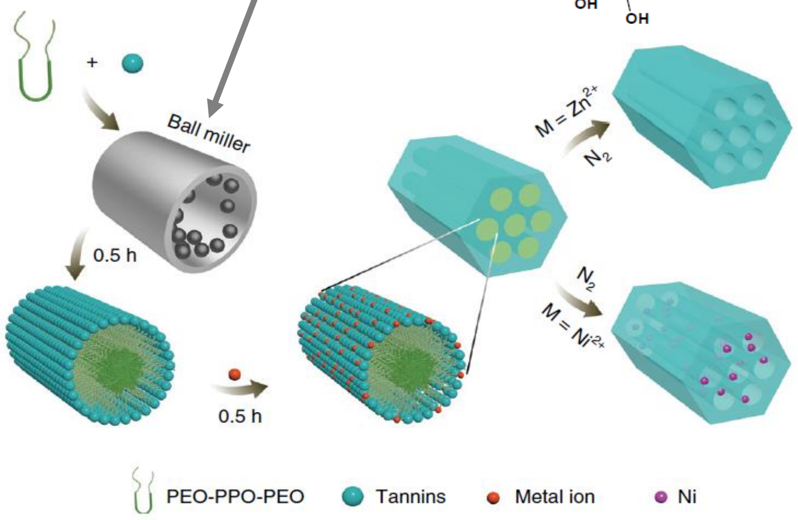
Solvent-Free Self-Assembly Synthesis of Mesoporous Polymers and Carbons via Mechanochemistry

Tannic Acid - Carbon Precursor

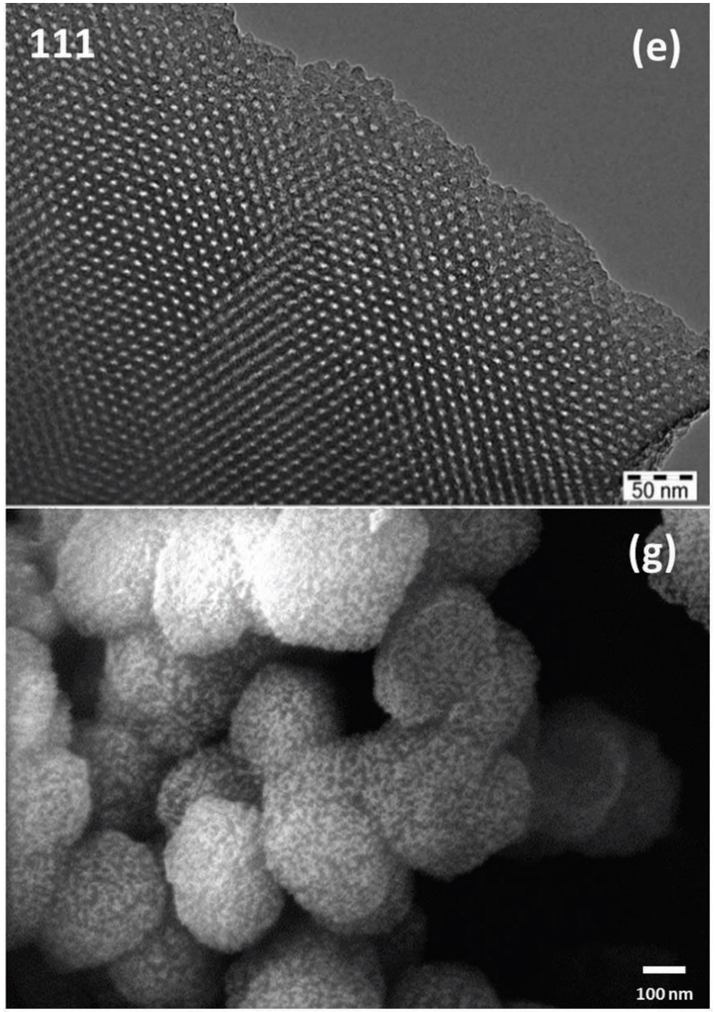
Low Solubility in Water & Alcohol



Mechanochemistry



TEM & SEM Images



- **The mechanochemically synthesized porous materials possessing abundant mesopores but negligible micropores, as well as nitrogen functionality**
- **High absorption selectivity (>200) by mesoporous polymers for CO_2 vs. N_2**
- **Temperature dependence of selectivity (entropic effect)**

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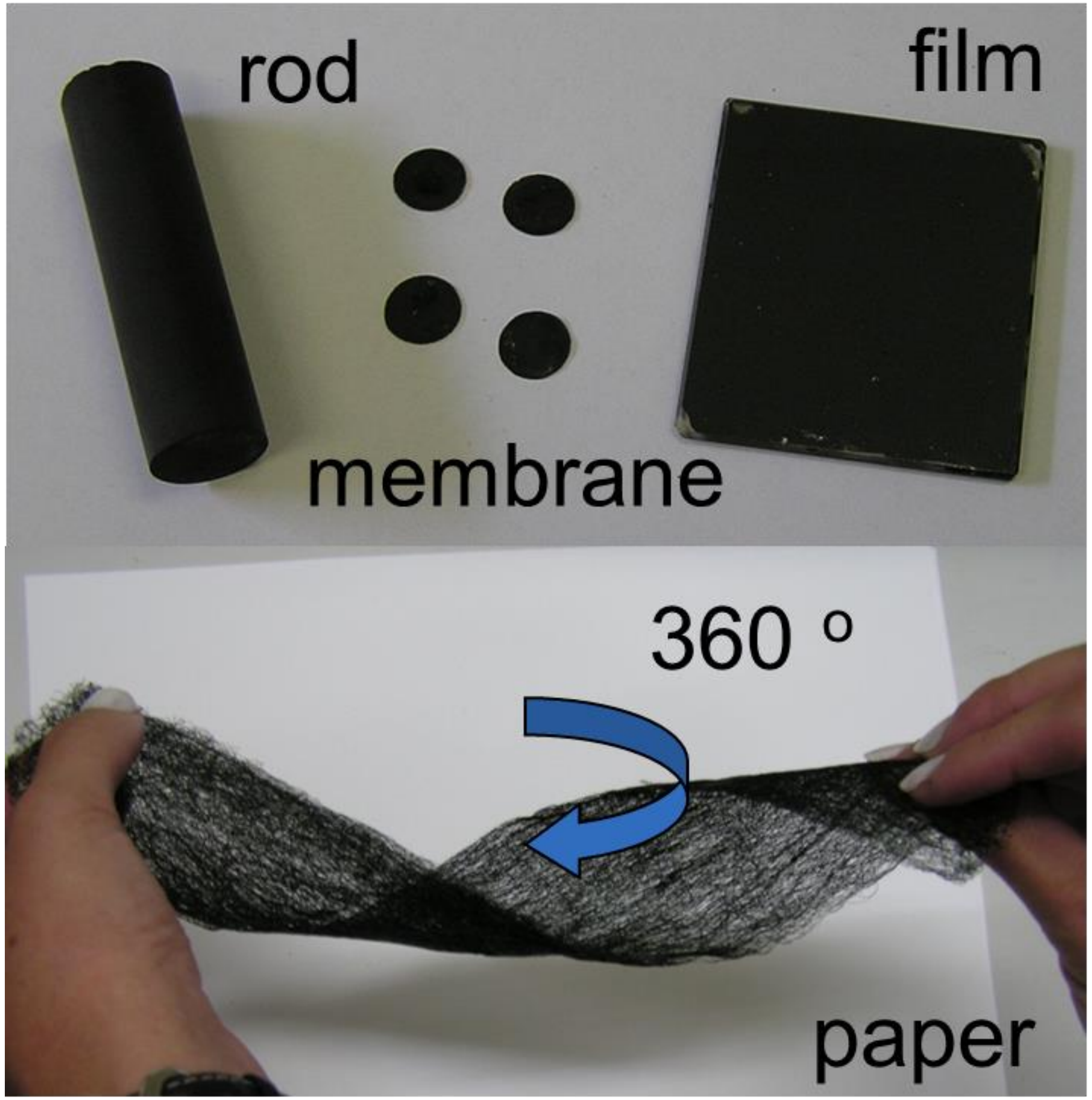
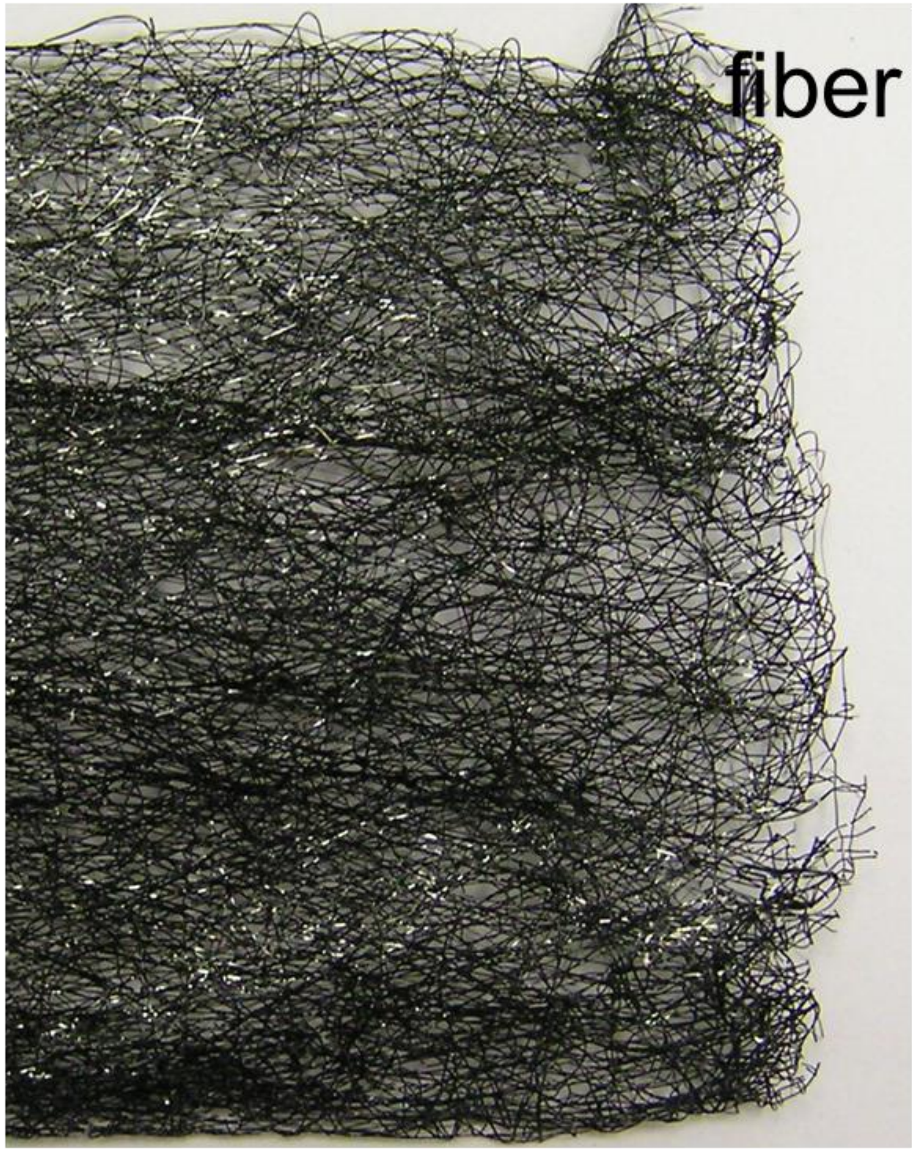
Liu, F. J.; Huang, K.; Wu, Q.; Dai, S. Solvent-Free Self-Assembly to the Synthesis of Nitrogen-Doped Ordered Mesoporous Polymers for Highly Selective Capture and Conversion of CO_2. *Adv. Mater.* **2017**, *29*, 1700445

Various Forms of Ordered Mesoporous Carbons

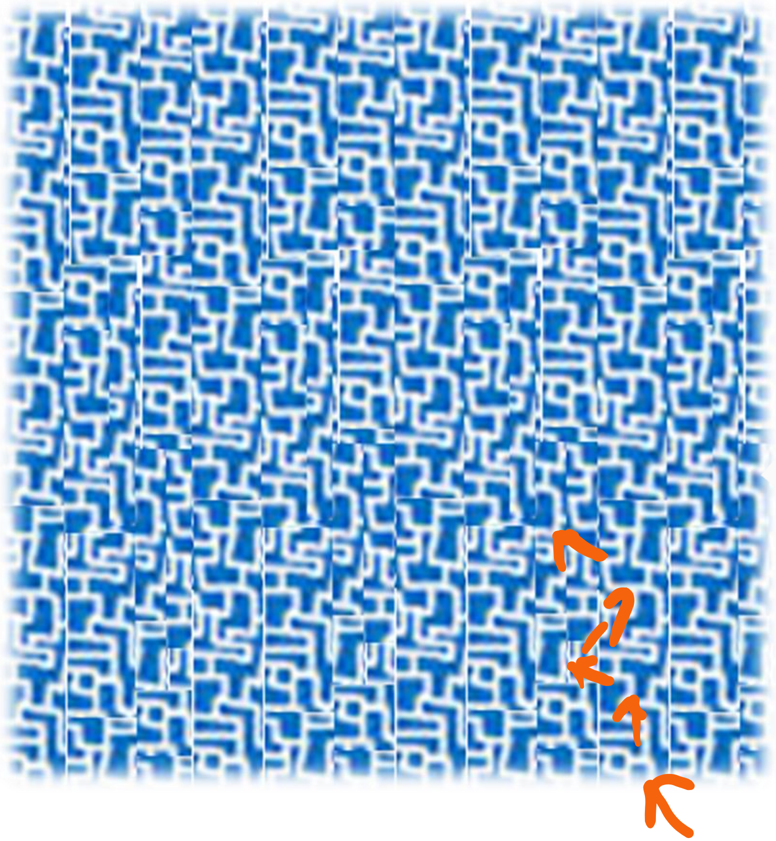




Liang, C. D.; Li, Z. J.; Dai, S. Mesoporous carbon materials: Synthesis and modification. *Angew. Chem.-Int. Edit.* **2008**, *47*, 3696-3717.

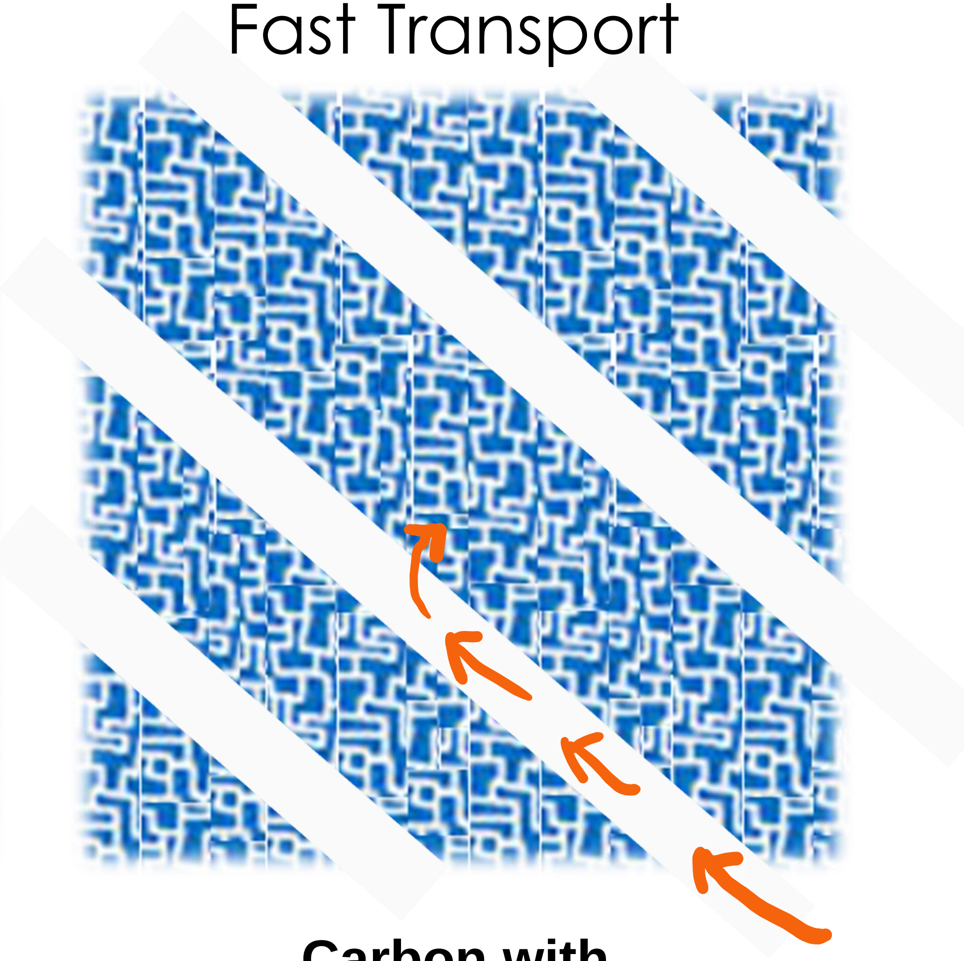
Schematic Comparison of Different Pore Morphologies

Slow Transport

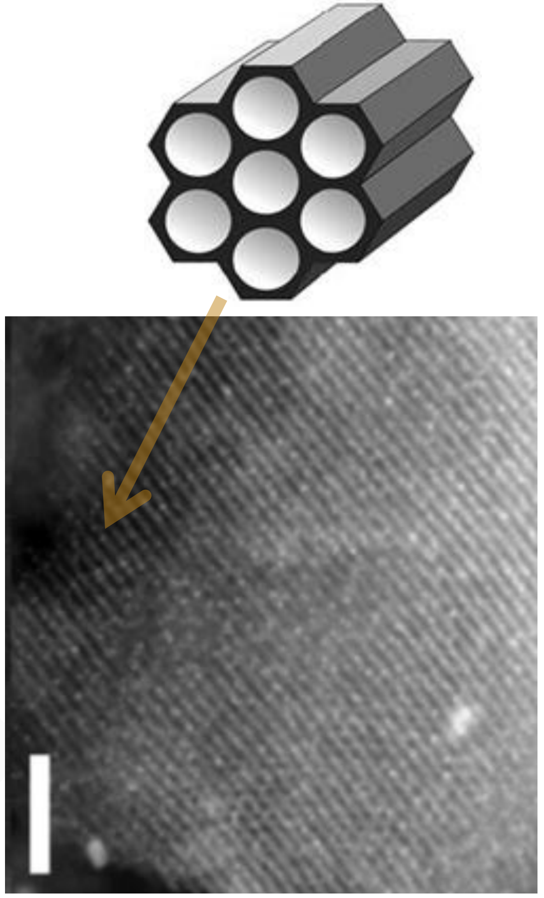


Carbon with Microporoes (< 2 nm)

Fast Transport



Carbon with Microporoes & Mesopores (< 2 nm & > 2 nm)



STEM-HAADF images of an OMC. Scale bar = 100 nm

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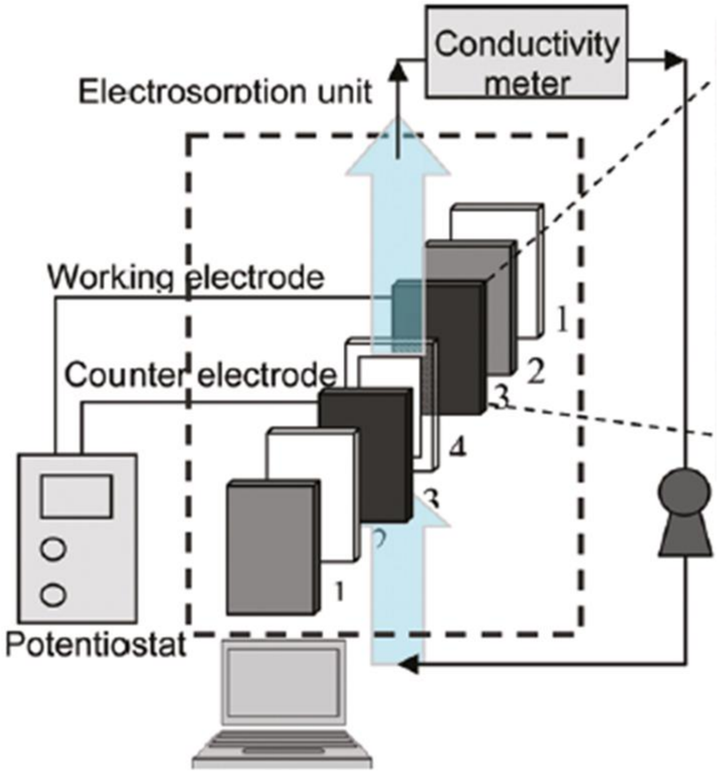
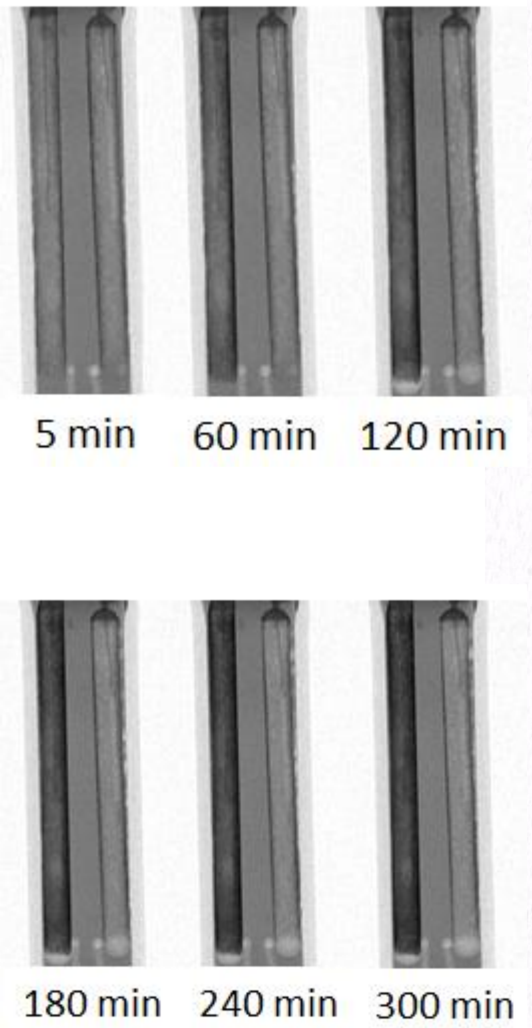
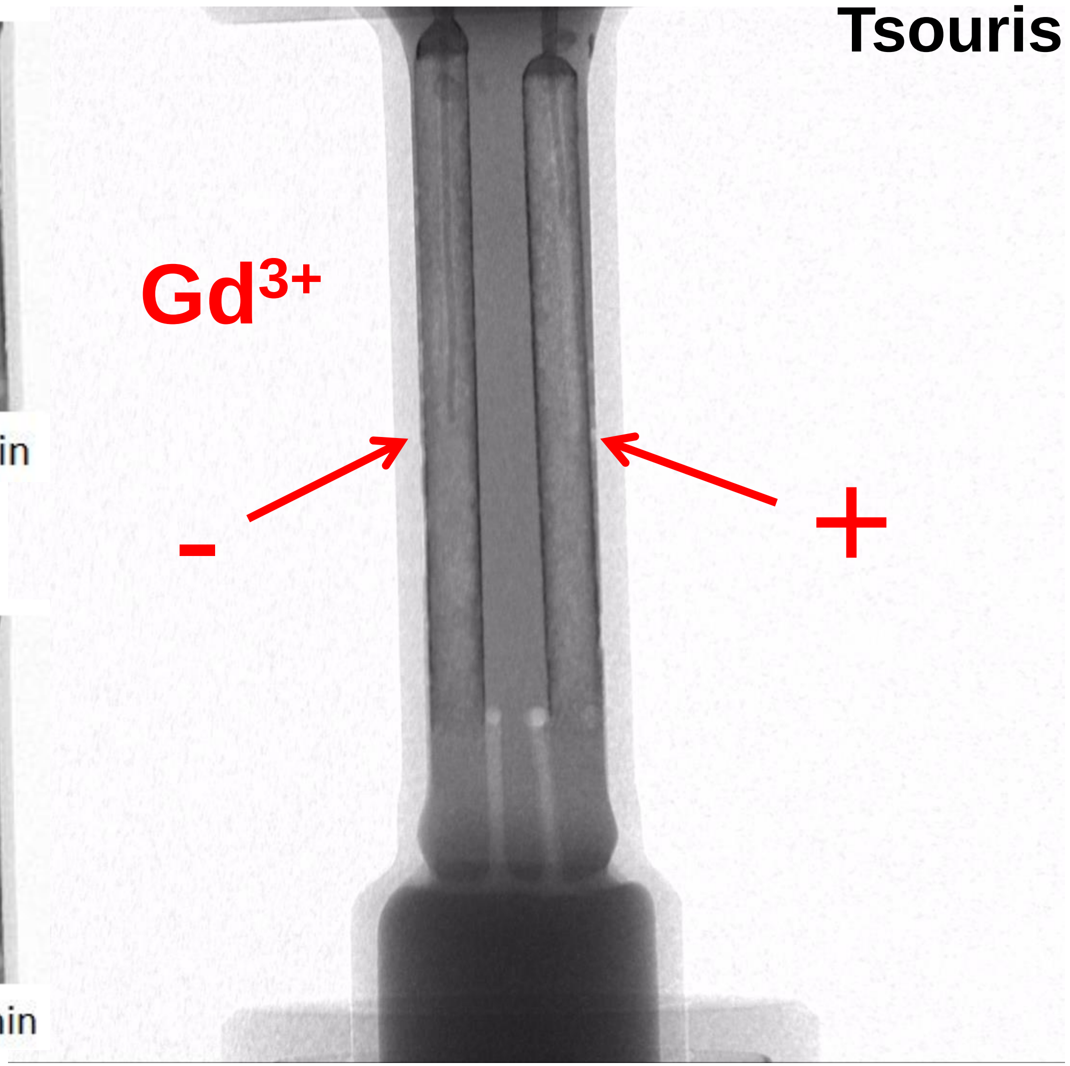
Neutron Imaging of Fast Ion Transport in Capacitive Desalination with Mesoporous Carbons





Tsouris



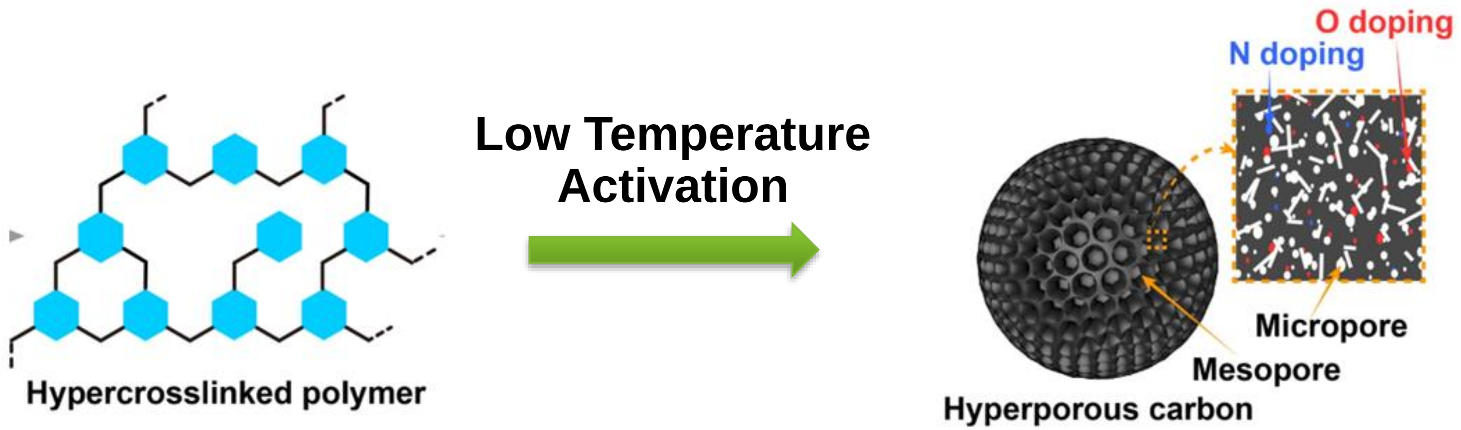
Needs:

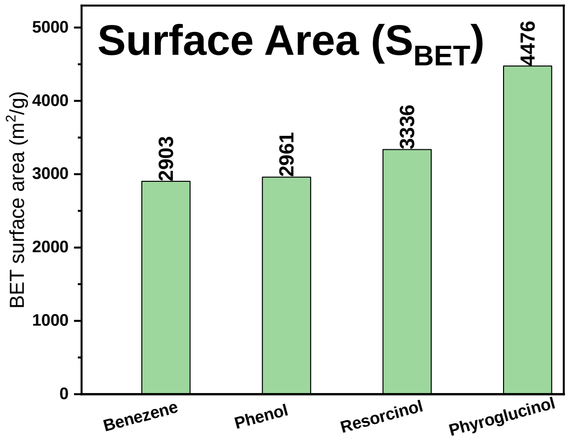
- Tunable hierarchical pore sizes
  - macropores, mesopores, micropores
- High conductive electrodes with
  - high accessible surface area

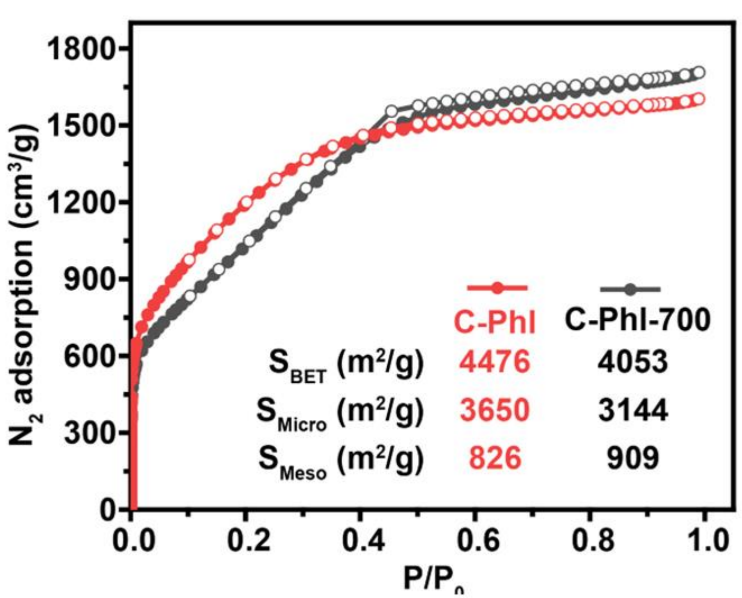
Sharma, K.; Bilheux, H. Z.; Walker, L. M. H.; Voisin, S.; Mayes, R. T.; Kiggans, J. O.; Yiacoumi, S.; DePaoli, D. W.; Dai, S.; Tsouris, C. Neutron imaging of ion transport in mesoporous carbon materials. *Phys. Chem. Chem. Phys.* **2013**, *15*, 11740-11747.

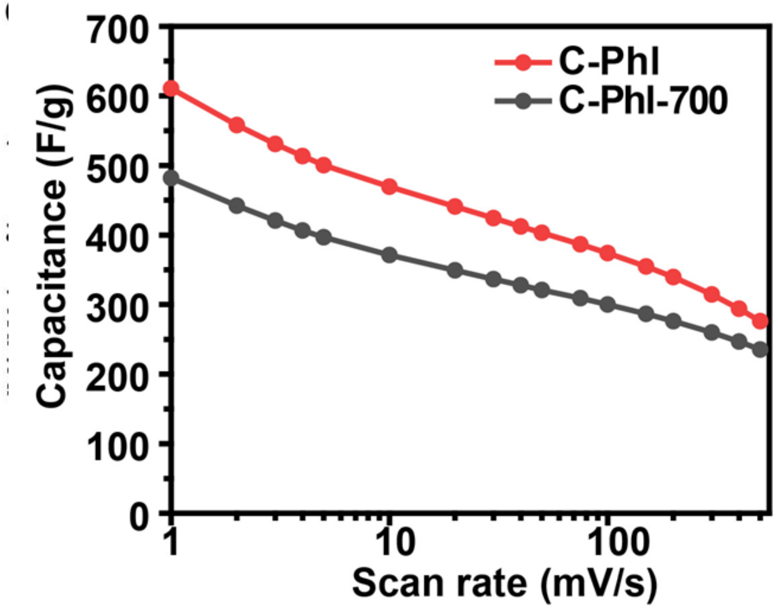
Hyperporous Mesoporous Carbons (C-Phl)

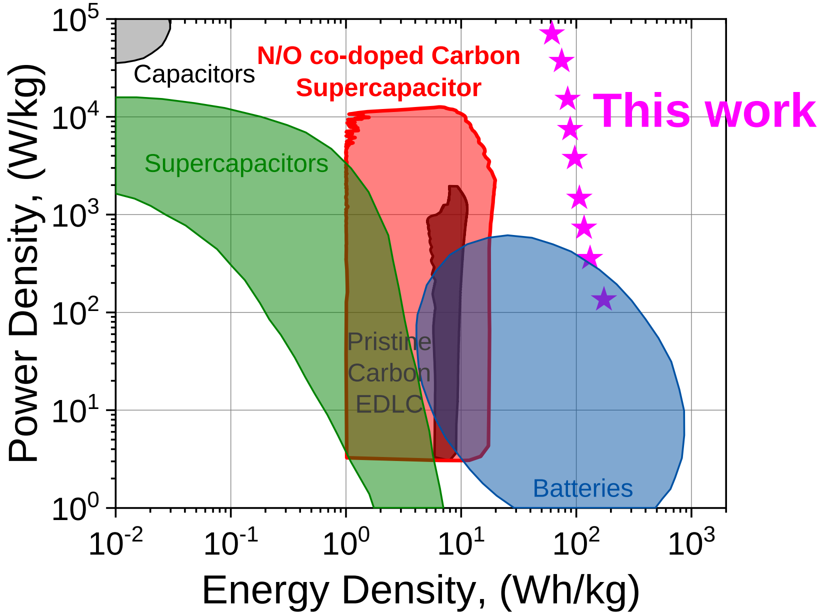
Approaching the Capacity Limit of Capacitive Energy Storage for Carbons









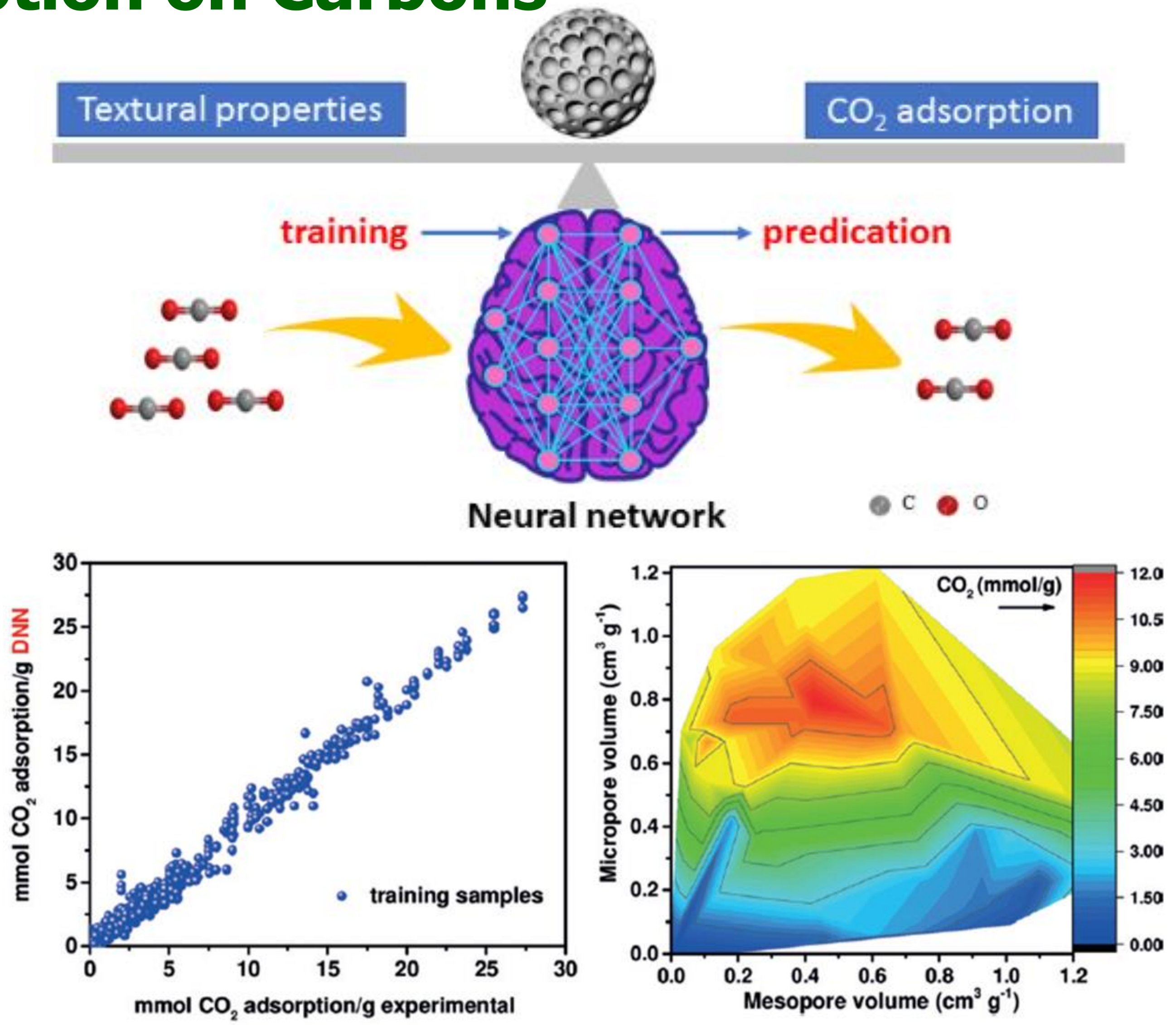


Wang, Wu, Dai, et al. *Nat. Comm.* **2023**, *14*, 4607

Deep Learning Reveals the Impact of Mesopores on Carbon Dioxide Adsorption on Carbons

Porous carbons with different textural properties exhibit great differences in CO_2 adsorption capacity. However, it is still unclear what role each variable in textural properties plays in CO_2 adsorption. Our work demonstrated that:

1) Surface area is an independent textural parameter that can be synergistically coupled with other **textural** parameters in determining gas-solid interactions and thus gas-uptake capacities.
2) **Mesopores** play a more important role on CO_2 adsorption under high pressure.



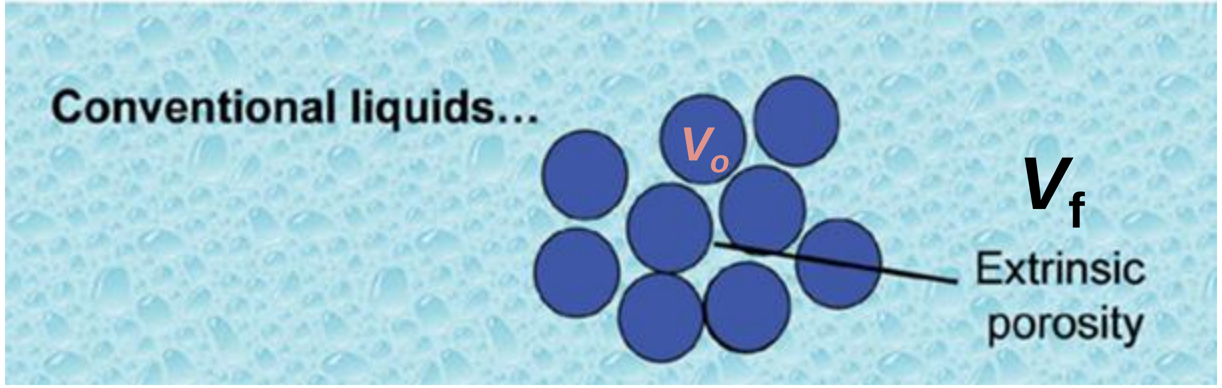
Zhang, Fu, Sumpter, Dai, et al., Prediction of Carbon Dioxide Adsorption via Deep Learning, *Angew. Chem. Int. Ed*. **2019**, *131*, 265.

Emerging Porous Liquids

Extrinsic Porosity in Molecular Solvents

- Extrinsic Porosity for Liquids
  - Transient cavities
  - Dynamic cavities

- The Concept of Free Volume in Liquids or Polymers



Interstitial Sites

V_o : Occupied by Solvent Molecules (Van der Waal's molecular volume)

V_t : Total Volume (Determined via Density Measurement)

V_f : Unoccupied "Free" Volume in bulk V_t

Free Volume = $V_f = V_t - V_o$ **Extremely Small!!!**

A. Pohorille; L. R. Pratt, *J. Am. Chem. Soc.*,**1990**, *112*, 5066

Absorption & transport properties of liquids are fundamentally connected to the free volume (V_f)!

Absorption

Gas Solubility in Liquids ∝ Traditional Sorption Terms (V_f)

Transport

Cohen-Turnbull Equation

D (Gas Diffusion) = $\alpha \exp[-\gamma(V_o/V_f)]$

Vogel-Tammann-Fulcher Empirical Equation

κ (Ion Conductivity) = $AC \exp[-\gamma(V_o/V_f)\, C]$

Yim, C. H.; Tam, J.; Soboleski, H.; Abu-Lebdeh, Y. On the Correlation between Free Volume, Phase Diagram and Ionic Conductivity of Aqueous and Non-Aqueous Lithium Battery Electrolyte Solutions over a Wide Concentration Range. *J. Electrochem. Soc.* **2017**, *164*, A1002-A1011.

Can we make liquids with intrinsic porosity instead of extrinsic porosity?

Porous Liquids (PLs):
Intrinsic porosity in a liquid

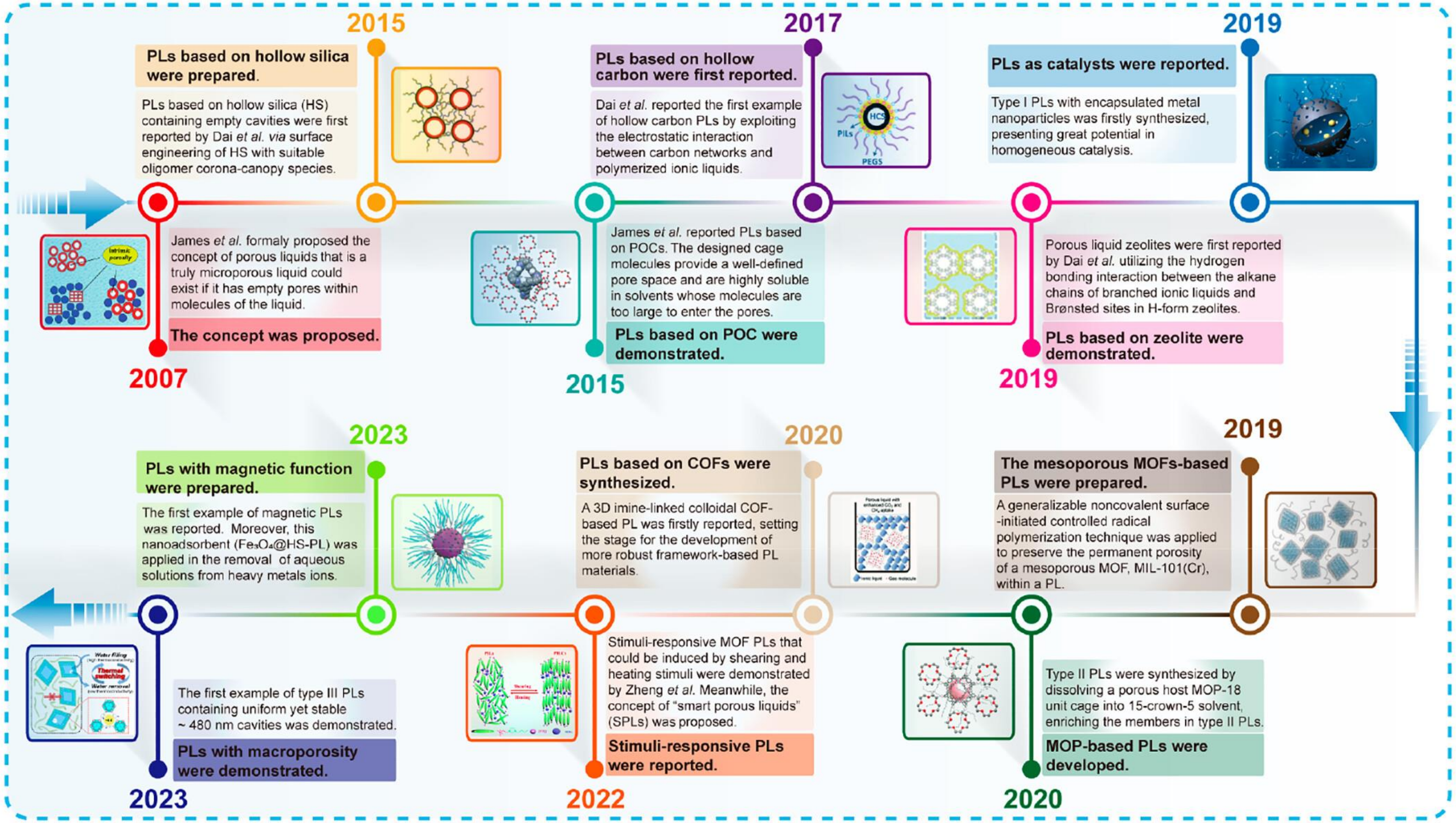
- Type 1
  - Constituent molecules are rigid
  - Pure liquid hosts with cavities
- Type 2
  - Empty hosts dissolved in sterically hindered solvent
- Type 3
  - Microporous frameworks dissolved in solvents

N. O'Reilly, et al., *Chem. Eur. J.*, **2007**, *13*, 3020

Porous liquids became reality in 2015!

Zhang, Mahurin, Dai, et al., *Angew. Chem. Int. Ed.* **2015**, *54*, 932 –936

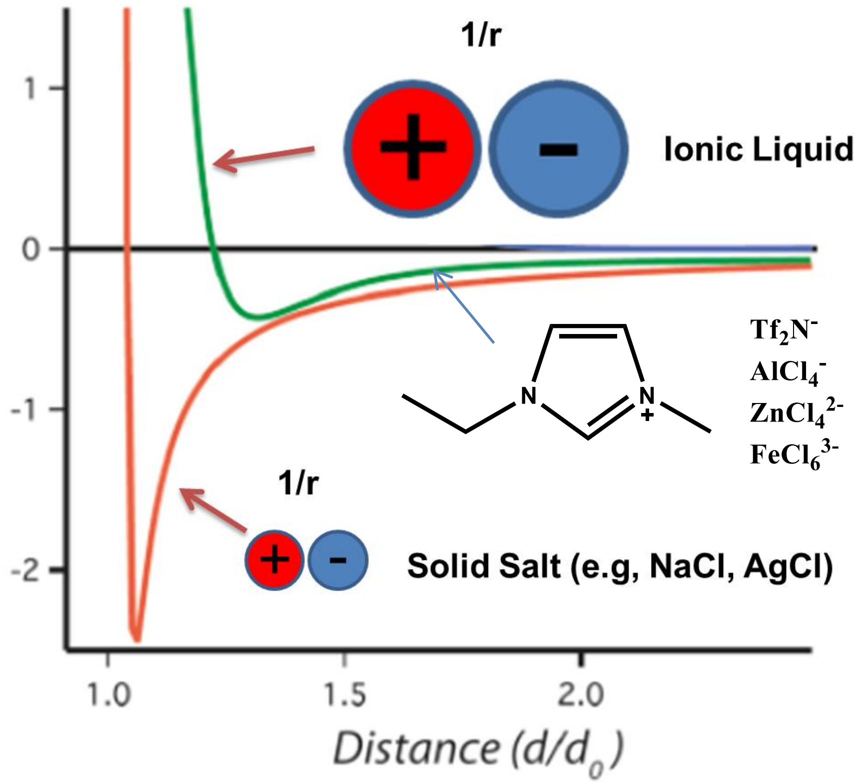
Free Volume: ~40%; Type I



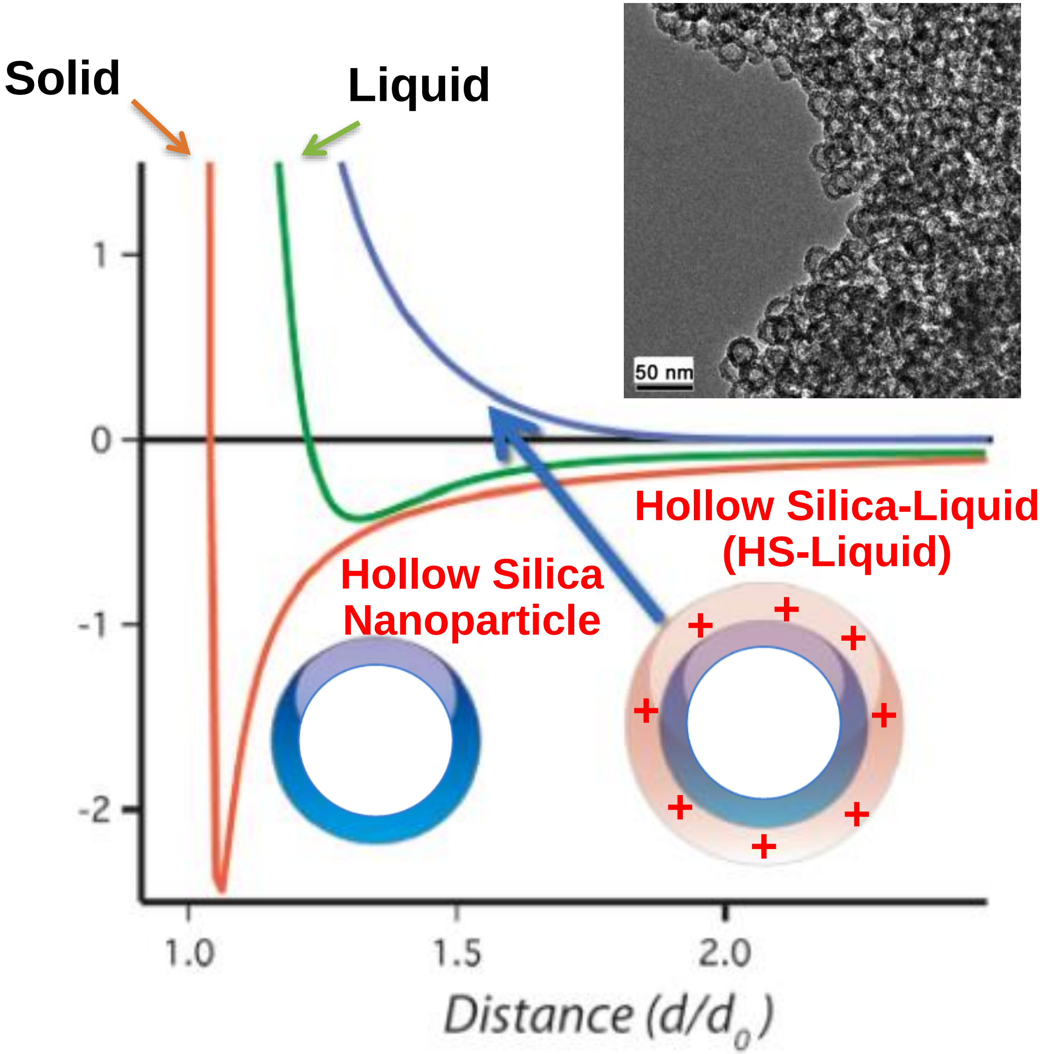
Timeline illustrating the development of PLs *Acc. Mater. Res.* **2023**, *4*, 854-866

Nanoscopic Ionic Liquids: our strategy for making porous liquids through the control of inter-particle interactions of hollow nanoparticles through interfacial functionalization

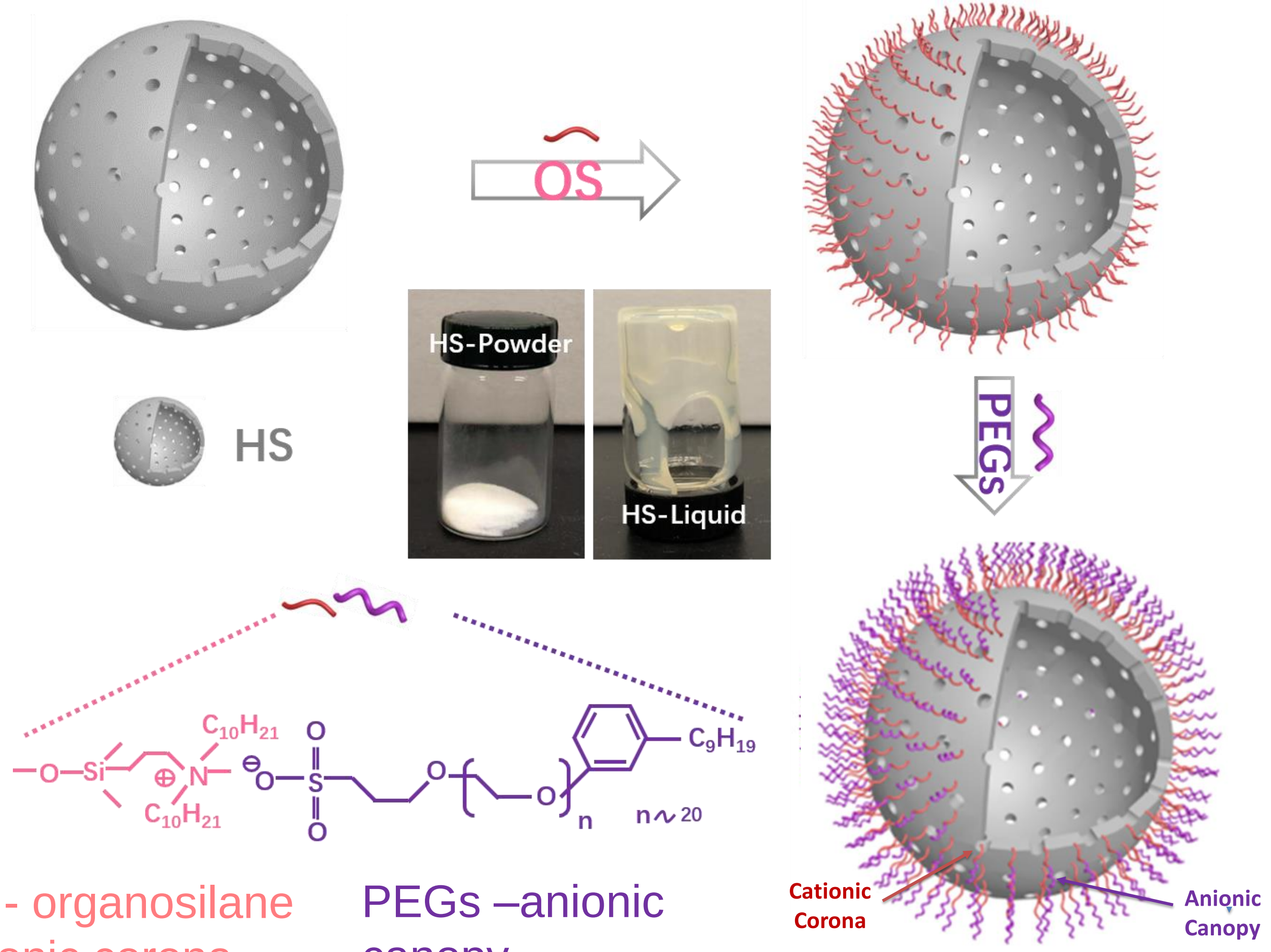
A shallow attractive well corresponding to a liquid molecular-size particle system.



Sun, X. Q.; Luo, H. M.; Dai, S. *Chem. Rev.* **2012**, *112*, 2100–2128.

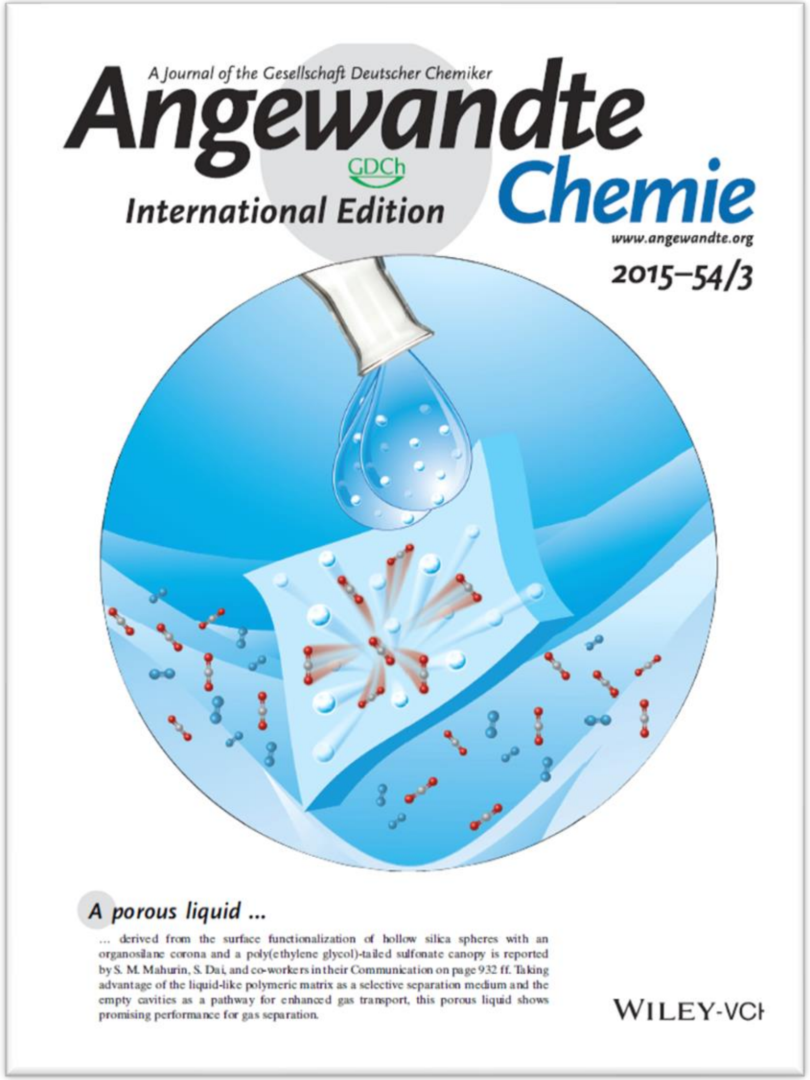


Two-step synthesis strategy for porous liquid fabrication (HS=hollow silica, OS=organosilane)



OS - organosilane cationic corona

PEGs –anionic canopy


A Journal of the Gesellschaft Deutscher Chemiker

Angewandte Chemie

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www.angewandte.org

2015–54/3

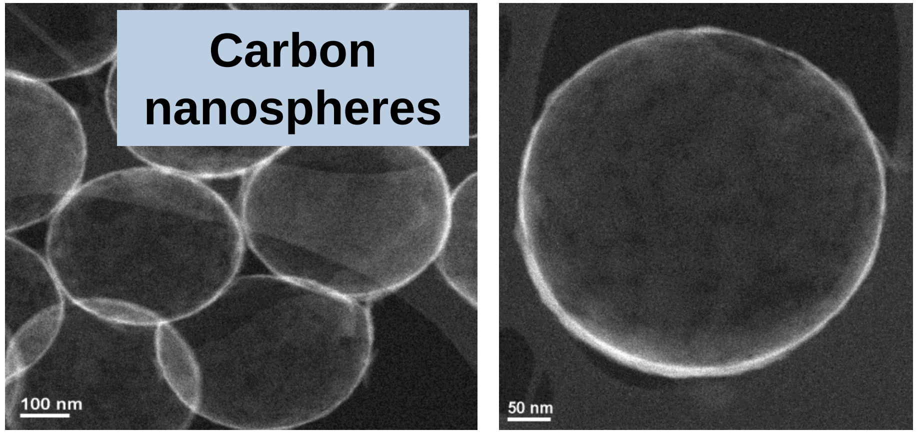
A porous liquid ...

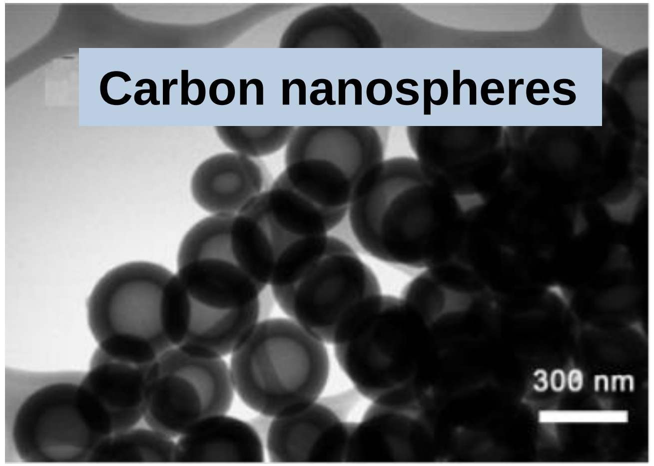
... derived from the surface functionalization of hollow silica spheres with an organosilane corona and a poly(ethylene glycol)-tailed sulfonate canopy is reported by S. M. Mahurin, S. Dai, and co-workers in their Communication on page 932 ff. Taking advantage of the liquid-like polymeric matrix as a selective separation medium and the empty cavities as a pathway for enhanced gas transport, this porous liquid shows promising performance for gas separation.

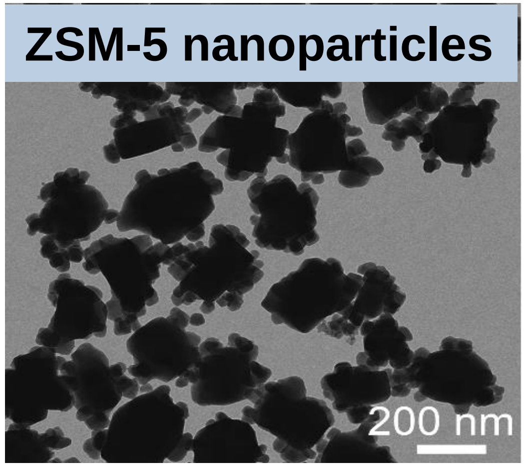
WILEY-VCH

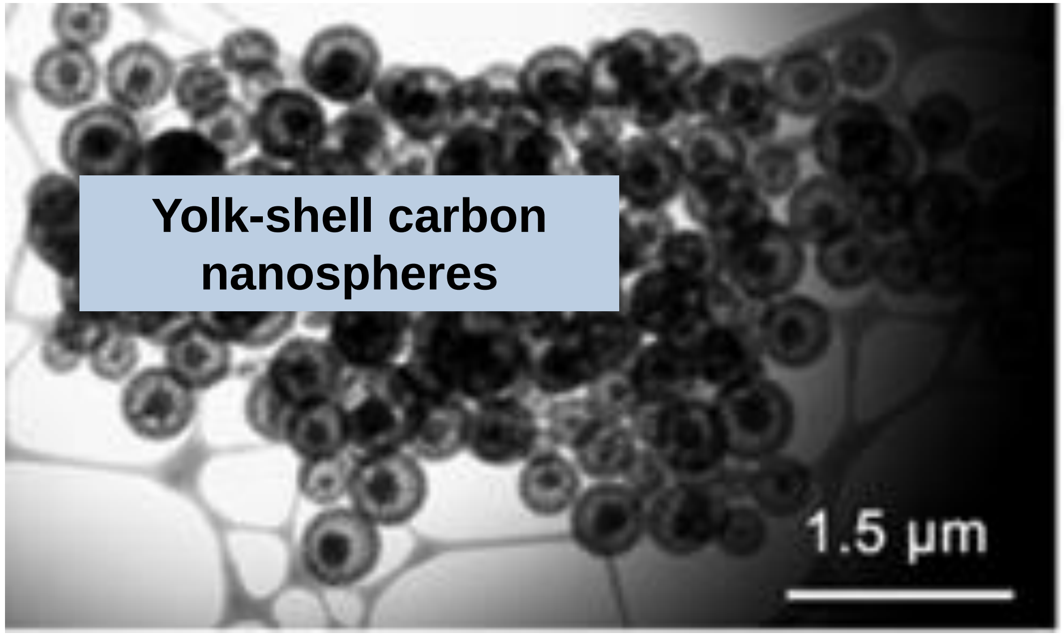
Zhang, J.; Chai, S.-H.; Qiao, Z.-A.; Mahurin, S. M.; Chen, J.; Fang, Y.; Wan, S.; Nelson, K.; Zhang, P.; Dai, S. *Angew. Chem. Int. Ed.* **2015**, *54*, 932 –936

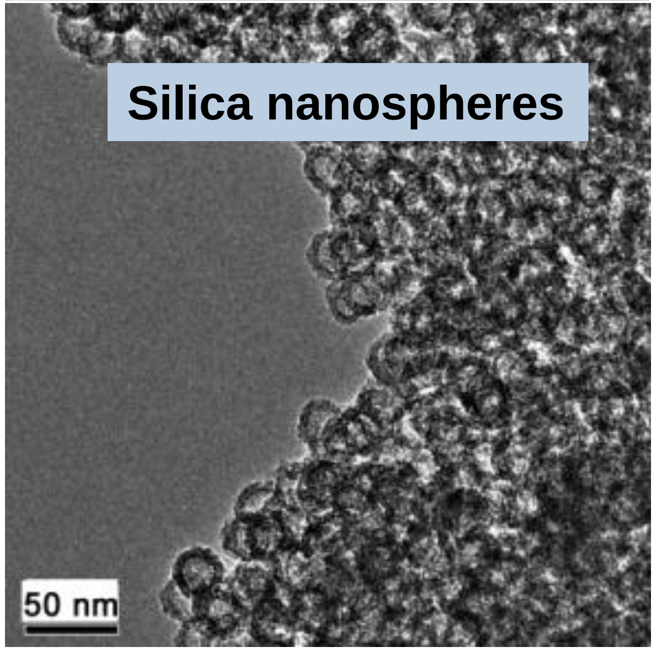
Diverse Building Blocks for Porous Liquids Based on Hollow Nanospheres

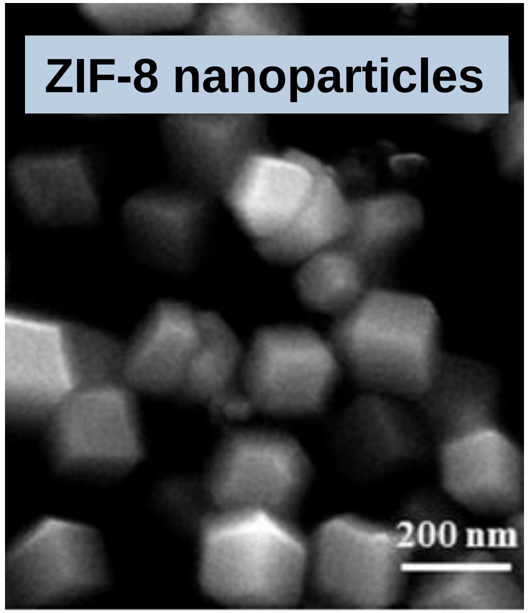






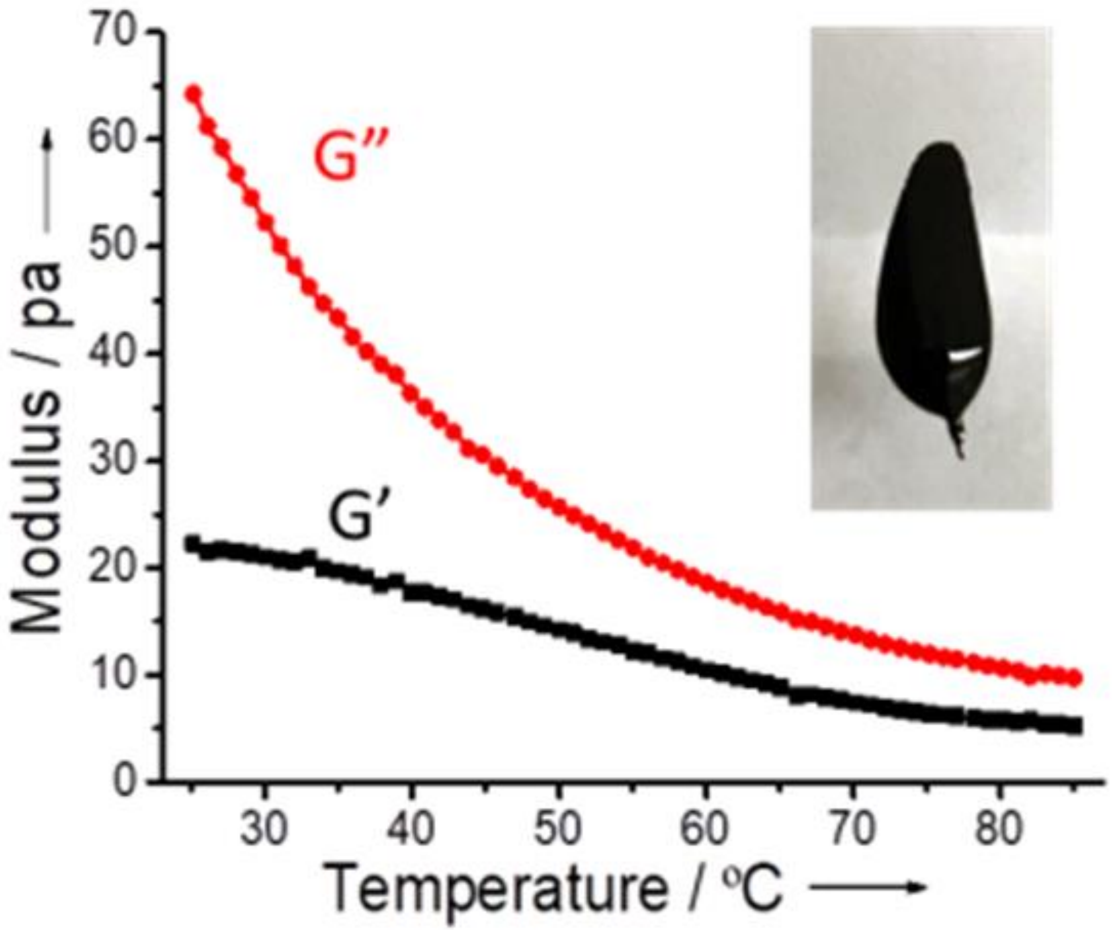


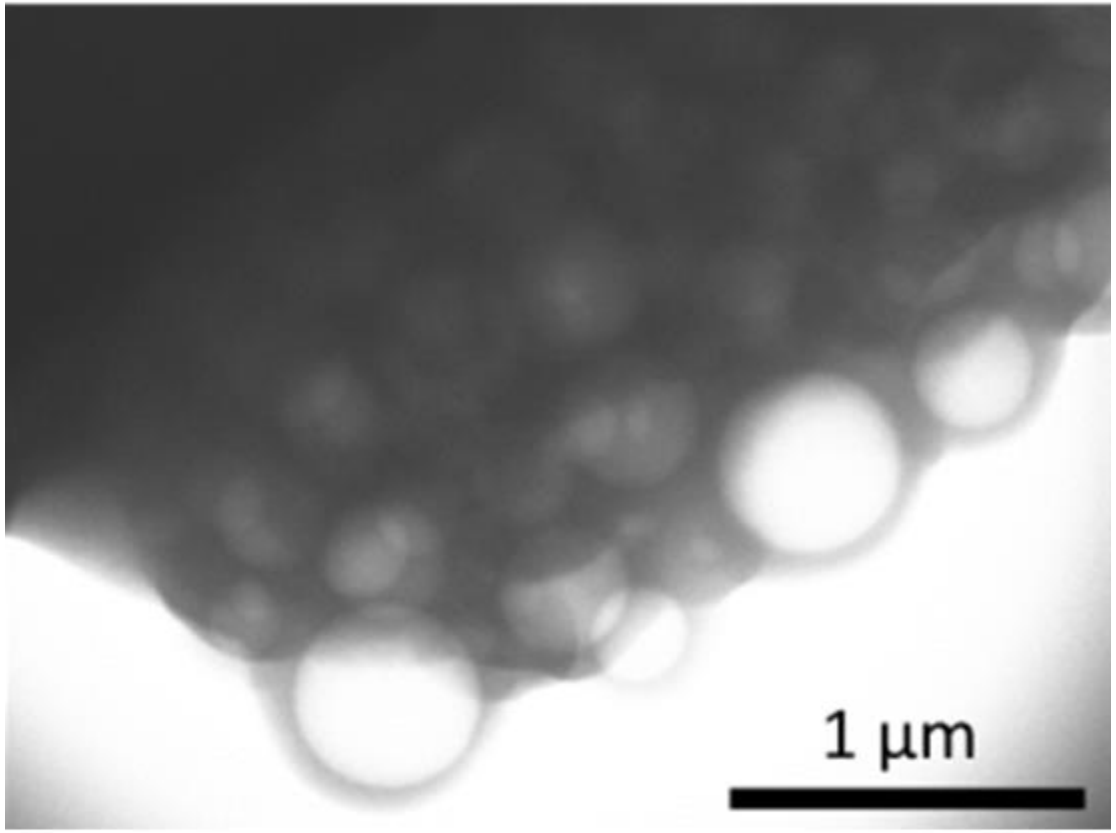




Zhang, Qiao, Dai, *Chem. Comm.* **2015**, *51*, 9246

Rheology and TEM Characterizations of Liquefied Hollow Carbon Spheres

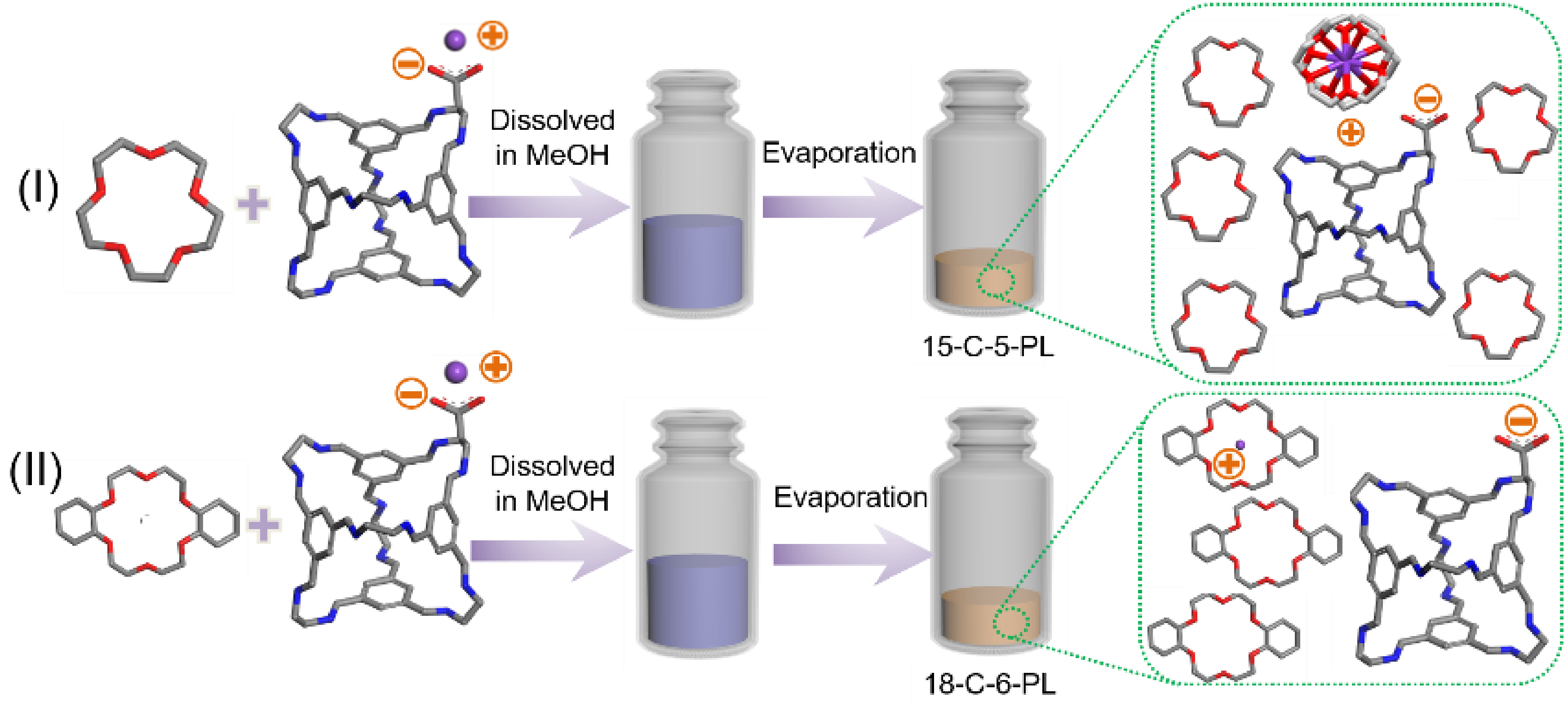


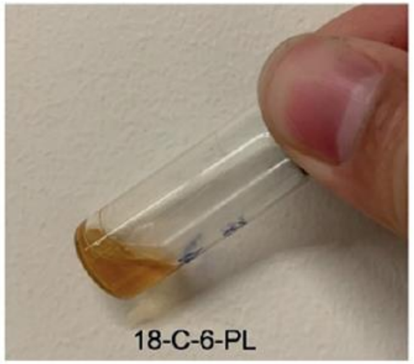


Li, P. P.; Zhang, J. S.; Dai, S. *et. al*. Electrostatic-Assisted Liquefaction of Porous Carbons. *Angew. Chem.-Int. Edit.* **2017**, *56*, 14958.

Supramolecular Approach to Cage-based Porous Ionic liquids (Type I) for Gas Storage and Separation

Scientific Achievement: A type I porous liquid, namely porous ionic liquid, based on anionic covalent cages and crown ethers via a supramolecular complexation strategy was successfully developed.

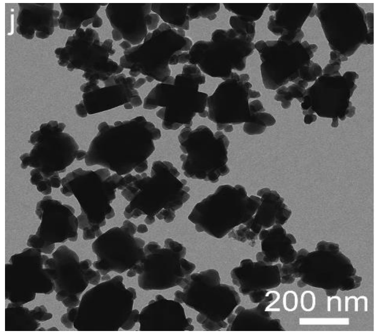


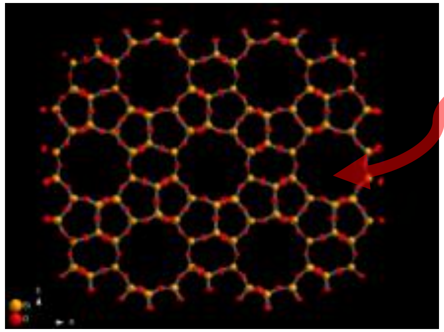


Jie, K.; Onishi, N.; Schott, J. A.; Popovs, I.; Jiang, D.-e.; Mahurin, H.; Dai, S. Transforming Porous Organic Cages into Porous Ionic Liquids via a Supramolecular Complexation Strategy. *Angew. Chem. In. Ed.* **2020**, DOI: 10.1002/anie.201912068.

Porous Liquid Zeolites

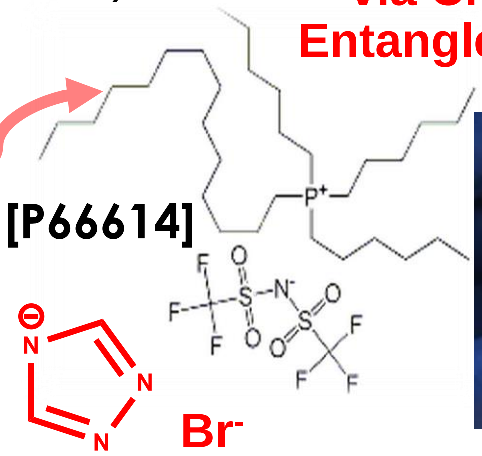
ZSM-5 Nanocrystals
(Zeolite Socony Mobil–5; Aluminosilicate Zeolite)

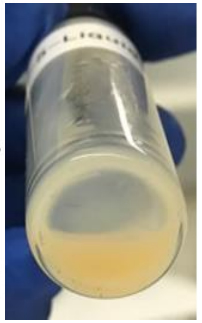




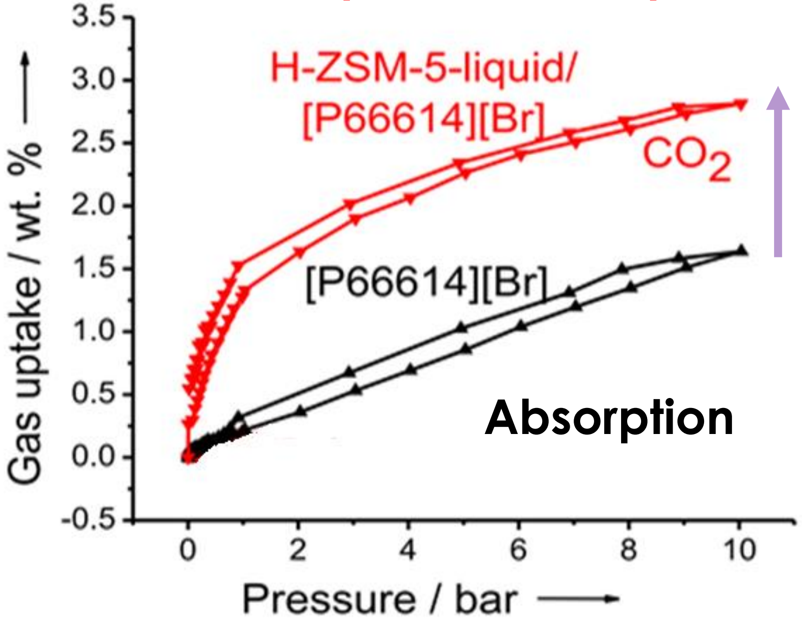
Negatively Charged Framework

Mechanical Bond via Chain Entanglement





Absorption + Adsorption



Li, Mahurin, Jiang, Dai, *et al.*, *Nanoscale*, **2019**, *11*, 1515-1519

Article

Microporous water with high gas solubilities

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Liquids with permanent microporosity can absorb larger quantities of gas molecules than conventional solvents[1], providing new opportunities for liquid-phase gas storage, transport and reactivity. Current approaches to designing porous liquids rely on sterically bulky solvent molecules or surface ligands and, thus, are not amenable to many important solvents, including water[2–4]. Here we report a generalizable thermodynamic strategy to preserve permanent microporosity and impart high gas solubilities to liquid water. Specifically, we show how the external and internal surface chemistry of microporous zeolite and metal–organic framework (MOF) nanocrystals can be tailored to promote the formation of stable dispersions in water while

Aug. 24, 2022
Jarad Mason

nature catalysis

May 15, 2023
Dan Nocera

Article

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Enhanced activity for the oxygen reduction reaction in microporous water

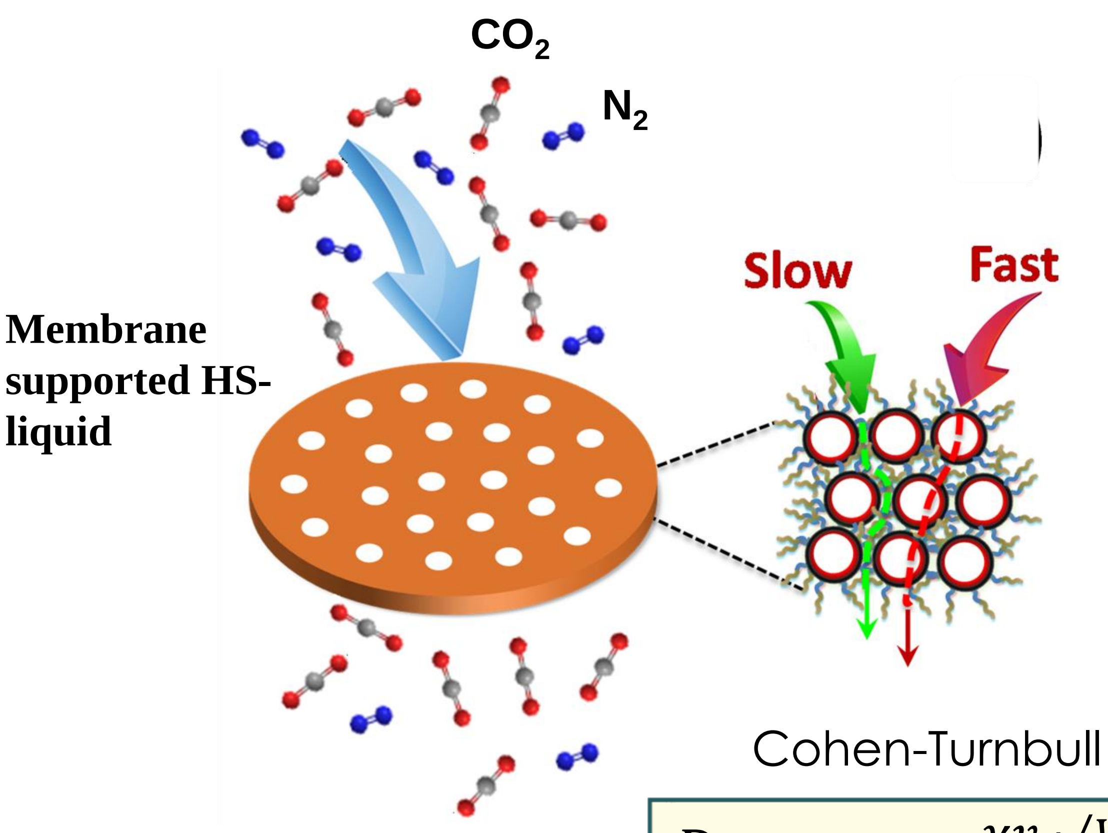
Received: 30 August 2022
Accepted: 7 April 2023
Published online: 15 May 2023
Check for updates

Agnes E. Thorarinsdottir[1,3], Daniel P. Erdosy[1,3], Cyrille Costentin[2], Jarad A. Mason[1] & Daniel G. Nocera[1]

Electrocatalysis of small gas molecules driven by renewable energy sources offers a promising route to carbon-neutral fuels and chemicals. Such small-molecule conversion reactions rely on water as a source of protons

OAK RIDGE National Laboratory

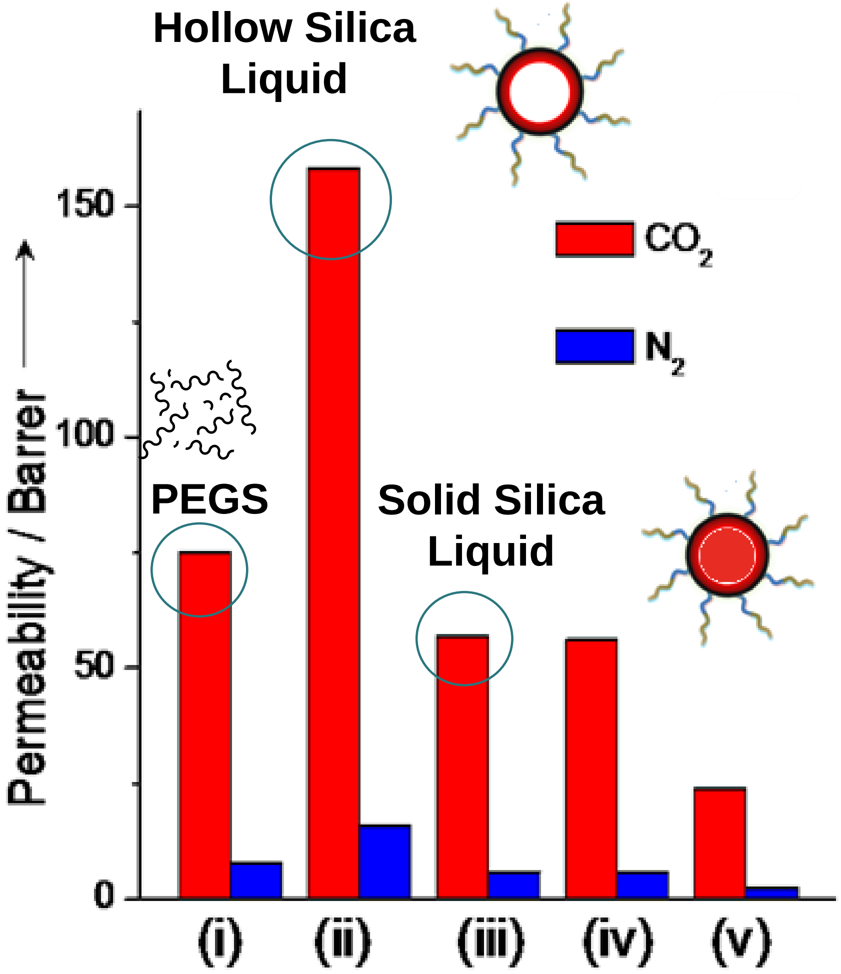
Gas separation properties of porous liquids



Cohen-Turnbull

$$D_A = \alpha \cdot e^{-\gamma v_A / V_{FV}}$$

Schematic representation of gas separation in membrane supported HS-liquid

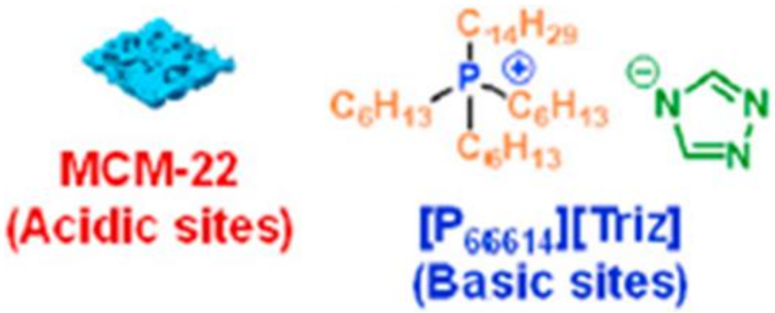


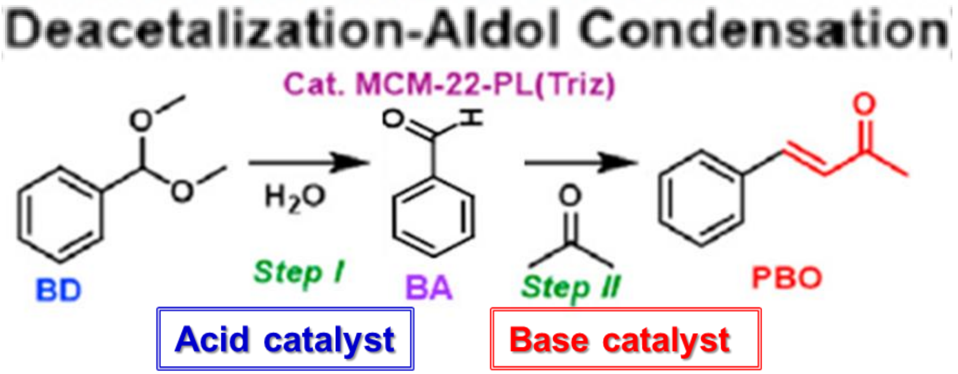
Gas permeability obtained on i) PEGS, ii) HS-liquid, iii) SS-liquid, iv) CS-liquid, and v) CS/Ni-liquid.

Zhang, J.; Chai, S.-H.; Qiao, Z.-A.; Mahurin, S. M.; Chen, J.; Fang, Y.; Wan, S.; Nelson, K.; Zhang, P.; Dai, S. *Angew. Chem. Int. Ed.* **2015**, *54*, 932 –936

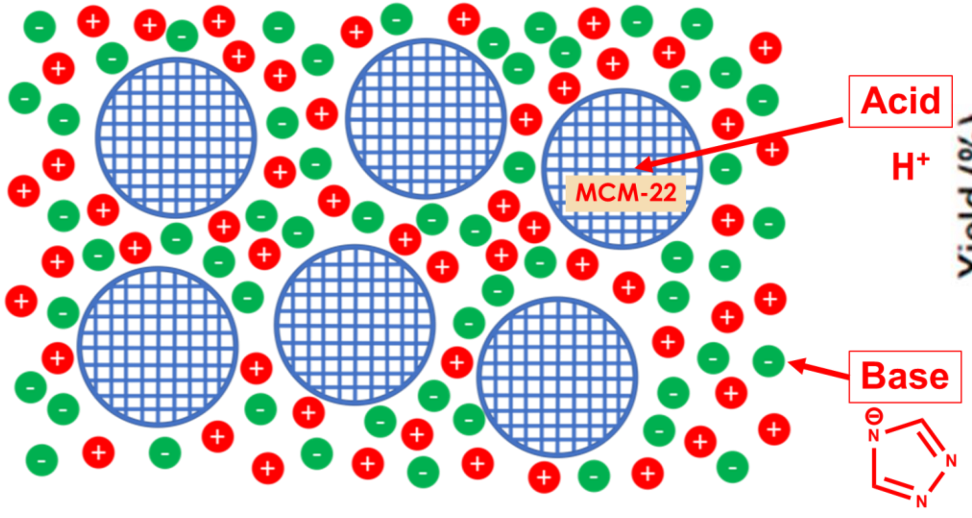
A Porous-Liquid Approach to Antagonistic Cascade Catalysis

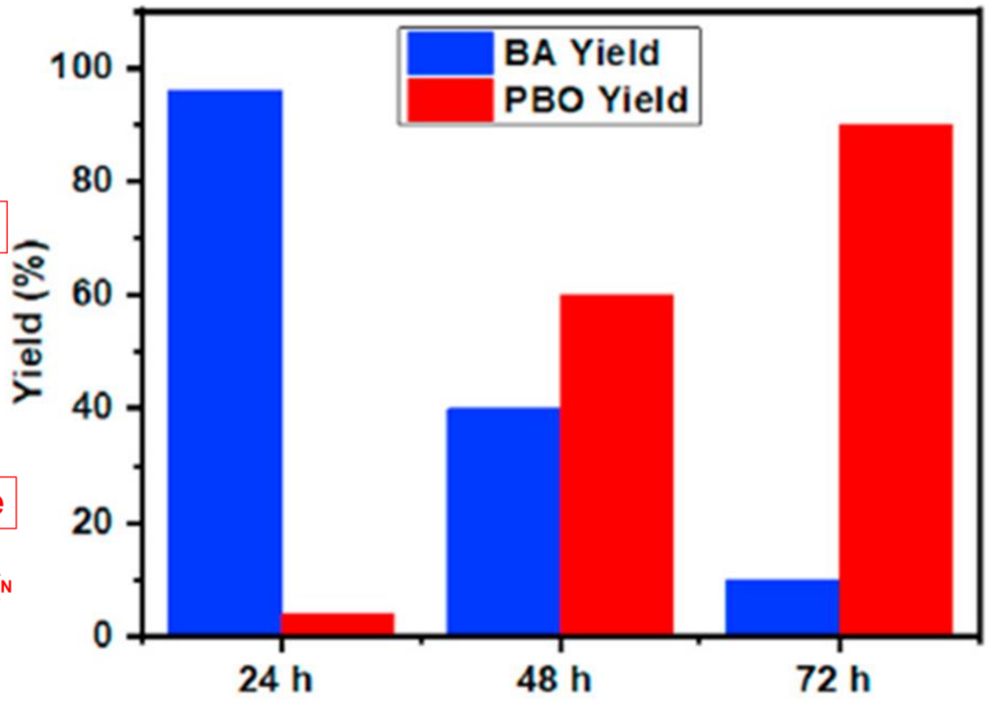
Microporous Ionic Liquids Based on MCM-22 Zeolite





- **Frustrated Lewis Pair (FLP) Ionic Liquids**
- **Strong Base & Strong Acid in the Same Solution**





Chen, Yang, Peng, Dai, *et al.*, A Bifunctional Zeolitic Porous Liquid with Incompatible Lewis Pairs for Antagonistic Cascade Catalysis. *Chem* **2021,** *7,* 3340-3358.

Synthesis of Graphite and Related Materials

Sources of Synthetic Graphite

Synthesis: High temperature synthesis of graphite

- Invented accidently by Edward Goodrich Acheson in 1890s

3C (coke) + SiO_2 → SiC + $2CO_{(g)}$ **T = ~2300 K**

SiC → C(graphite) + $Si_{(g)}$ **T = ~4500 K**

- Current Process:

C(coke) = C(graphite) **T = ~3300 K**

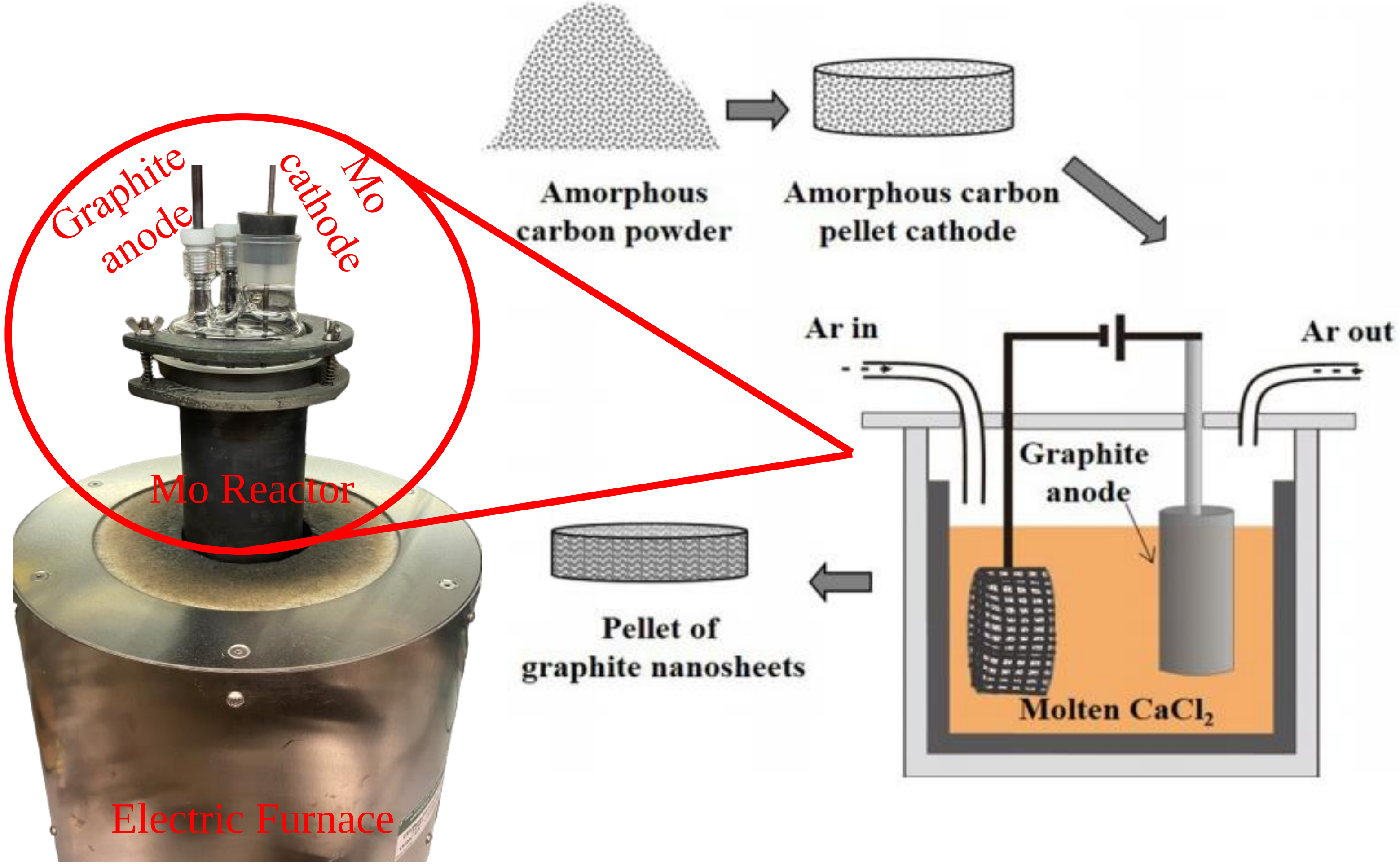
Graphitizable sources of amorphous carbon required

Edward Goodrich Acheson
(March 9, 1856 – July 6, 1931)

https://www.sciencehistory.org/historical-profile/edward-goodrich-acheson

A New Approach to Graphitization (Crystallization)

Electrochemical Graphitization



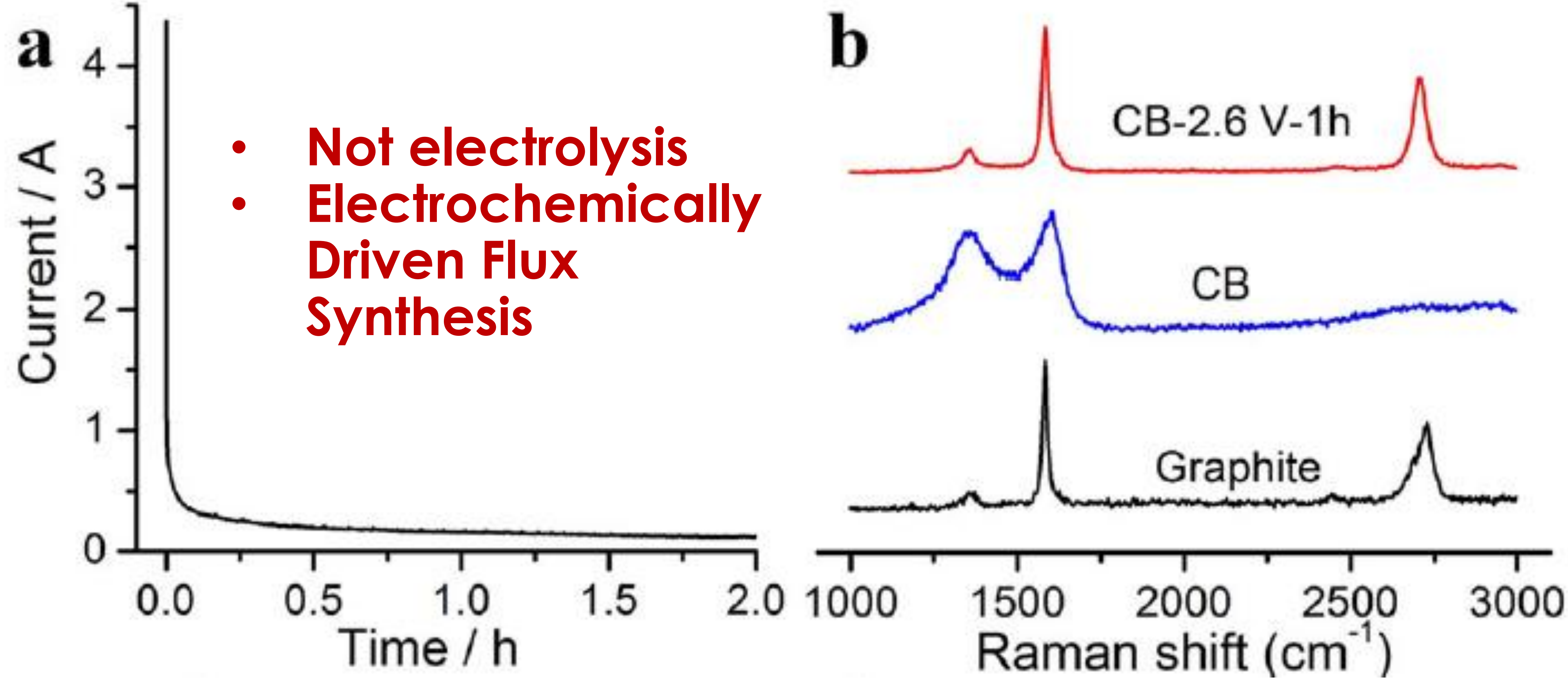
V = -2.6 V

T = 850 °C

Molten $CaCl_2$

- Peng, Dai, Jin, et. al., *Angew. Chem. Int. Ed.* **2017**, *56*, 1751-1755
- Bagri, Luo, Dai et. al., *Chem. Commun.* **2020**, *56*, 2783-2786

Electrochemical graphitization of carbon black (CB) in molten $CaCl_2$: (a) Current response at a constant cell voltage of 2.6 V,1093 K. (b) Raman spectra of CB before and after 1 h graphitization and commercial graphite powder.

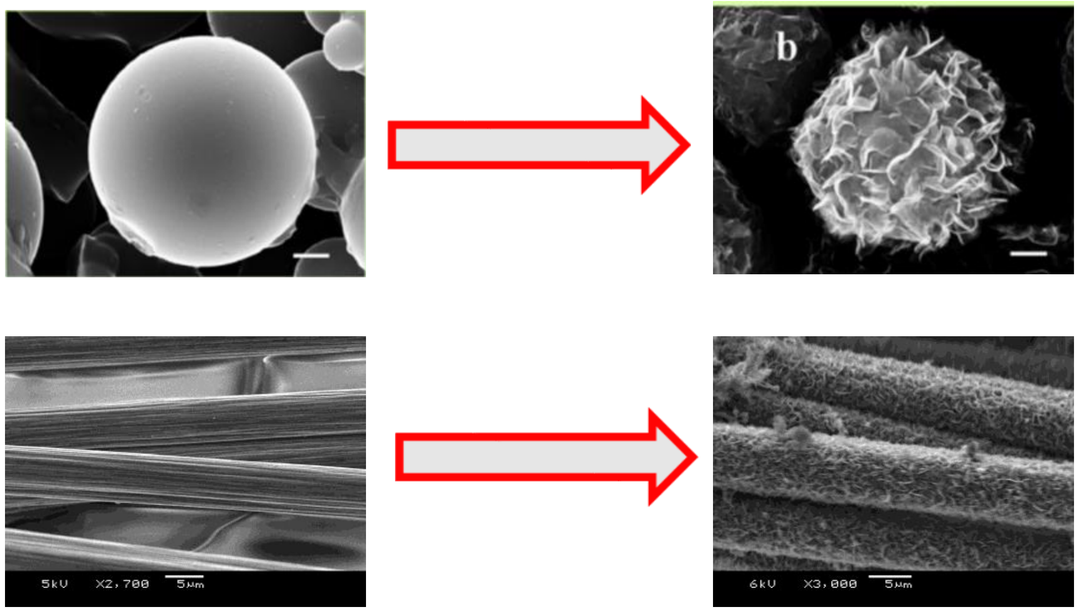


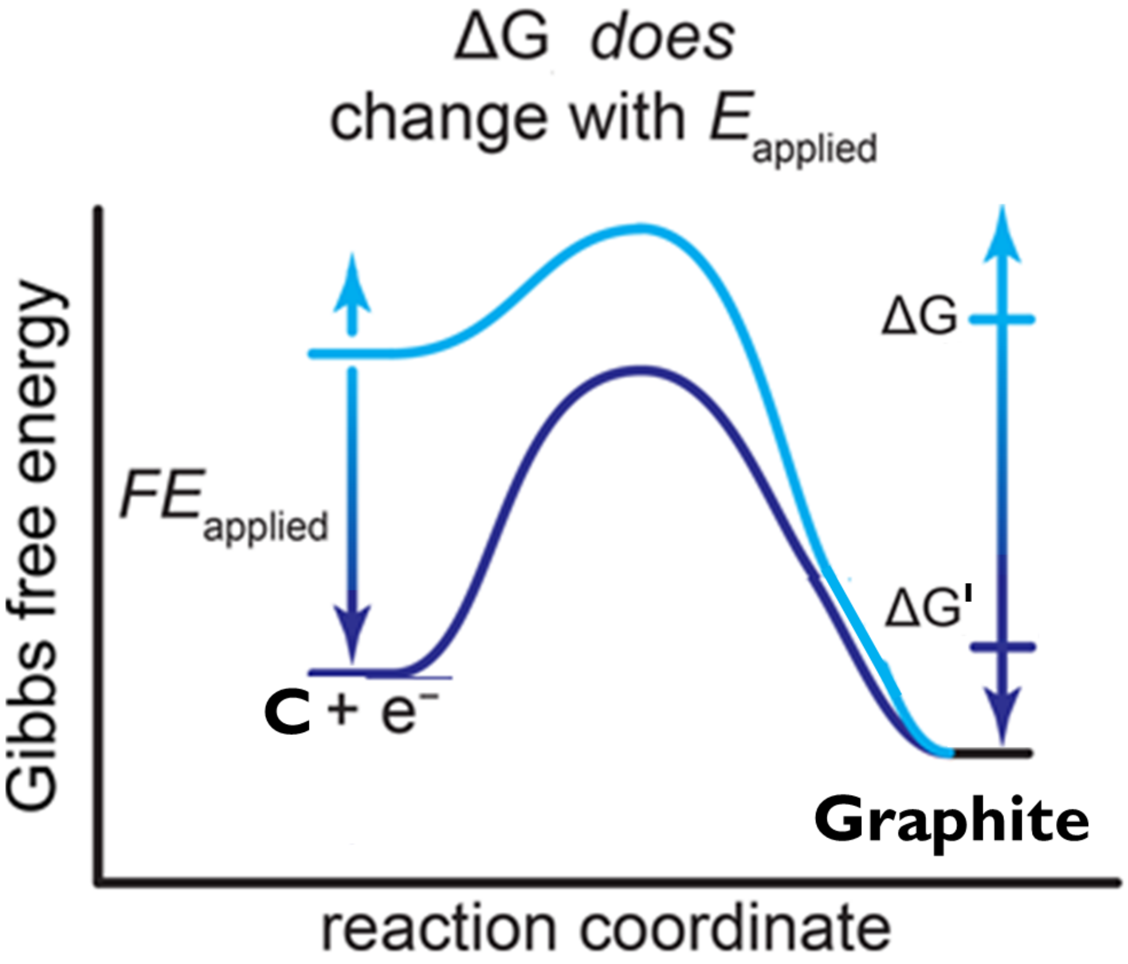
- Not electrolysis
- Electrochemically Driven Flux Synthesis

Peng et. al., *Angew. Chem. Int. Ed.* **2017**, *56*, 1751-1755

Potential Mechanism for Electrochemically Driven Flux Synthesis

- Electrochemical graphitization through unpinning of Fermi
- Solid phase transformation (topotactic)

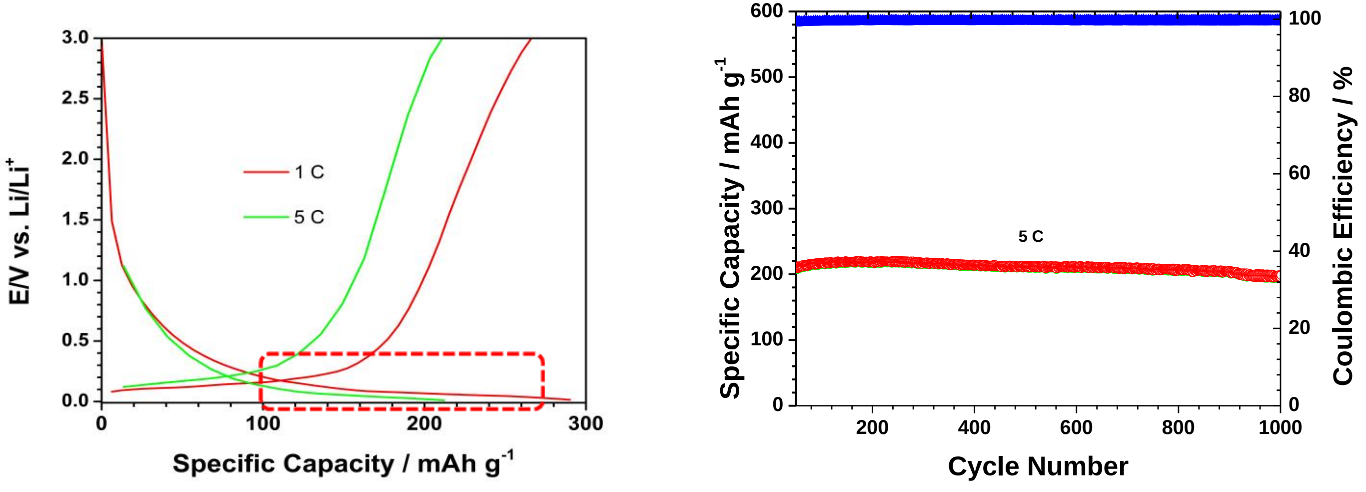




Jackson and Surendranath, *Acc. Chem. Res.* **2019**, *52*, 3432

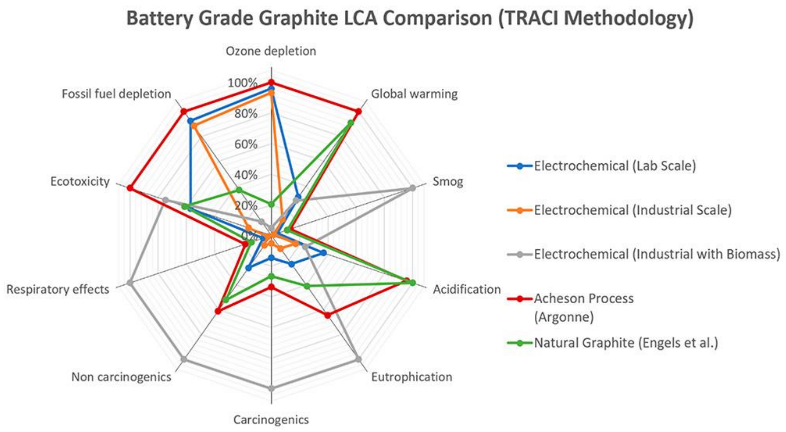
Electrochemical graphitization of activated coconut charcoals and coal chars

- Electrochemically graphitized activated coconut charcoal (EG-ACC) exhibits highly enhanced energy storage performance even at higher charging and discharging rates. (at 5C rate for 1000 cycles with capacity > 195 mAh g^{-1}).
- Energy storage capacity of EG-ACC much higher (5 times) than commercial graphite at 5C rate (~25-40 mAh g^{-1}).



Thapaliya, Luo, Dai, et. al.; *ACS Appl. Mater. Interfaces* **2021**, *13*, 4393

- The key usage of synthetic graphite is in electric vehicles.
- Graphite is one of just four metals and minerals on the critical materials list for which the United States is 100 % import reliant.
- Our BES-initiated research impacts on both EERE and FECM.

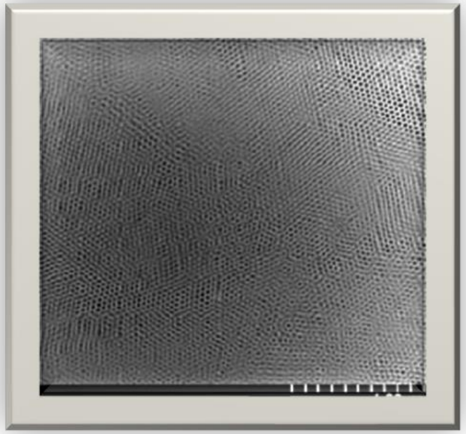


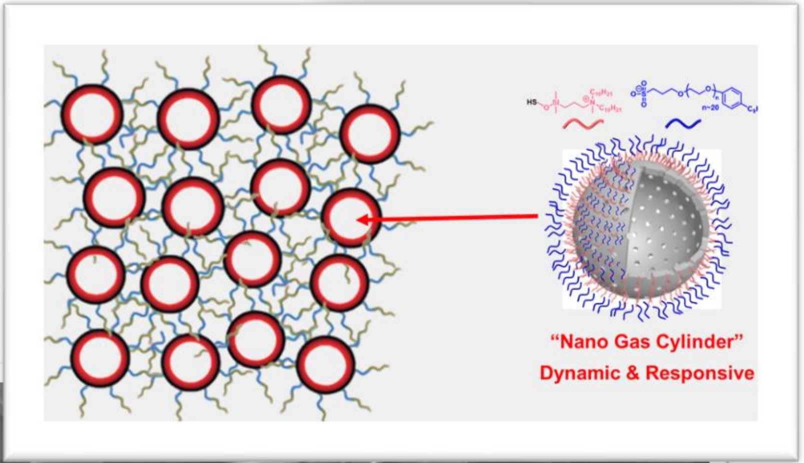
S. Kulkarni, T. Y. Huang, B. Prasad Thapaliya, H. M. Luo, S. Dai, F. Zhao, Prospective Life Cycle Assessment of Synthetic Graphite Manufactured via Electrochemical Graphitization, *ACS Sustain. Chem. & Eng.* 2022, 10, 13607−13618

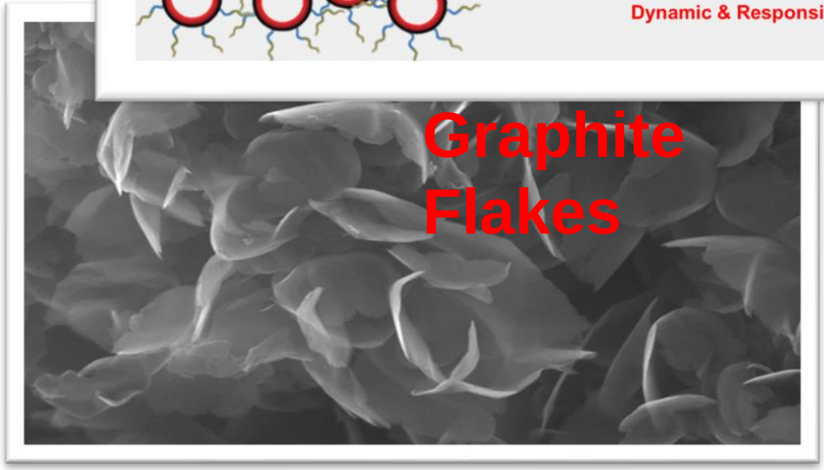
Oak Ridge National Laboratory
CMI Critical Materials Institute
AN ENERGY INNOVATION HUB

Conclusions

- Soft-templating methodologies (solvent & solvent-free) have been developed for synthesis of nanoporous carbons
  - Fast transport
  - Importance of mesopores in gas separation & energy storage
- Liquid porous materials including liquid zeolites were developed
  - Intrinsic free volumes for separation & catalysis
  - Soft adsorbents (dynamic & responsive)
- Crystallization strategies for carbon and related materials were developed
  - Low temperature graphitization technology
  - Electrochemically facilitated flux synthesis







Thanks for your attention!