Next Generation Fiber-Encapsulated Nanoscale Hybrid Materials for Direct Air Capture with Selective Water Rejection

Project Number DE-FE0031963

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Columbia University

U.S. Department of Energy

National Energy Technology Laboratory

2021 Carbon Management and Oil & Gas Research Project Review Meeting

August 18, 2021

Program Overview

a. Funding: $800,000 DOE + $200,000 Cost Share

b. Overall Project Performance Dates: 01/01/2021 – 06/30/2022

c. Project Participants:

Columbia University (lead institution: Alissa Park (PI))

Cornell University (Yong L. Joo)

Oak Ridge National Laboratory (Michelle Kidder)

d. Overall Project Objectives

We aim to address direct air capture (DAC) challenges by developing the **next generation fiber-encapsulated DAC sorbent** employing an electrospun, solid sorbent embedded with liquid-like Nanoparticle Organic Hybrid Materials (NOHMs) that will **selectively reject water while allowing facile CO_2 diffusion.**

Team Members

Design, Synthesis and Testing of NOHMs for CO_2 capture

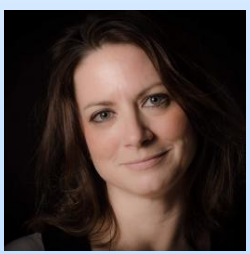


Alissa Park (PI) Annie Lee (GRA) Jeffrey Xu (Postdoc)

Fabrication of nanofibers via electrospinning technology


Kyle Kersey (GRA) Yong Joo (co-PI)

Design and characterization of polymeric materials

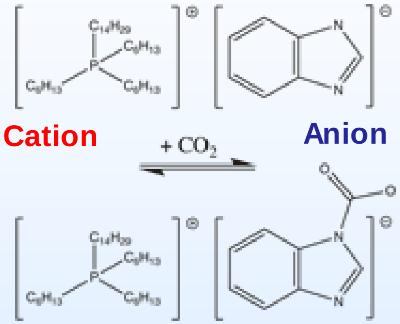


Michelle Kidder (co-PI)

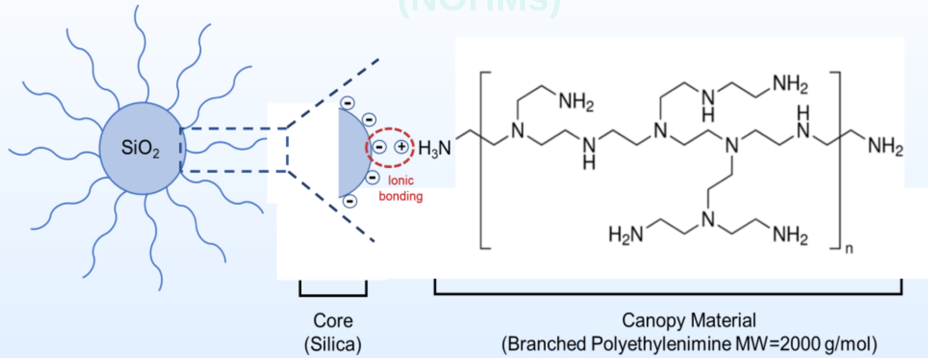
Technology Background

Water-lean Solvents for CO_2 Capture

Ionic Liquids

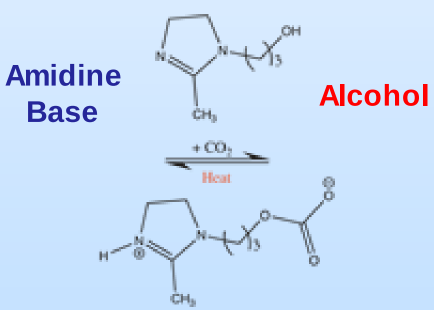


Liquid-like Nanoparticle Organic Hybrid Materials (NOHMs)



CO_2BOLs

CO_2 Binding Organic Liquids



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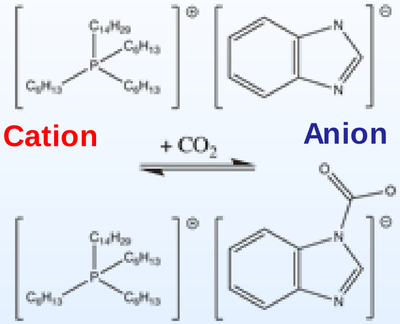

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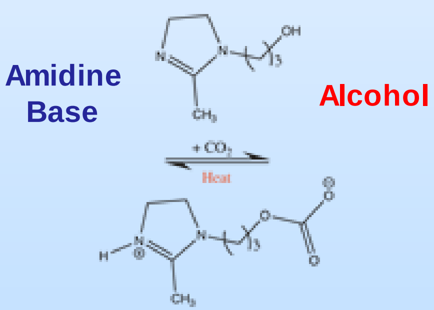

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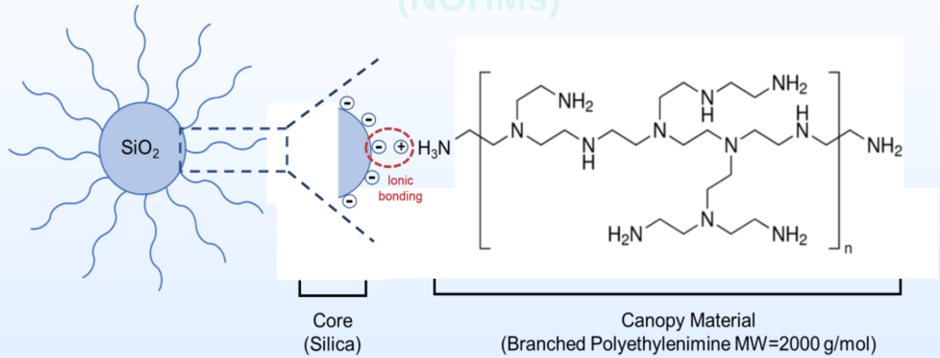
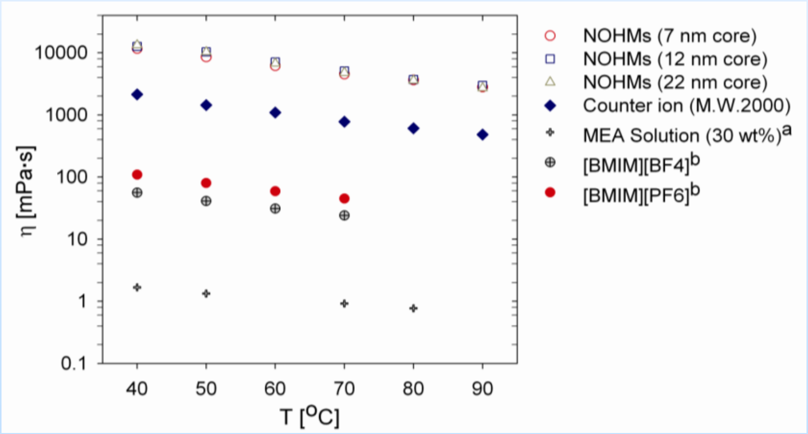
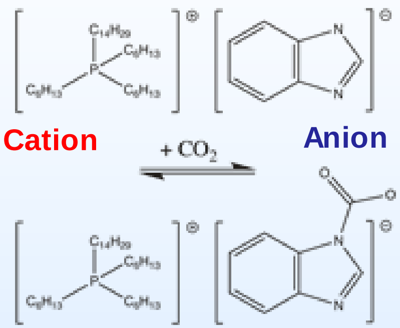




Petit, Bhatnagar & Park, *Journal of Colloid and Interface Science* (2013)

Water-lean Solvents for CO_2 Capture

Ionic Liquids



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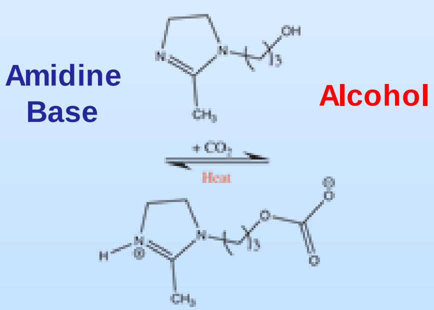
CO_2 Binding Organic Liquids



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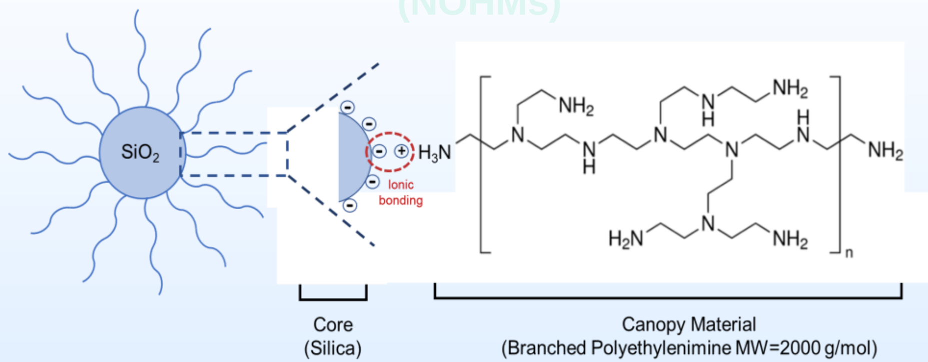
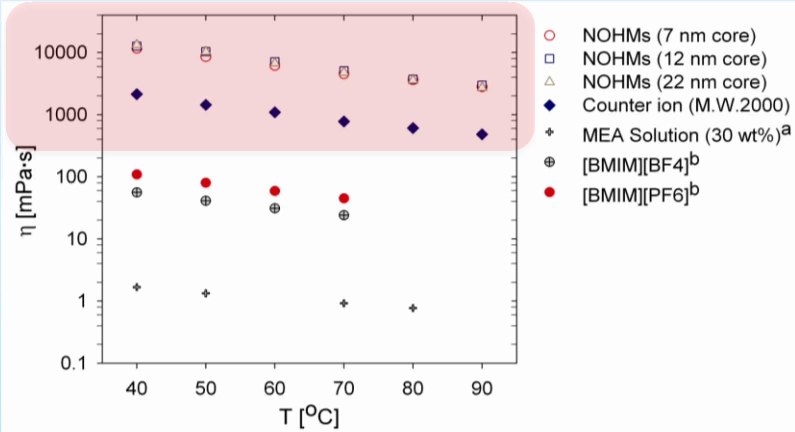
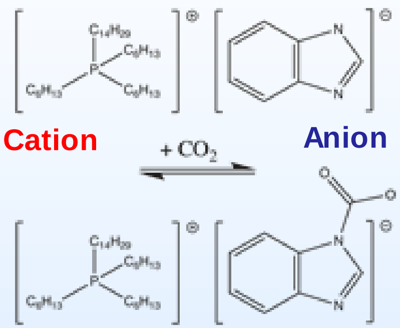




Petit, Bhatnagar & Park, *Journal of Colloid and Interface Science* (2013)

Water-lean Solvents for CO_2 Capture

Ionic Liquids

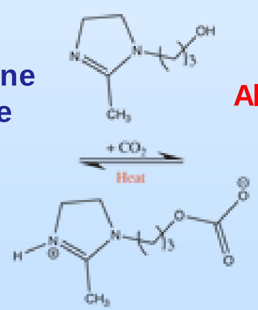


CO_2BOLs

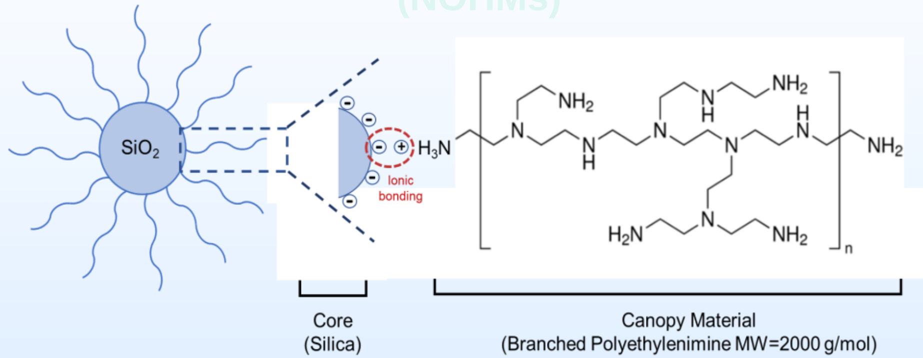
CO_2 Binding Organic Liquids

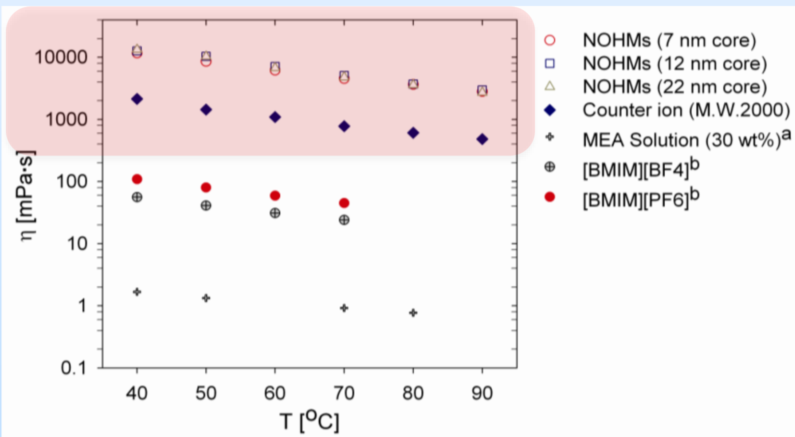
Amidine Base

Alcohol



Liquid-like Nanoparticle Organic Hybrid Materials (NOHMs)



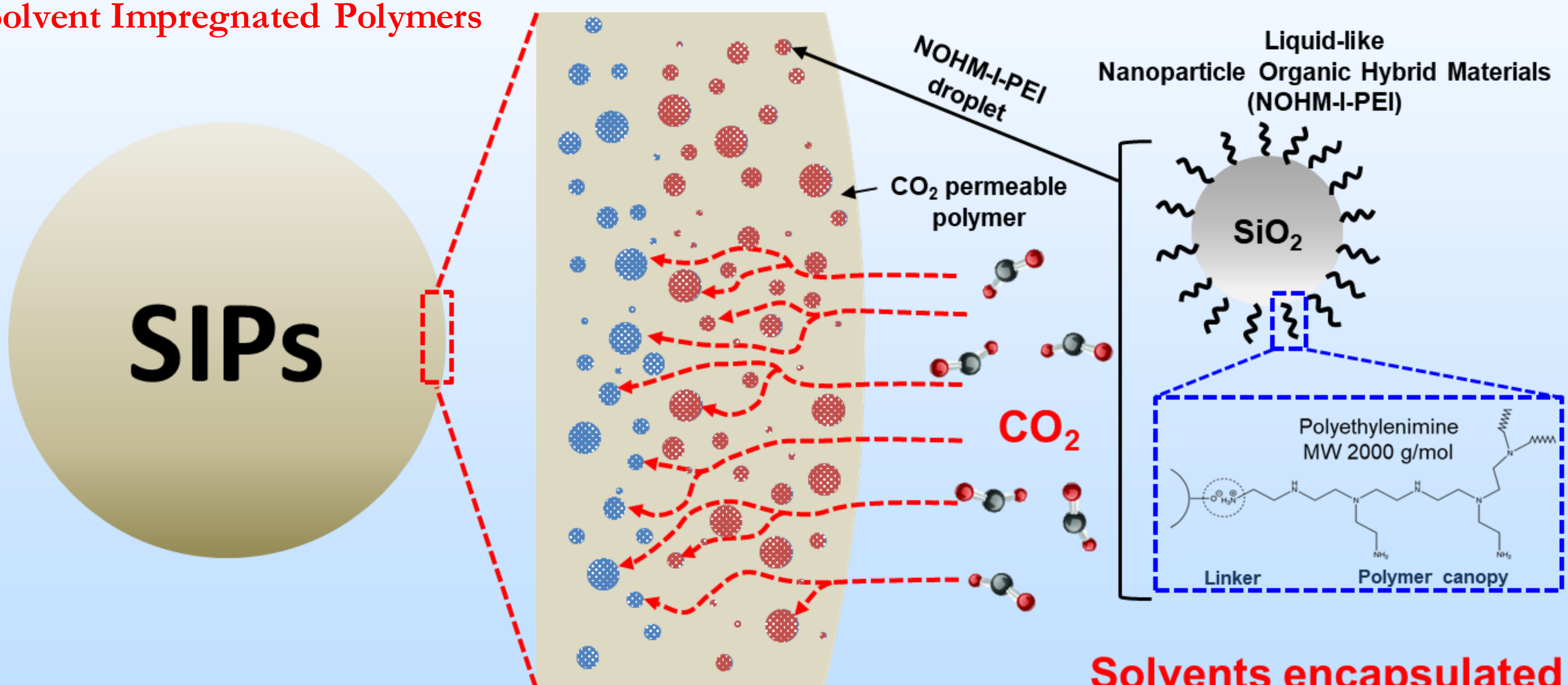


Petit, Bhatnagar & Park, *Journal of Colloid and Interface Science* (2013)

Introduction of nanoparticles increases the viscosity of the system
→ Need to develop **novel carriers** of NOHMs

Encapsulation of NOHM-I-PEI for CO_2 Capture

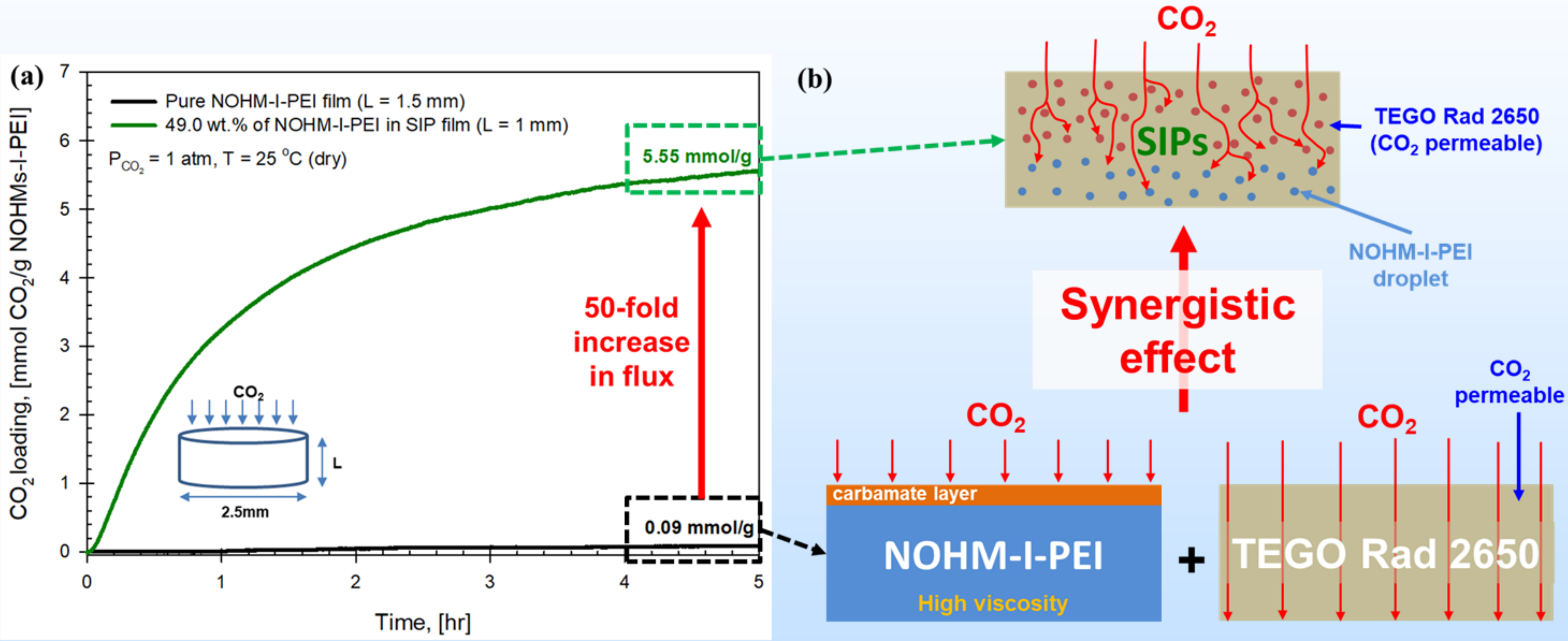
Solvent Impregnated Polymers



Solvents encapsulated
solid sorbents

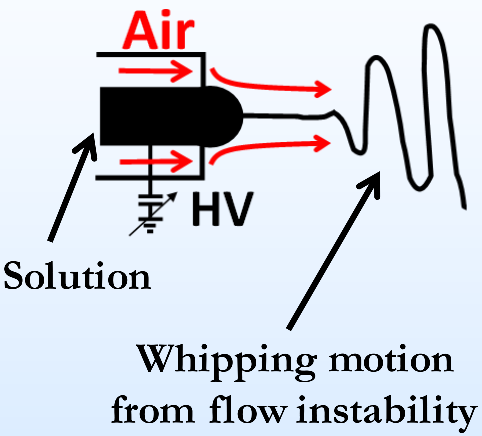
Rim et al., *Advanced Functional Materials* (2021)

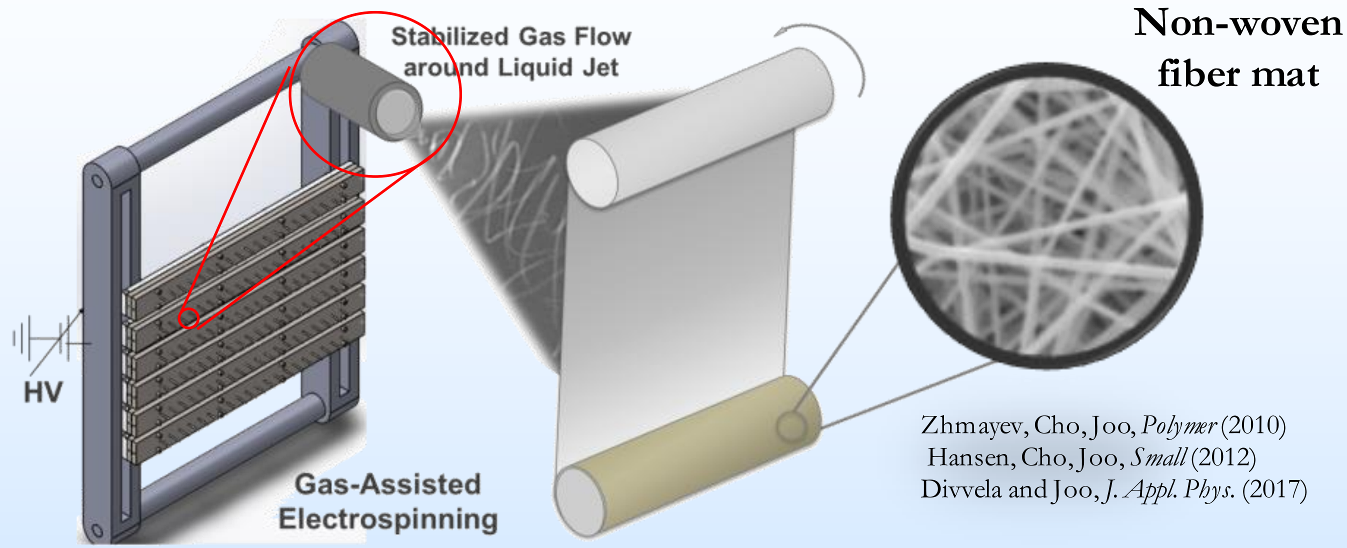
Accelerated CO_2 Sorption Kinetics of NIPEI via Increased Interfacial Area



Rim et al., *Advanced Functional Materials* (2021)

Gas-Assisted Electrospinning



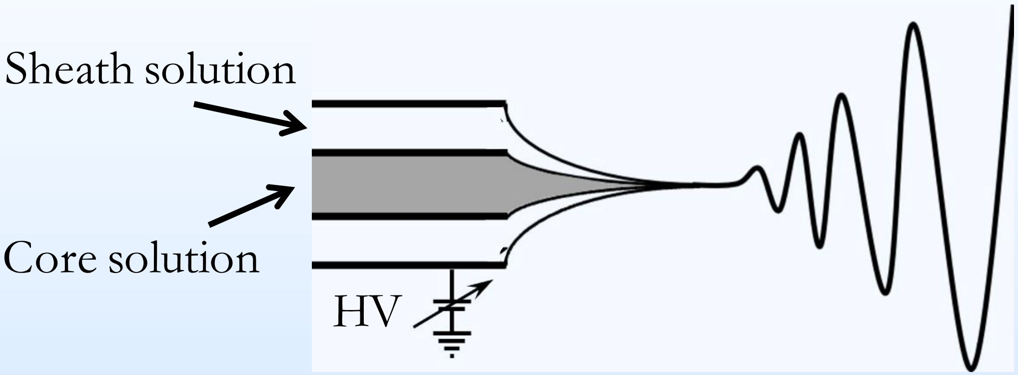


Zhmayev, Cho, Joo, *Polymer* (2010)
Hansen, Cho, Joo, *Small* (2012)
Divvela and Joo, *J. Appl. Phys.* (2017)

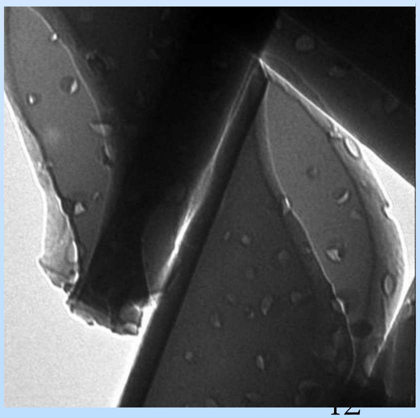
- Sheath of high-speed air promotes faster solvent evaporation than in traditional electrospinning
- Able to utilize faster flow rates to decrease processing time

Core-Sheath Fiber Morphology

- Coaxial electrospinning allows control of internal fiber assembly



Hollow
V_2O_5/SiO_2 Nanofibers



Panels and Joo, *J. Nanomater.* (2006)

Core-Sheath Fiber Morphology

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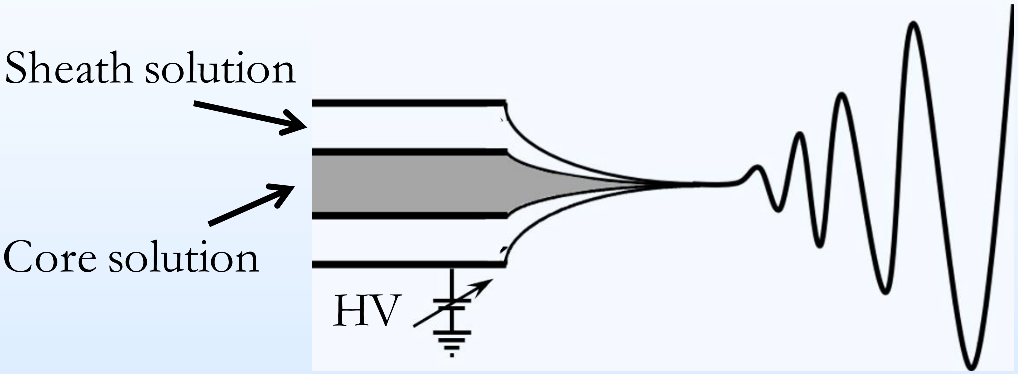
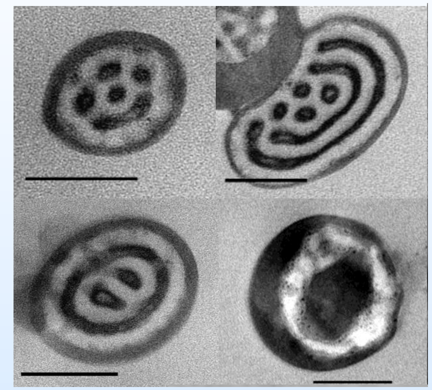
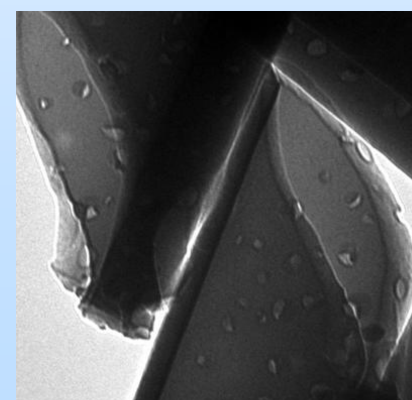




SiO_2 Nanoparticles in PI-*b*-PS Nanofibers

Kalra and Joo, *Small* (2008), (2009)

Hollow V_2O_5/SiO_2 Nanofibers



Panels and Joo, *J. Nanomater.* (2006)

Core-Sheath Fiber Morphology

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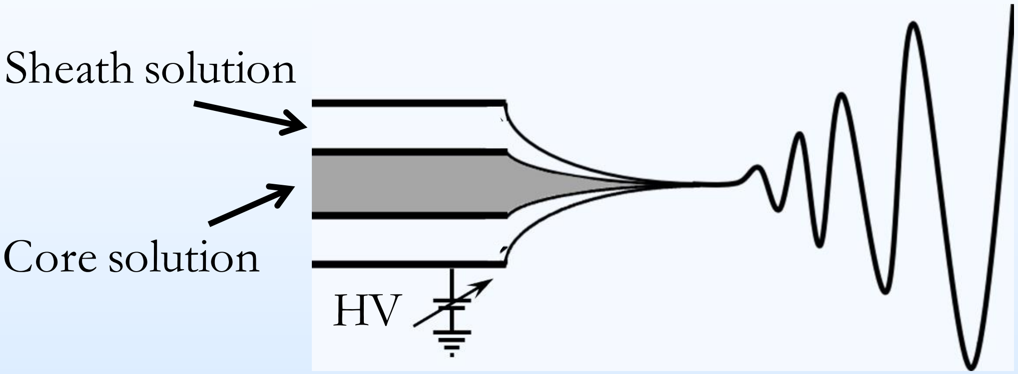
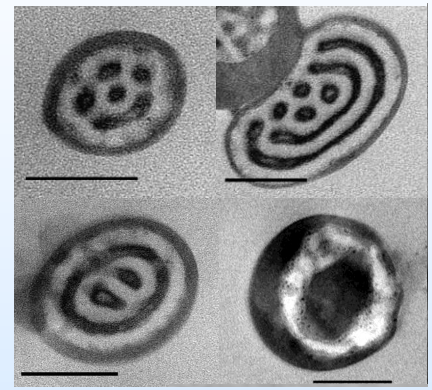
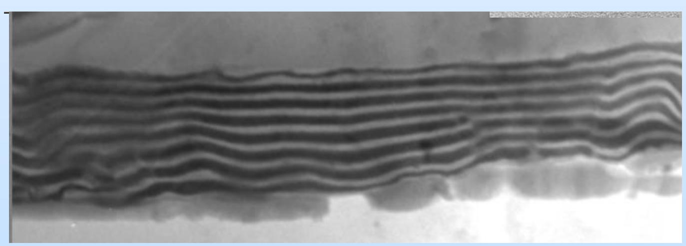


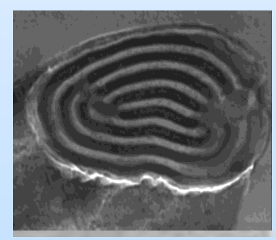


SiO_2 Nanoparticles in PI-*b*-PS Nanofibers

Kalra and Joo, *Small* (2008), (2009)

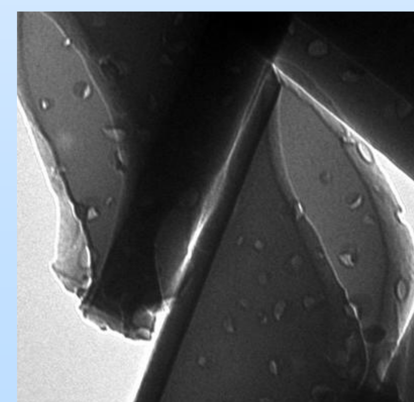
Alternating Layers of PI-*b*-PS Nanofibers





Kalra and Joo, el al., *Macromol.* (2006), *Adv. Mater.* (2006)

Hollow V_2O_5/SiO_2 Nanofibers



Panels and Joo, *J. Nanomater.* (2006)

Core-Sheath Fiber Morphology

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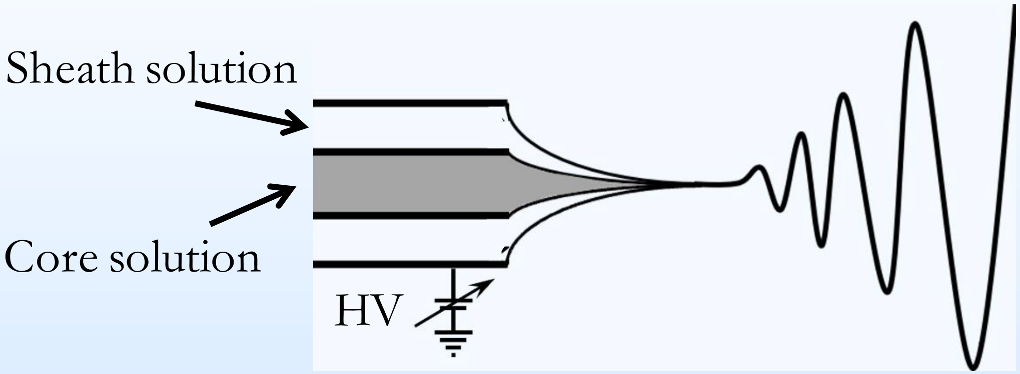

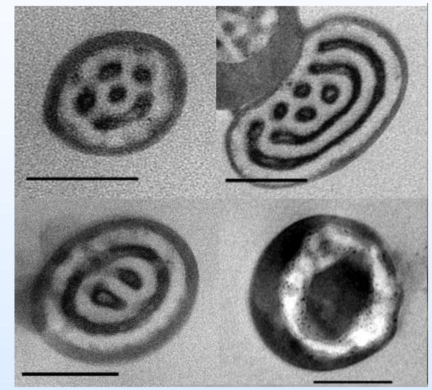

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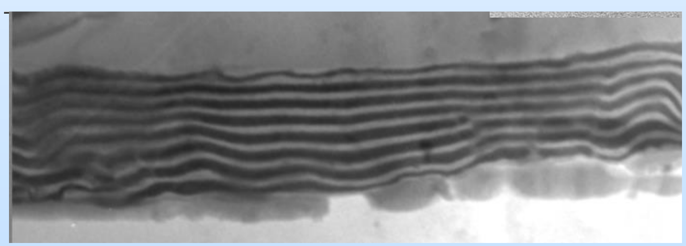
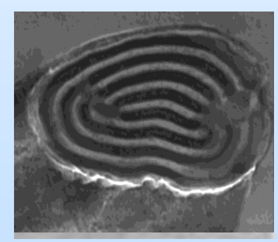
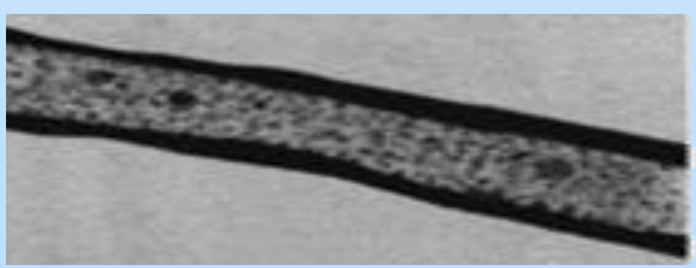
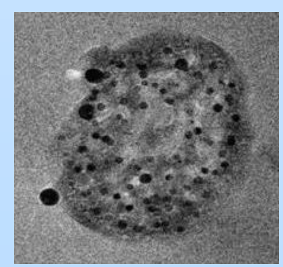




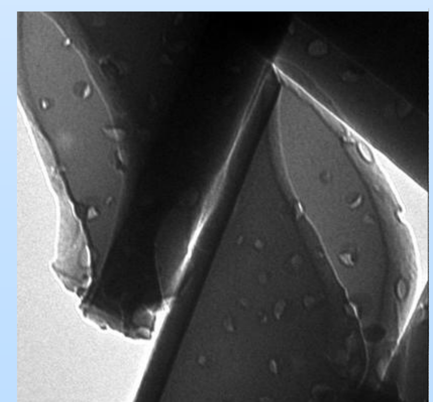
Kalra and Joo, el al., *Macromol.* (2006), *Adv. Mater.* (2006)

Core (SiO_2)/Sheath (Ni) Nanofibers



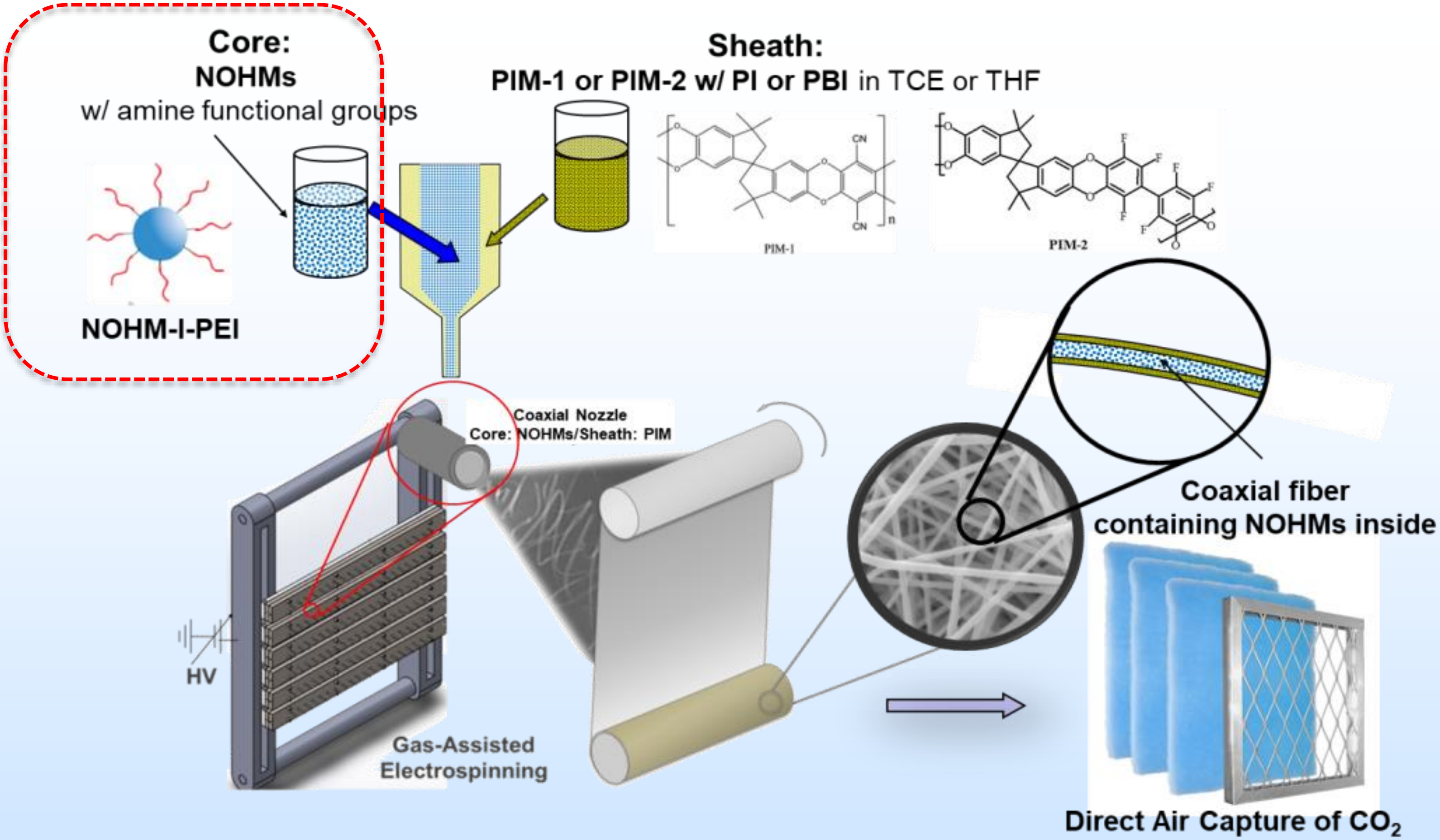


Hollow V_2O_5/SiO_2 Nanofibers



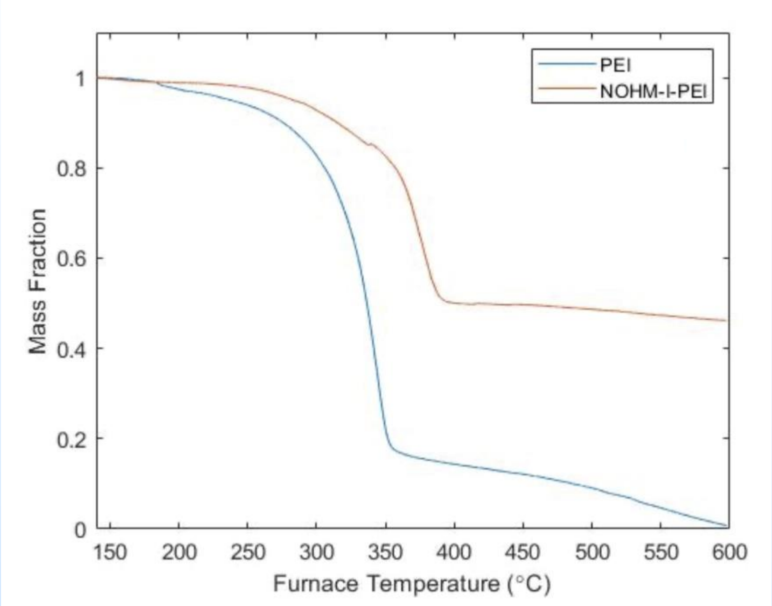
Panels and Joo, *J. Nanomater.* (2006)

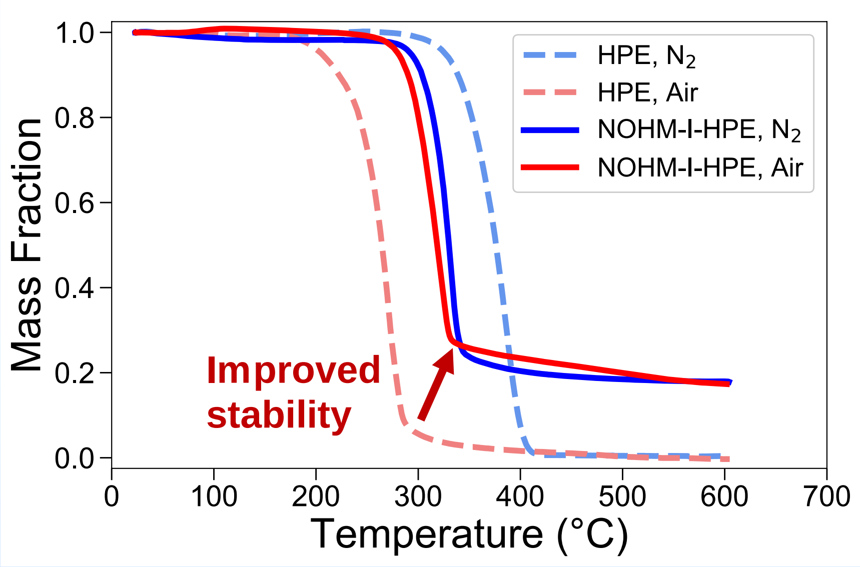
Progress and Current Status of Project



Objective: To address direct air capture (DAC) challenges by developing the **next generation fiber-encapsulated DAC sorbent** employing an electrospun, solid sorbent embedded with liquid-like Nanoparticle Organic Hybrid Materials (NOHMs) that will **selectively reject water while allowing facile CO_2 diffusion**.

Thermal Oxidative Stability of NOHMs





Feric T., et al., Submitted manuscript

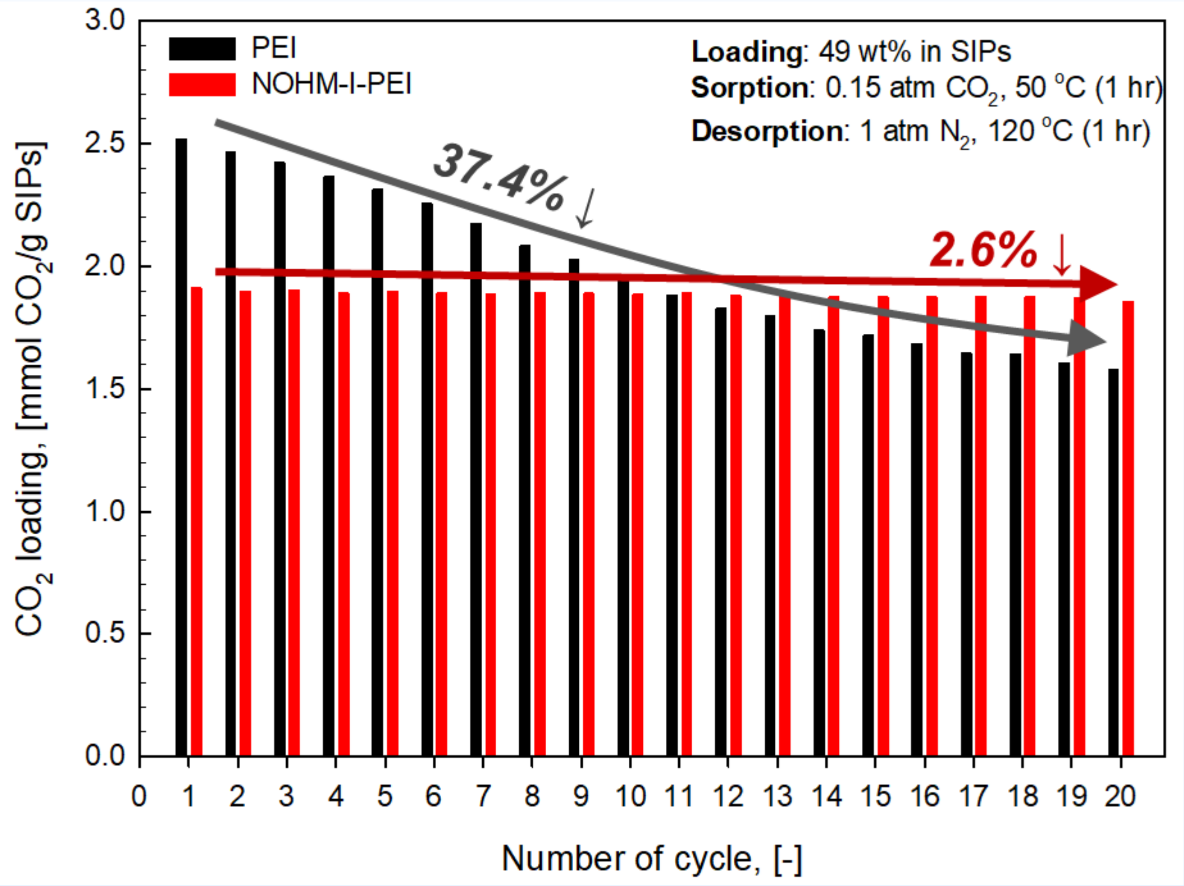
TGA temperature scan under Air, 0 – 600 C

Rate: 10 K/min

TGA temperature scan, Rate: 5 K/min

- **Synthesized NOHMs exhibit improved thermal stability than free polymers (e.g., HPE and PEI)**

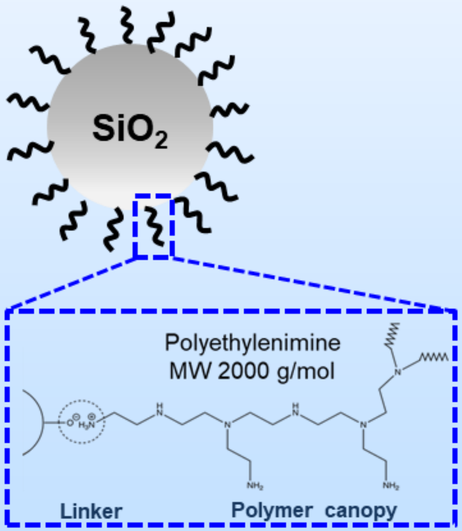
Recyclability of Thermally Stabile NIPEI-SIPs

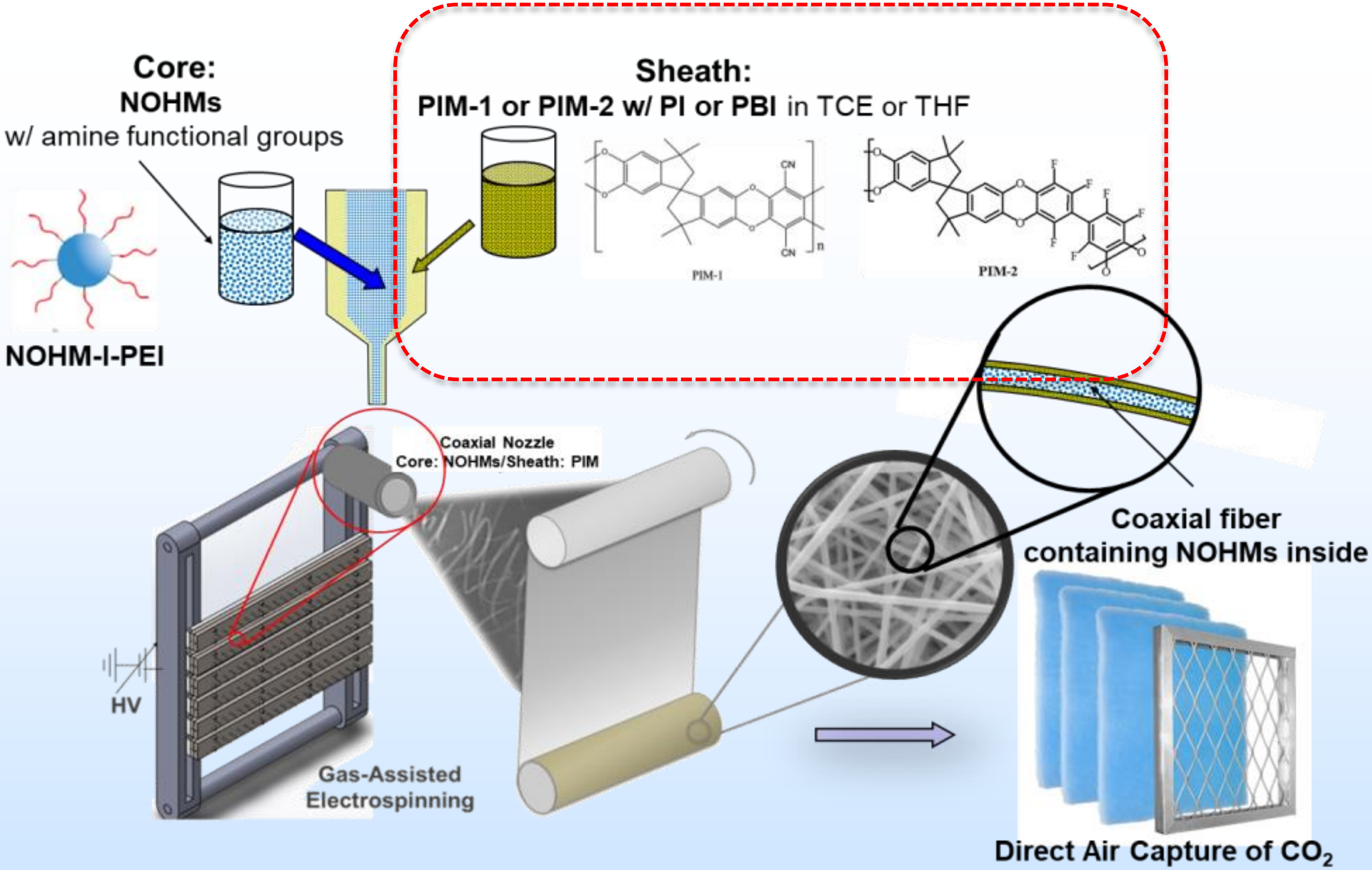


1st cycle

PEI-SIPs > NPEI-SIPs

→ 20 wt% of inert silica nanoparticles





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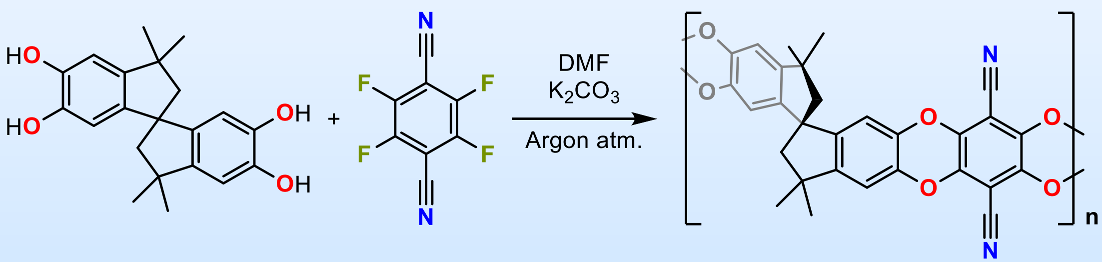
Synthesis of Polymers of Intrinsic Microporosity (PIM-1 and PIM-2)

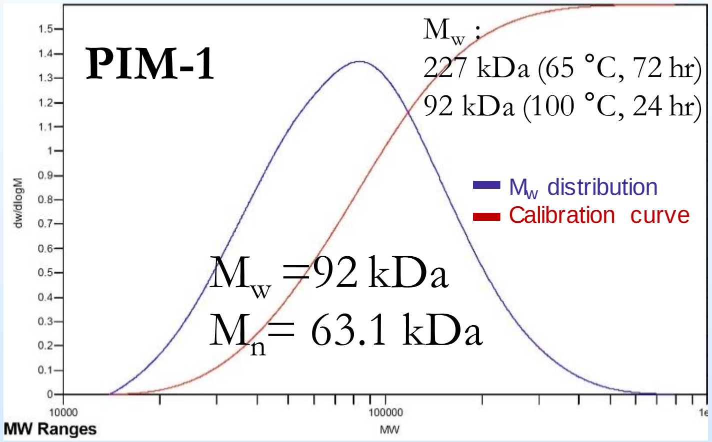
Incorporate axial chirality into polymeric structure through monomers

Tuning M_w and M_n via reaction time and/or temp.:

PIM-1 BET Surface Area : 743.3 ± 9.1 m^2/g

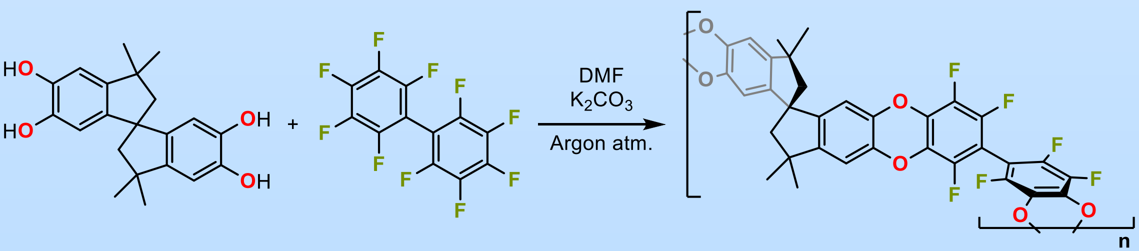
Literature Range: 600-875 m^2/g

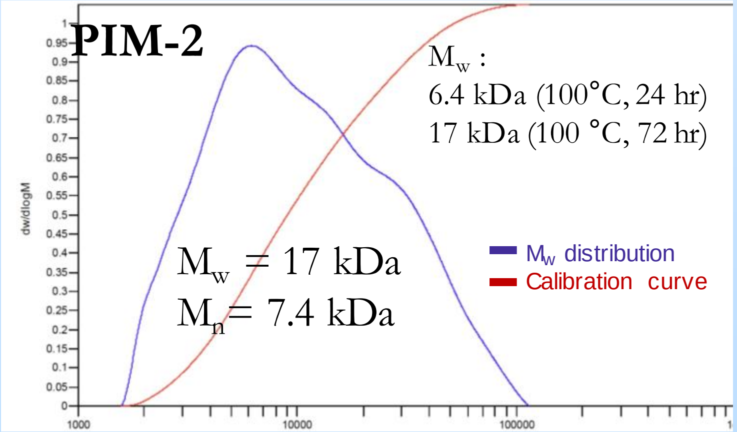




PIM-2 BET Surface Area : 513.0 ± 9.5 m^2/g

Literature Range: ~600 m^2/g

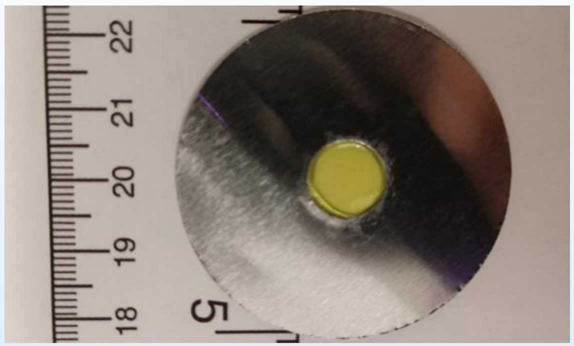




McKeown, N., *Macromolecules* 2010, 43, 12, 5163–5176

PIM-1 Membranes Exhibit High Permeability and Selectivity of CO_2

Thin PIM-1 membranes via solution casting



Permeability test setup

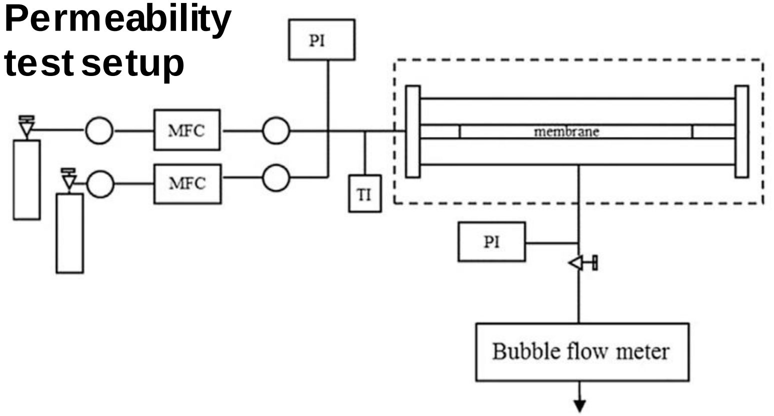
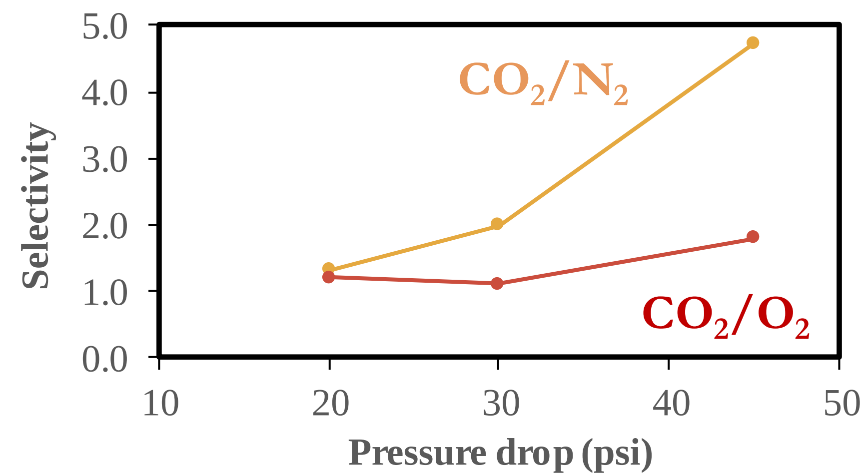
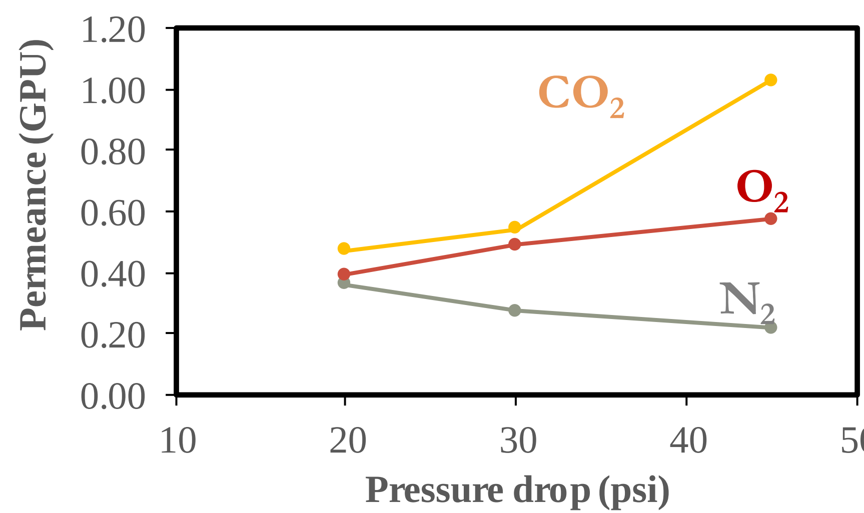


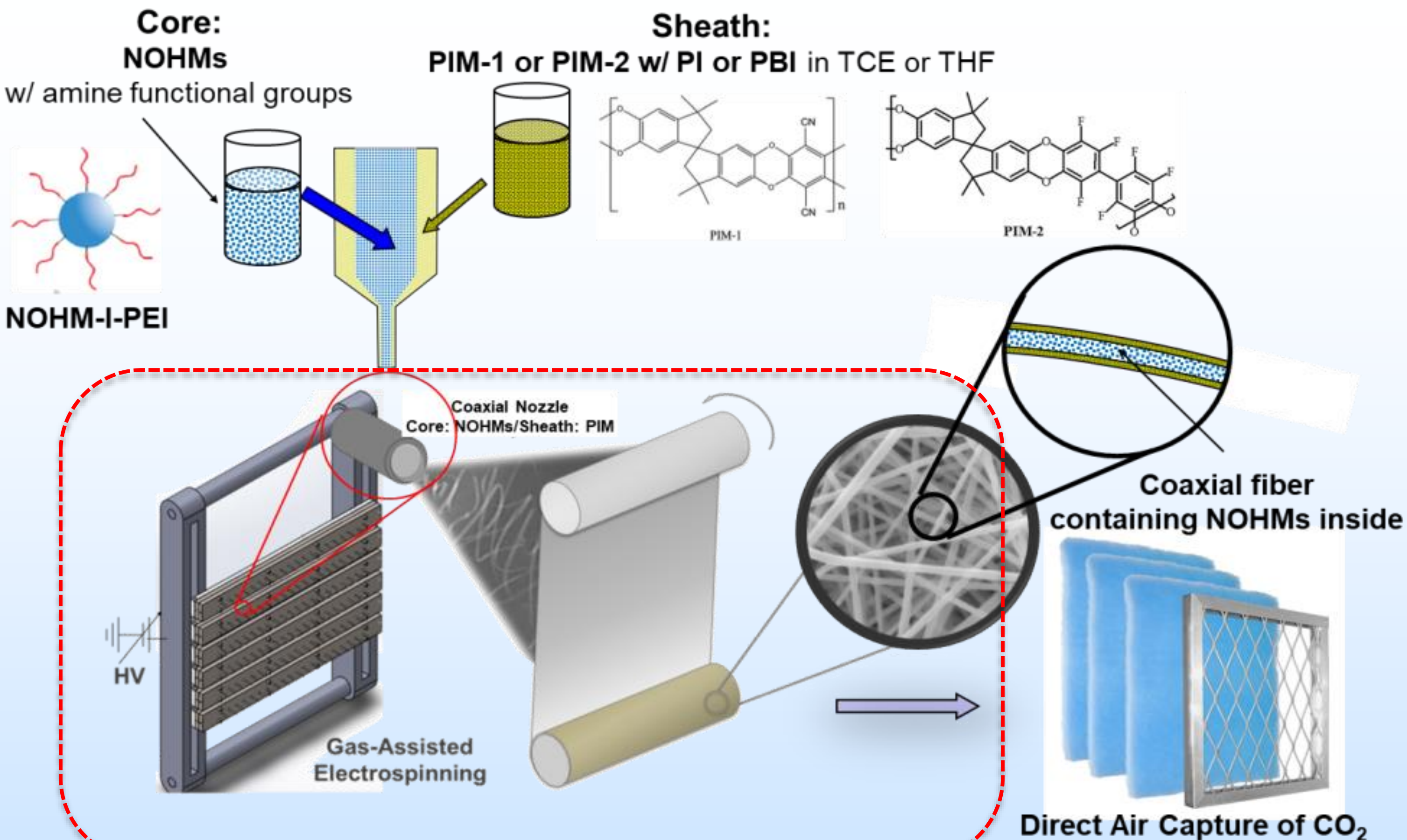
Fig. 2. Schematic of gas permeation test system (MFC: mass flow controller, PI: pressure indicator, TI: temperature indicator).

P.-S. Lee et al. / Microporous and Mesoporous Materials 224 (2016) 332–338





Dry conditions, 25°C, after methanol treatment



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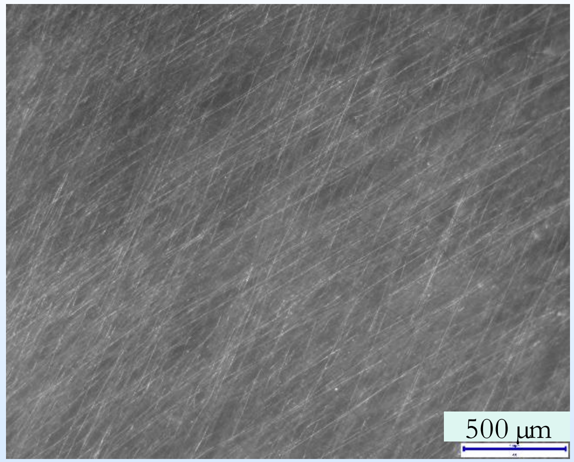
Development of Micron-Scale PIM-1 Fibers

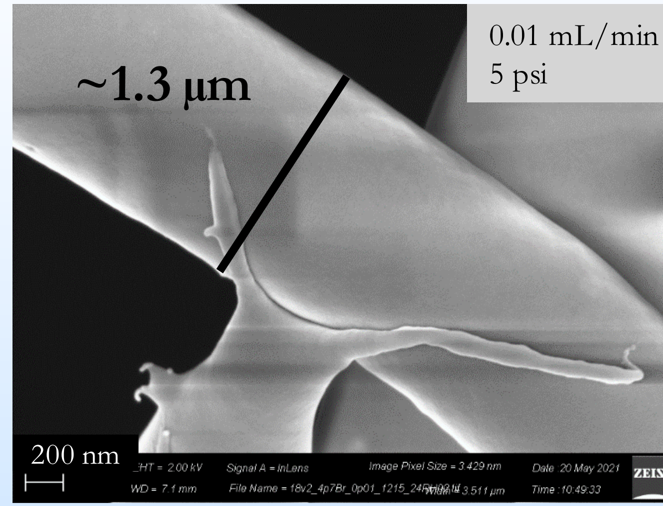
Electrospinning PIM-1 polymer in 1,1,2,2-tetrachloroethane produces highly uniform micron-scale fibers.

The organic electrolyte $[NBu_4]Br$ is employed to increase the polymeric solution conductivity to decrease fiber dimensions

Common to all images: 18% PIM-1, 2.5% $[NBu_4]Br$, 12 kV, 15 cm collector distance, 34% relative humidity

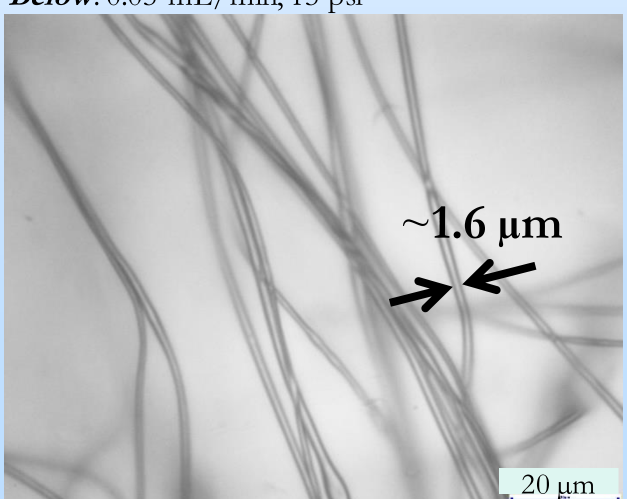
Right: 0.05 mL/min, 15 psi



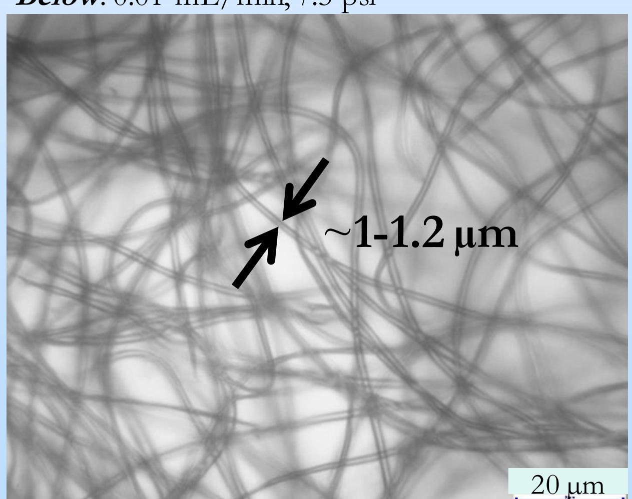


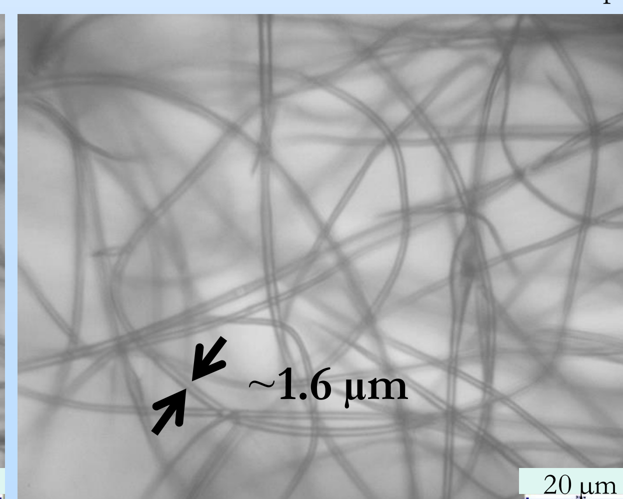
Below: 0.01 mL/min 10 psi

Below: 0.05 mL/min, 15 psi



Below: 0.01 mL/min, 7.5 psi



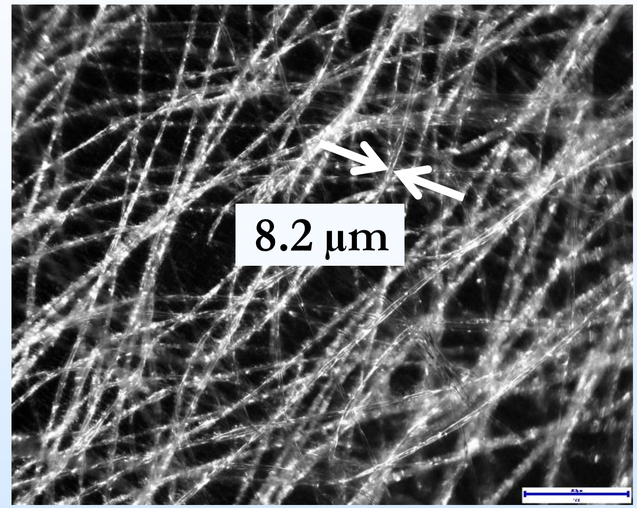


Electrospinning Micron-Scale PIM-2 Fibers

Apply methodology for PIM-1 in tetrachloroethane to PIM-2 polymer higher molecular weight (M_w = 6,400 kDa).

Consistent fiber production in the 5-10 µm range across flow rates, concentrations, and air pressure.

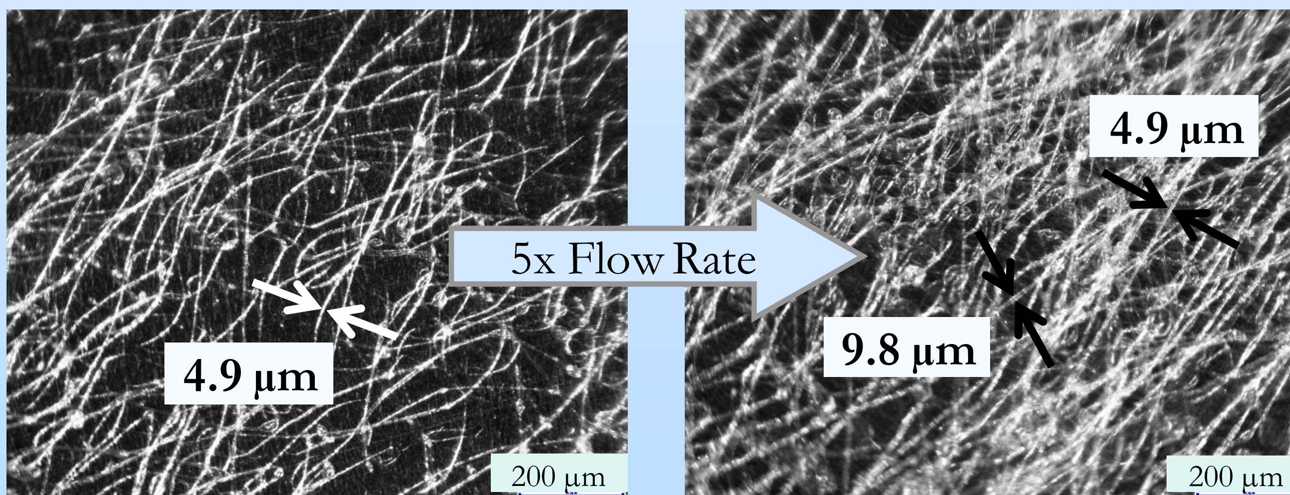
Right: 17% PIM-2, 0.025 mL/min, 12 kV, 20 cm collector distance, 0 psi, 31% relative humidity



***Below*:** 0.05 mL/min 12 kV 3 psi

***Below*:** 0.01 mL/min, 12 kV, 3 psi

Bottom images: 15% PIM-2, 20 cm collector distance, 45% relative humidity

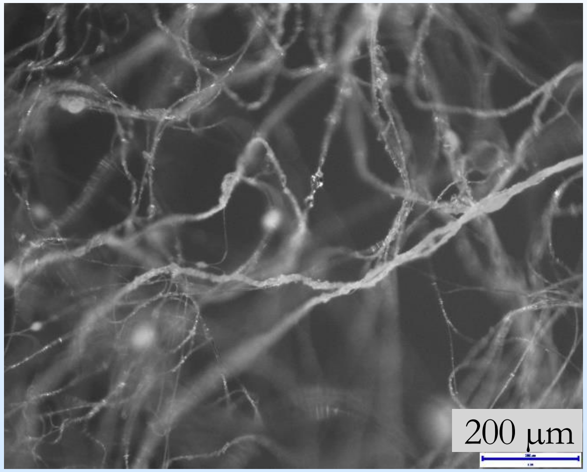


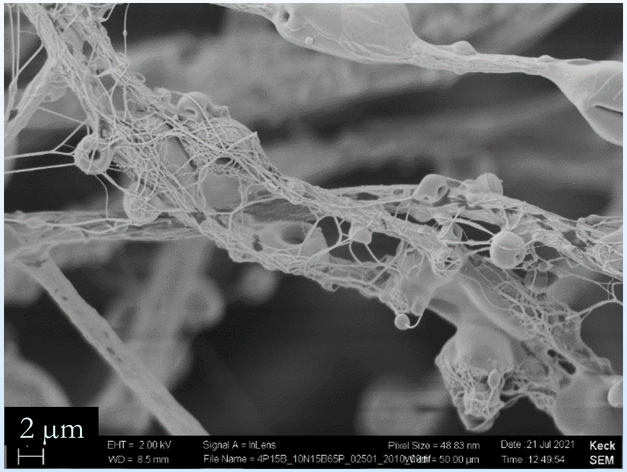
Incorporating NOHM-I-PEI into PIM-1 Fibers via Coaxial Spinning

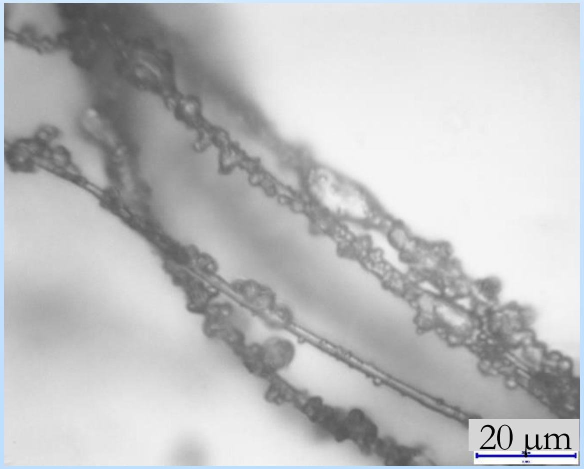
Incompatibility between NOHM-I-PEI and PIM-1 solubilities prevent monoaxial spinning approach

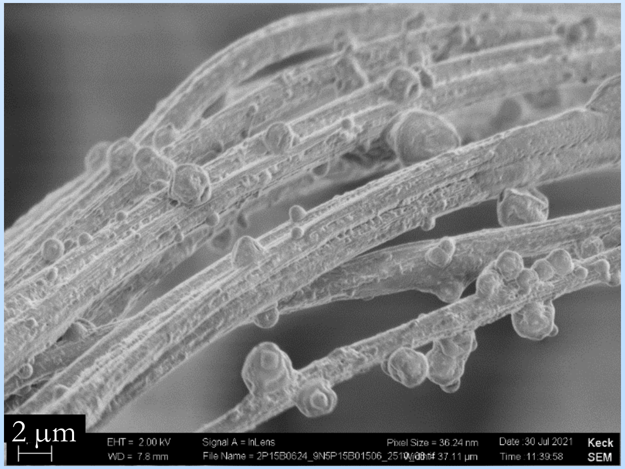
Investigating coaxial techniques using NOHM-I-PEI core supported by poly(acrylonitrile) framework and coated with a thin layer of PIM-1. Exploring decoupled vs. equal flow rates

Right: 4 wt% PIM-1, 1.5% NBu4Br, EtCl4 (Shell). 10% NOHM, 6.5% PAN, 1.5 NBu4Br, DMF (Core). 0.025 mL/min, 20 kV, 10 cm distance, 45% relative humidity. (35% NOHM loading)





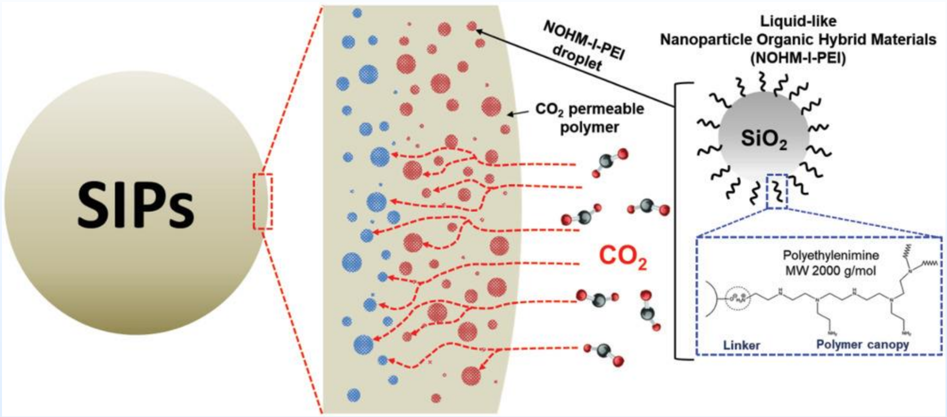


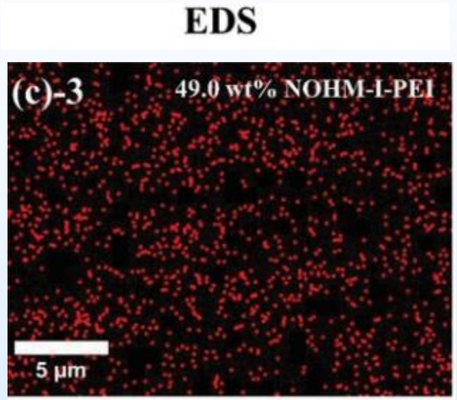


Phase separation during coaxial spinning creates distinct polymer and NOHM-I-PEI domains.

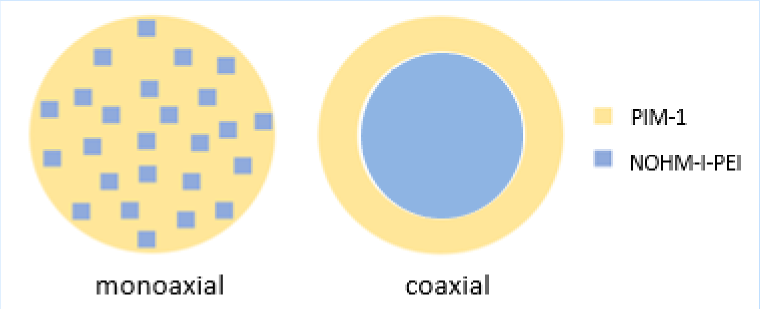
Left: 2 wt% PIM-1, 1.5% NEt_4Br, 0.06 mL/min, $EtCl_4$ (Shell). 9% NOHM, 5% PAN, 1.5% NEt_4Br, 0.015 mL/min, DMF. 22.5 kV, 10 cm distance

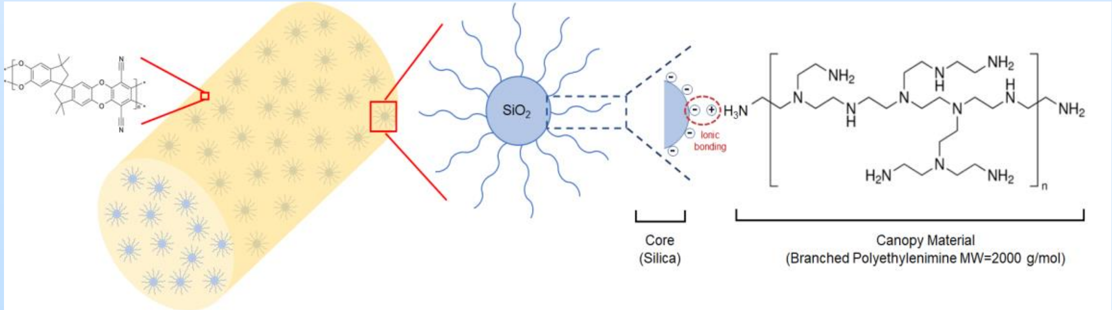
Solvent Impregnated Polymers & Encapsulated NOHMs in PIM via Electrospinning





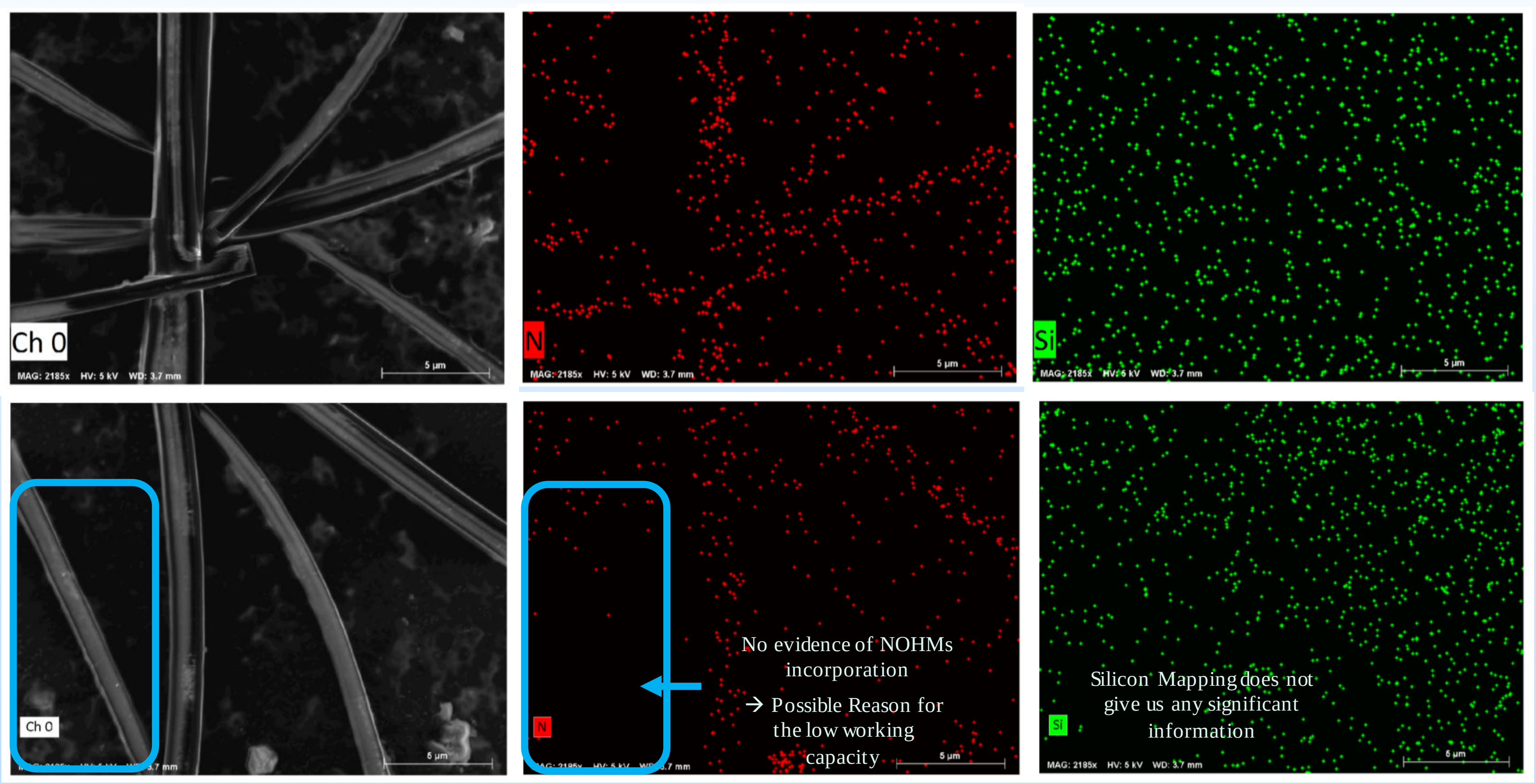
High interfacial surface area of microdroplets achieved from high shear emulsification (> 30,000 rpm)
yielded faster CO_2 sorption kinetics



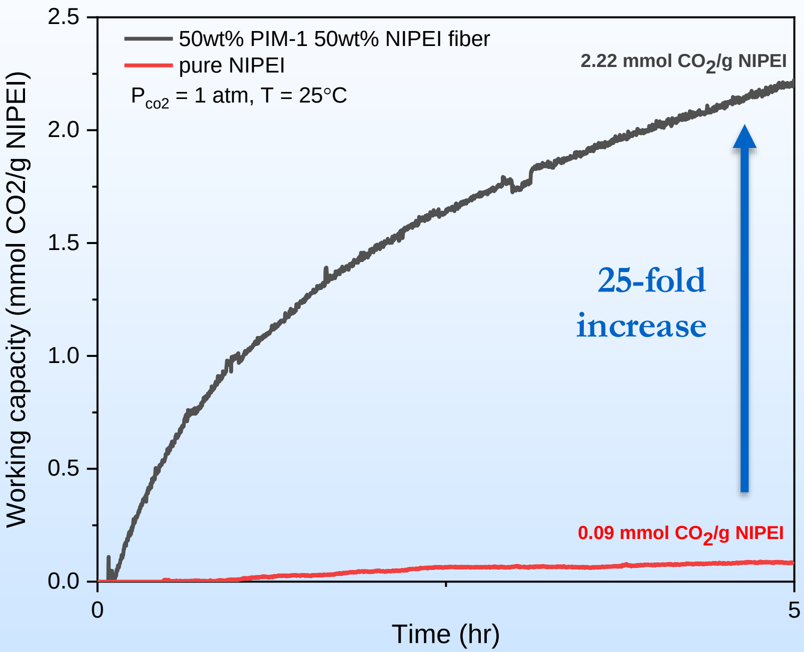


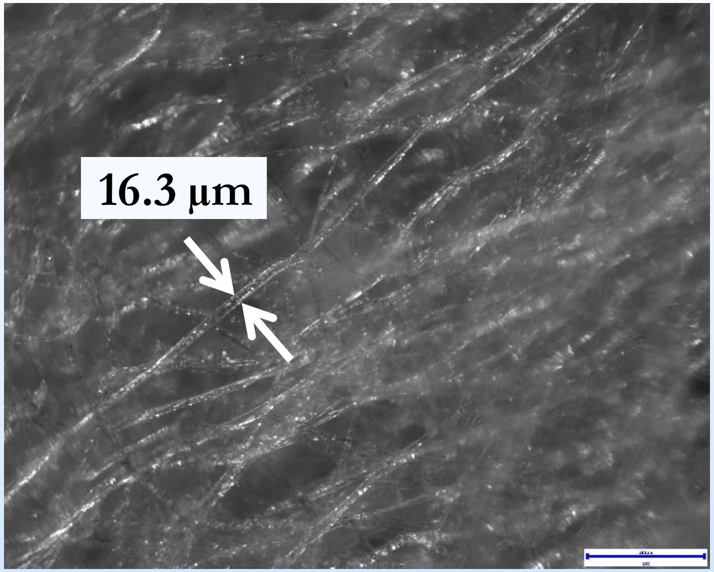
50 wt% NOHMs loaded monoaxially spun fiber yielded
higher CO_2 capture capacity than coaxial fiber

SEM-EDS (nitrogen & silicon mapping) of the coaxially electrospun fiber



Enhanced CO_2 Sorption Kinetics of the Monoaxially-Electrospun Fiber





Left: 5 wt% PIM-1, 5% NOHM-I-PEI, 0.5 mL/min, 25 kV, 10 cm collector distance, THF solvent.

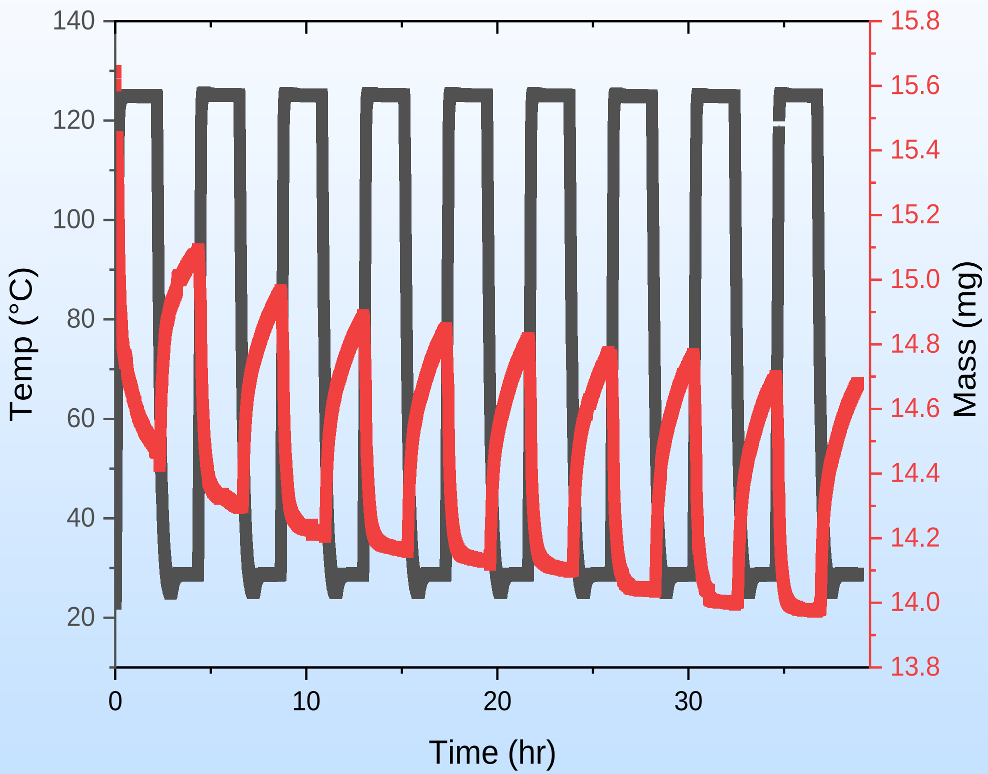
Remarkable increase in kinetics of the CO_2 adsorption behavior of the electrospun fiber

Electrospinning technology **eliminates the mass transfer limitation** occurring due to the high viscosity of pure NIPEI

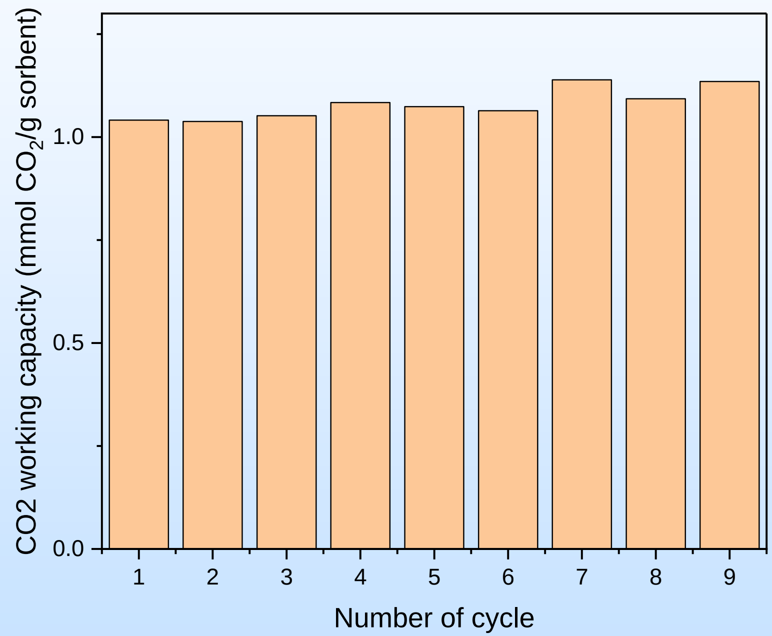
PIM-1 possess **high CO_2 permeability** allowing the rapid CO_2 capture by NIPEI encapsulated in the electrospun fiber

Multi-Cycle CO_2 Capture Test of the Monoaxially-Electrospun Fiber

On average 1.08±0.04 mmol CO2/g sorbent



Initial mass loss attributed to solvent evaporation



Coaxially electrospun fiber retained its working capacity after 9 cycles, exhibiting a long-term stability.

Initial activation with N_2 at 120°C for 2 hours

Sorption: 1 atm CO_2, 25°C – 2hr; **Desorption**: 1 atm N_2, 120°C – 2hr

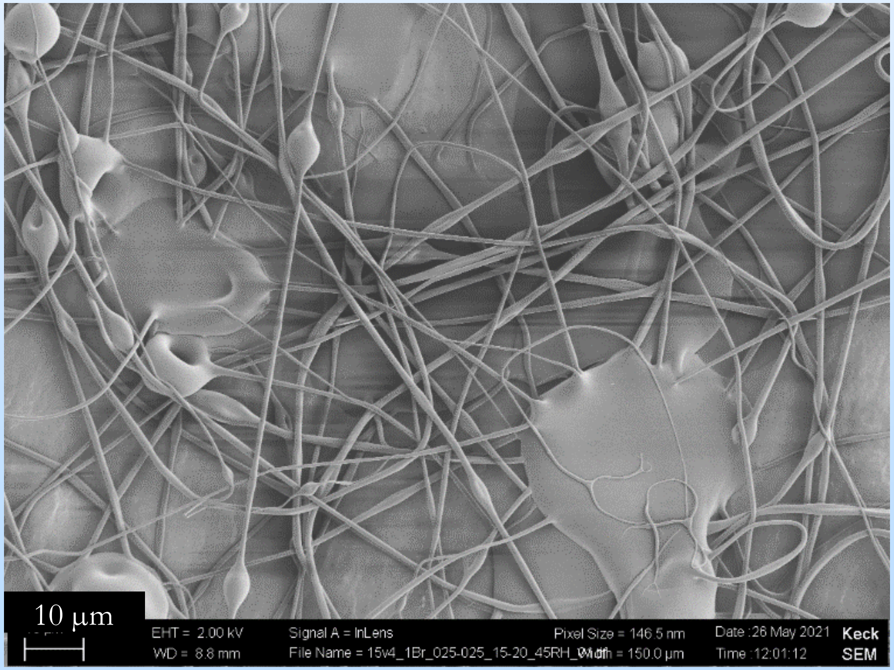
Plans For Future Testing/Development/ Commercialization

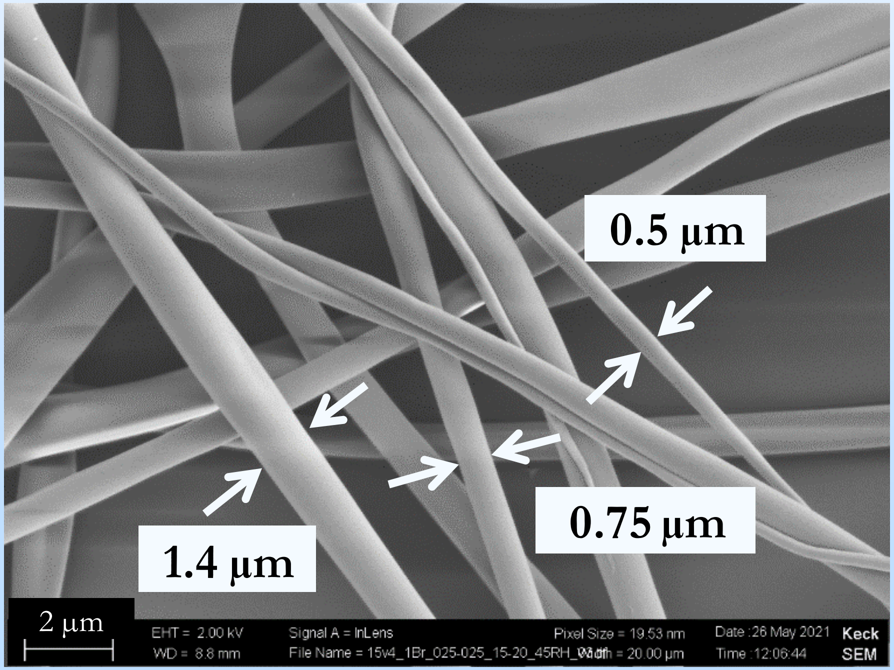
In Progress: Improving Quality of PIM-2 Micron-Scale Fibers

SEM imaging of electrospun PIM-2 fibers using 1,1,2,2-tetrachloroethane and $[NBu_4][Br]$.

Although beading is significant, connecting fibers are the correct morphology and are indicative of increased solution dielectric. Fibers are cylindrical and in the 0.5-1.5 micron fiber regime.

Images below:
14 wt% PIM-1 v.2, 1 wt% **$[NBu_4]$ [Br]**, 0.025 mL/min, 15 kV, 20 cm collector distance, 45% relative humidity, 0 psi





In Progress: Refining Coaxial Architecture through Solvent and Core Choice

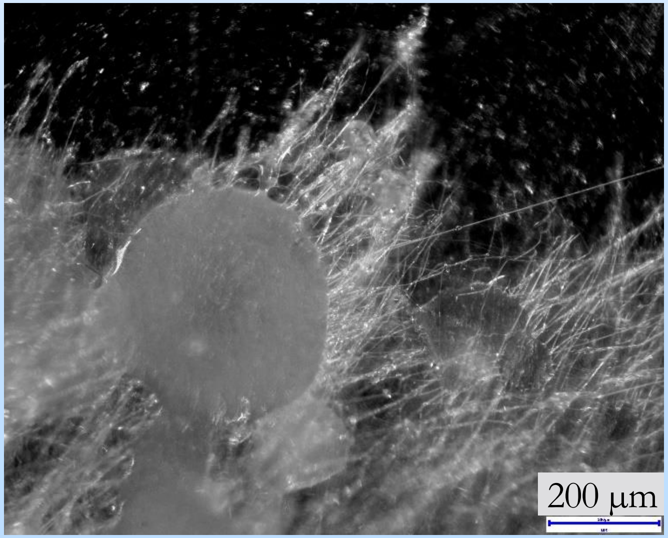
Solvent	Polymer for Core Architecture Study							
DMF	PI (P84)	PAN (200k)	PVA (25k)	PAA (450k)	PVP (1.3M)	PMMA (15k)	PEI (2k)	PVDF (180k)
NMP	PI (P84)	PAN (200k)	PVA (25k)	PAA (450k)	PVP (1.3M)	PMMA (15k)	PEI (2k)	PVDF (180k)
DMSO	PI (P84)	PAN (200k)	PVA (25k)	PAA (450k)	PVP (1.3M)	PMMA (15k)	PEI (2k)	PVDF (180k)

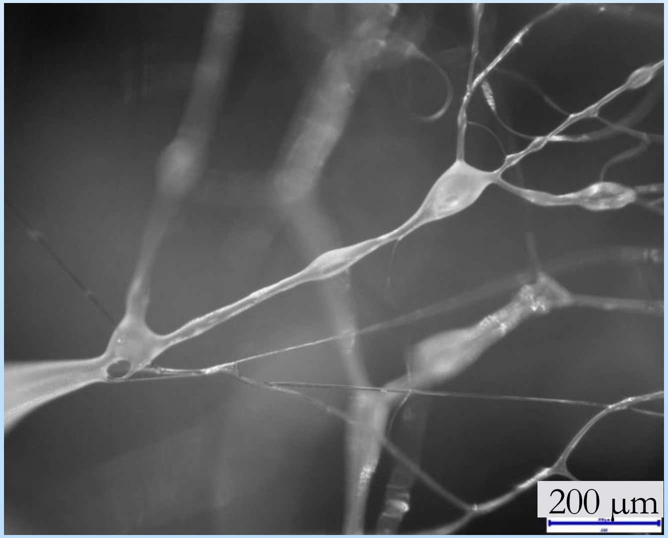
Screening polymers of various chemical moieties, chain lengths, and solubilities in three polar aprotic solvents.

Exploring encapsulation of branched poly(ethyleneimine) in PIM-1 sheath.

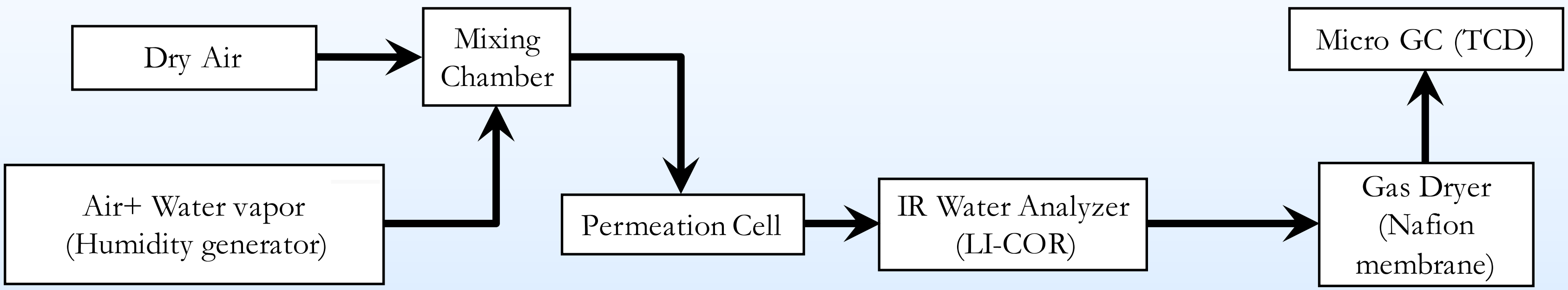
Left: 9 wt% PIM-1, 1.5% NEt_4Br, 0.02 mL/min, $EtCl_4$ (Shell). PEI-B, 0.005 mL/min (Core). 20 kV, **10 cm distance**.

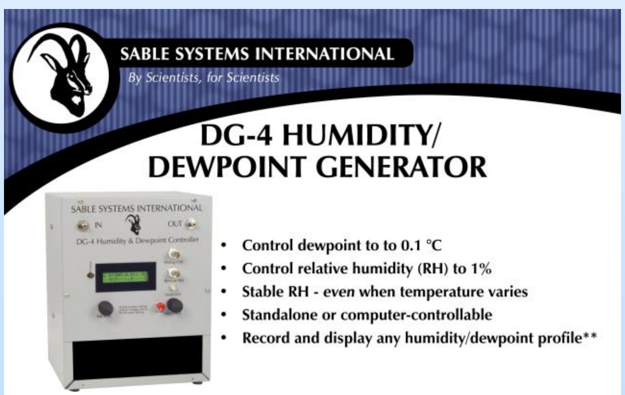
Right: 9 wt% PIM-1, 1.5% NEt_4Br, 0.02 mL/min, $EtCl_4$ (Shell). PEI-B, 0.005 mL/min (Core). 20 kV, **15 cm distance**.

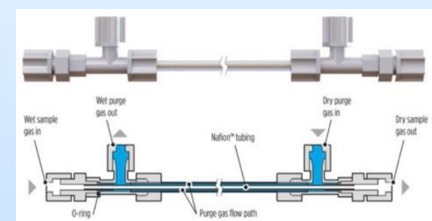




In Progress: Combined Multi-gas and Humidity Permeability Cell



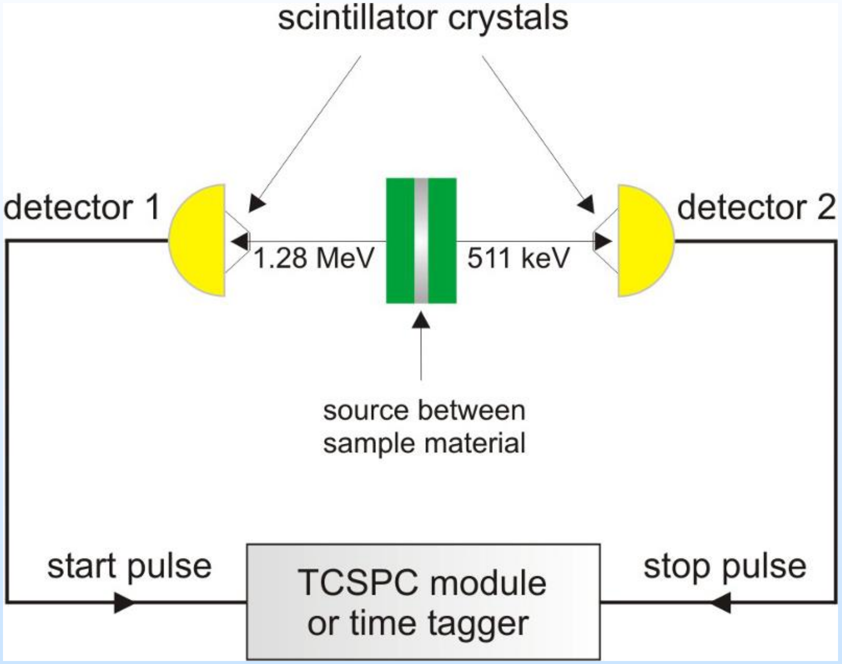


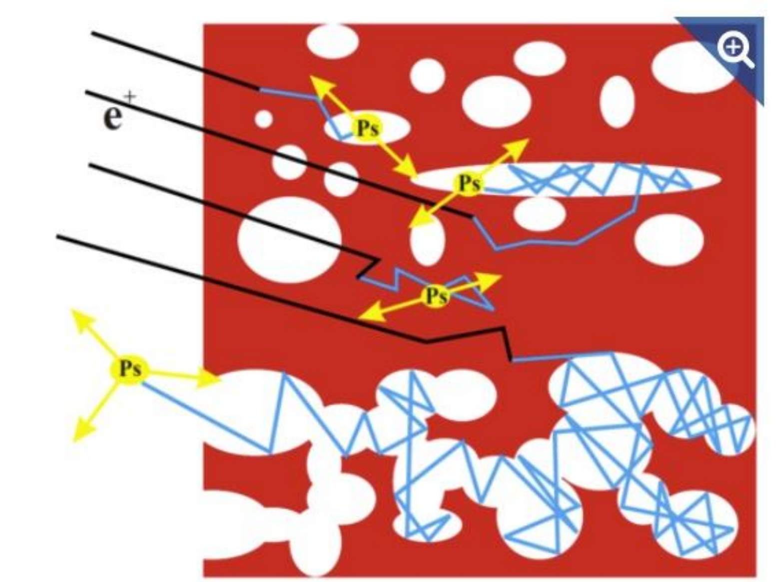


In Progress: PALS Characterization at NIST

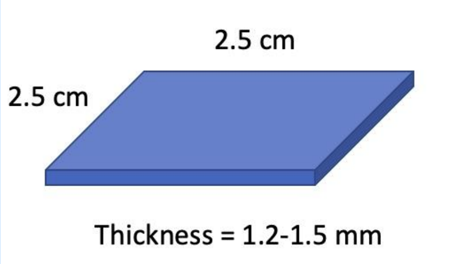
Positron Annihilation Lifetime Spectrometer

1) Apply positron beam
2) Positron react with electrons to produce e^+
3) Larger pores → longer e^+ residence time → more gamma rays detected





Positronium formation inside polymer materials [1].



Form factor of the sample

Summary

- Successfully synthesized NOHMs with oxidative thermal stability
- Optimized techniques to successfully electrospin PIM-1 and PIM-2 fibers in the 0.8-2-micron dimensional range.
- Tested encapsulated NOHMs and shown promising thermal cyclability and CO_2 capture performance across multiple loading/regeneration cycles
- Milestone: After extensive synthetic optimization, we identified the top 3 candidate polymeric materials to encapsulate NOHMs
    - PIM-1, PIM-2, and TEGO Rad
- Electrospinning polymeric fiber mats onto coarse filter media for increased structural stability

Future Research Plan

		Completed Tasks	Start date	End date
Columbia U	Task 1	**Project management and planning**		
Columbia	Task 2	**Design and Synthesis of NOHMs for CO_2 Capture**	1/1/21	3/31/21
ORNL		ST 2.1. Synthesis of NOHMs with different amine group	1/1/21	3/31/21
Cornell		ST 2.2. Optimization between CO_2 capture capacity and viscosity of NOHMs	1/1/21	3/31/21
		ST 2.3. Characterization and evaluation of pure NOHMs for encapsulation and CO_2 capture	1/1/21	3/31/21
ORNL	Task 3	**Fabrication of NOHMs/PIM coaxial nanofibers**	4/1/21	3/31/22
Cornell		ST 3.1. Enhancement of PIM's hydrophobicity, thermal stability, and mecahnical properties	4/1/21	9/30/21
Columbia		ST 3.2. Electrospining of NOHMs/PIM coaxial nanofibers	7/1/21	3/31/22
		ST 3.3. Charaterization of NOHMs/PIM coaxial nanofibers	7/1/21	3/31/22

Pending Tasks

			Q3 07/01/21-09/30/21	Q4 10/01/21-12/31/21	Q5 01/01/2022-3/31/2022	Q6 04/01/2022-06/30/2022
Cornell	Task 4	**Fabrication of NOHMs (core)/ceramic (sheath) nanofibers**				
ORNL		ST 4.1. Control hydrophobicity of ceramic (OPSZ)				
Columbia		ST 4.2. Conventional monoaxial electrospining of NOHMs and OPSZ mixture				
		ST 4.3. Coaxial electrospining of NOHMs (core) and OPSZ (sheath)				
		ST 4.4. Characterization of NOHMs/ceramic nanofibers				
Cornell	Task 5	**Fabrication of air filters with NOHMs/(PIM or ceramic) nanofibers**				
Columbia		ST 5.1. Deposition of nanofibers on a coarse filter media				
ORNL		ST 5.2. Characterization of nanofibers bearing air filter media				
		ST 5.3. CO_2 capture using air filters - fixed bed testing				
		ST 5.4. Long term CO_2 capture testing in a lab scale unit with simulated air (with moistu				
		ST. 5.5. Develop thermodynamic and kinetic models for laboratory phase equilibria resi				
ORNL	Task 6	**Process Modeling and TEA/LCA**				
Columbia		ST 6.1. Development of full-scale process models for direct air capture				
Cornell		ST 6.2. Operation of process models to achieve DOE targets				
		ST 6.3. Economic Analysis and Life Cycle Analysis				

Acknowledgements

U.S. DEPARTMENT OF ENERGY

NIST

Dr. Ajay Krishnamurthy
Dr. Amanda Forster