Energy Efficient GO-PEEK Hybrid Membrane Process for Post-combustion CO_2 Capture

DOE Contract No. DE-FE0026383

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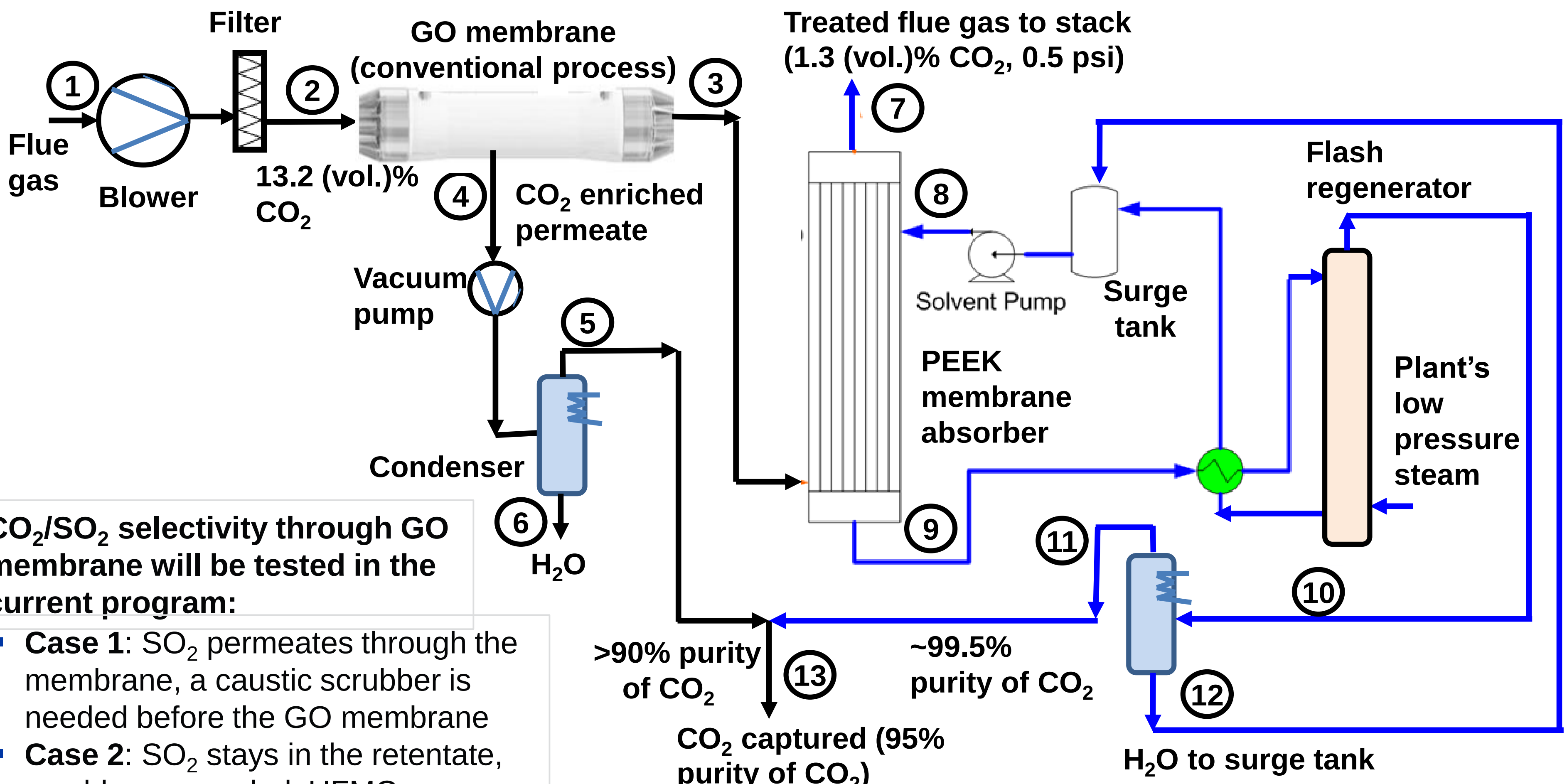
CO_2 Capture Technology Project Review Meeting

August 21 - 25, 2017, Pittsburgh, PA

Process description

GO for bulk/partial CO_2 removal

PEEK HFMC to further capture CO_2



CO_2/SO_2 selectivity through GO membrane will be tested in the current program:

- **Case 1**: SO_2 permeates through the membrane, a caustic scrubber is needed before the GO membrane
- **Case 2**: SO_2 stays in the retentate, scrubber unneeded; HFMC can handle 150 ppmv SO_2 (DE-FE-0004787)

GO = graphene oxide

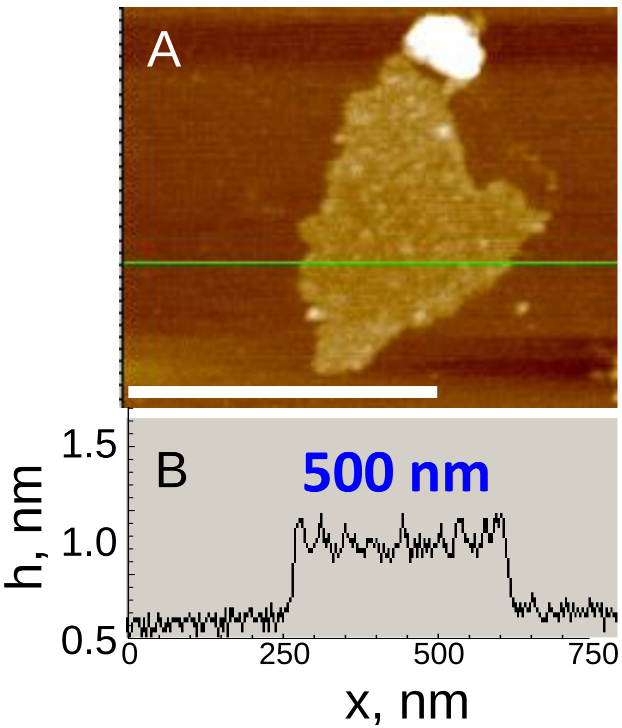
GO-PEEK project overview

- **Performance period**: Oct. 1, 2015 – Sep. 30, 2018
- **Funding**: $1,999,995 from DOE; $500,000 cost share
- **Objectives**: Develop a hybrid membrane process combining a graphene oxide (GO) gas separation membrane configuration unit and a PEEK hollow fiber membrane contactor (HFMC) unit to capture ≥90% of the CO_2 from flue gases with 95% CO_2 purity at a cost of electricity 30% less than the baseline CO_2 capture approach
- **Team:**

Member	Roles
gti	• Project management and planning • Quality control and CO_2 capture performance tests
University of South Carolina; Rensselaer Polytechnic Institute	• GO membrane development
Air Liquide Advanced Business & Technologies (ALaS)	• PEEK membrane development
Trimeric Corporation	▪ High-level technical & economic feasibility study

GO membrane technology based on our pioneering work published in *Science (2013, 342 (6154) 95)*

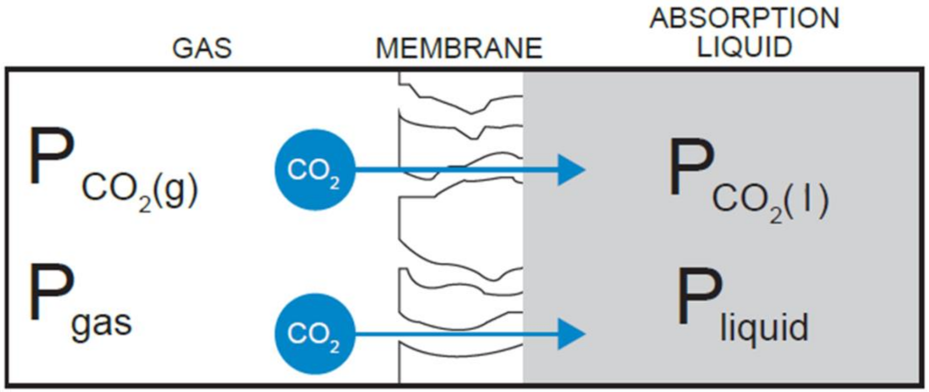
Ultrathin, Molecular-Sieving Graphene Oxide Membranes for Selective Hydrogen Separation
Hang Li *et al.*
Science **342**, 95 (2013);
DOI: 10.1126/science.1236686



Single-layered GO flake prepared as thin as 1 nm

- **Contribution of the paper**:
  - Structural defects on GO flakes can be controlled as transport pathway for selective gas separations

Singular PEEK HFMC technology currently at pilot scale development stage (DE-FE0012829)



Membrane contactor: high surface area device that facilitates mass transfer

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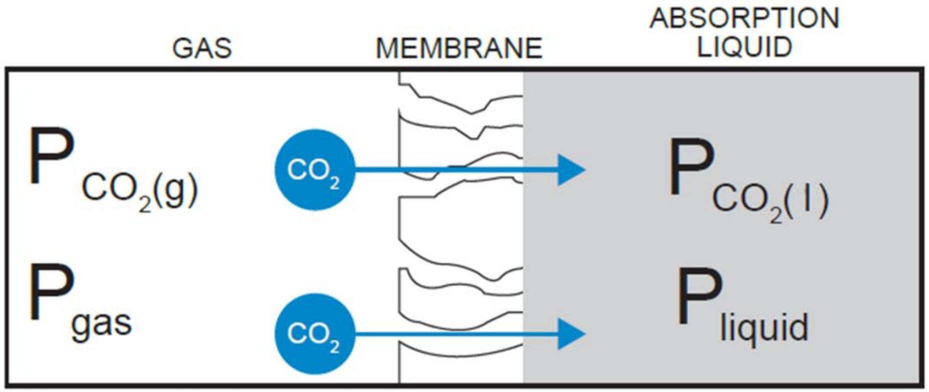

Membrane contactor: high surface area device that facilitates mass transfer

Commercial-sized modules

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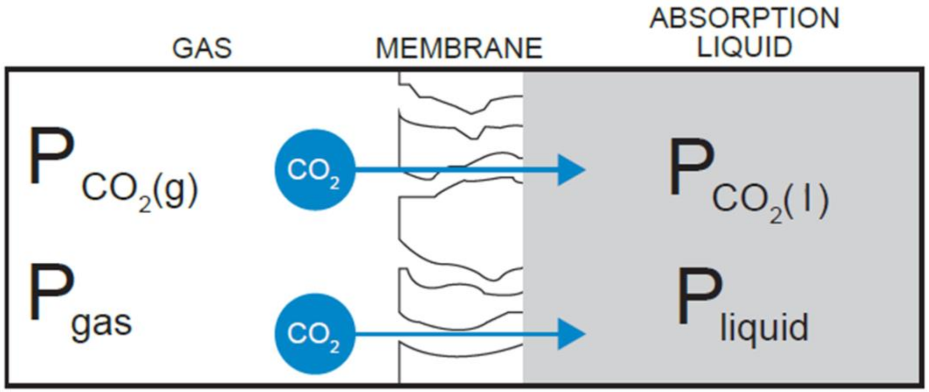

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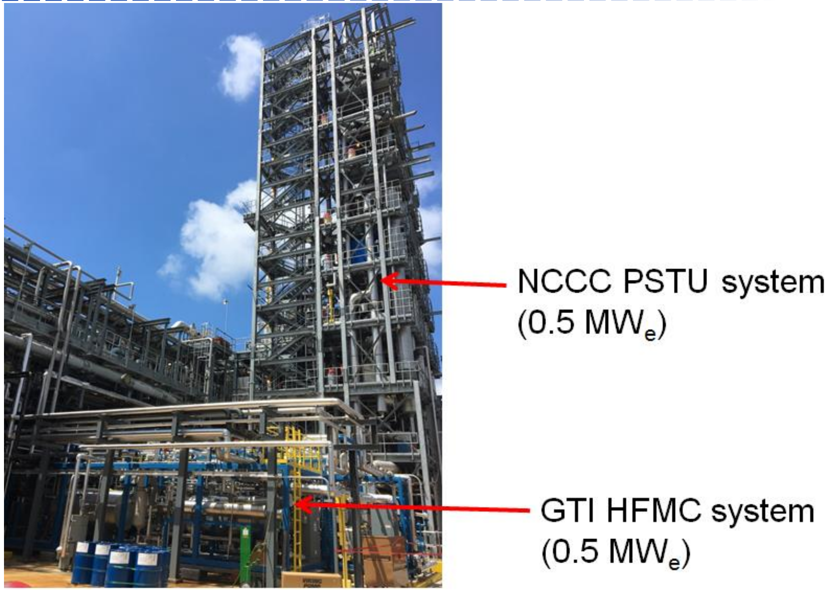

Plant constructed and installed at NCCC

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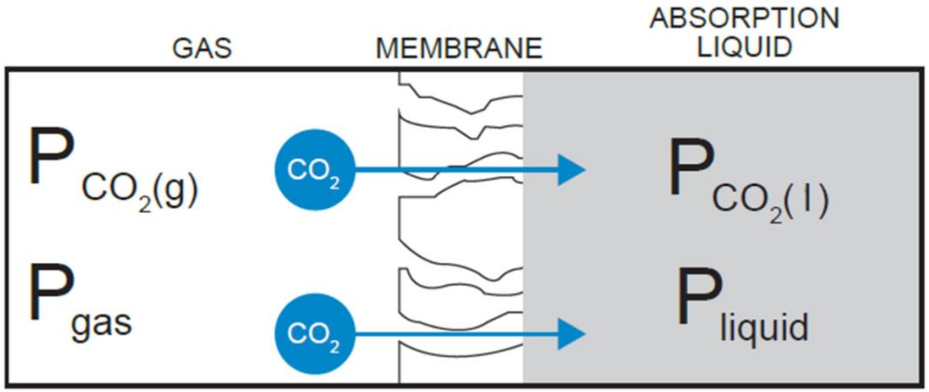

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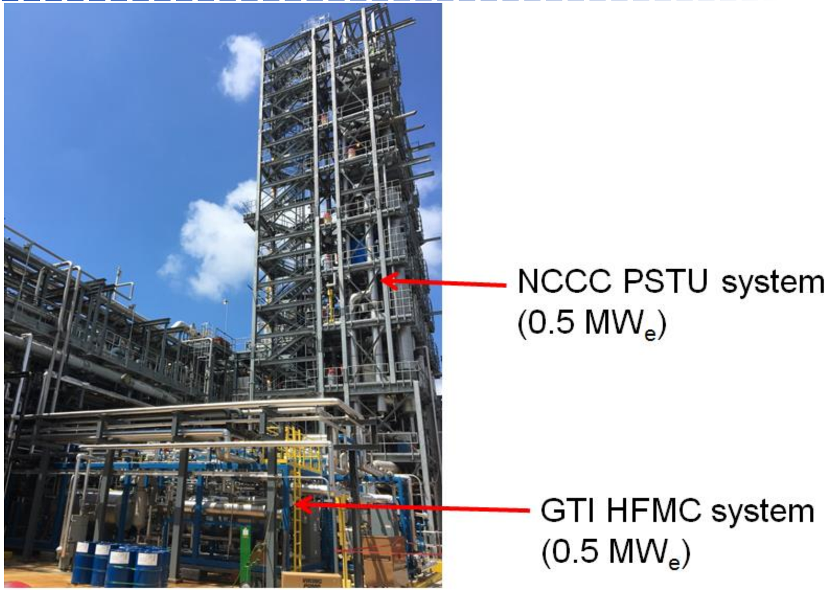
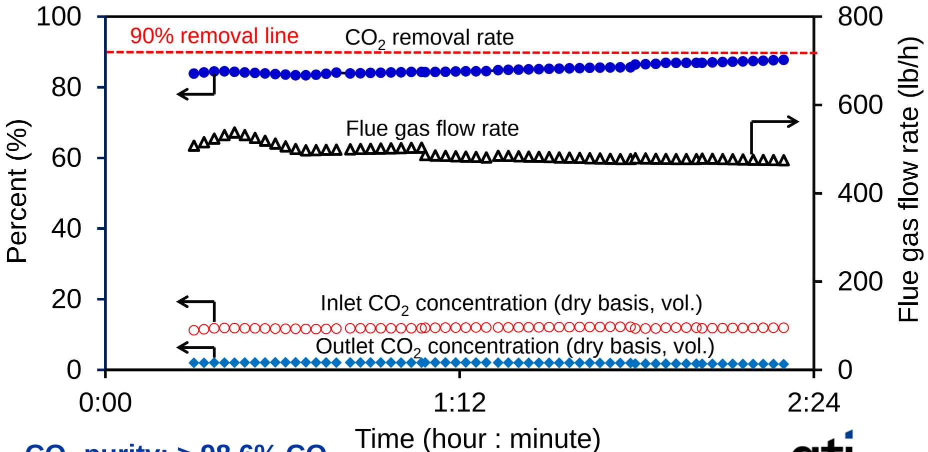


Plant constructed and installed at NCCC

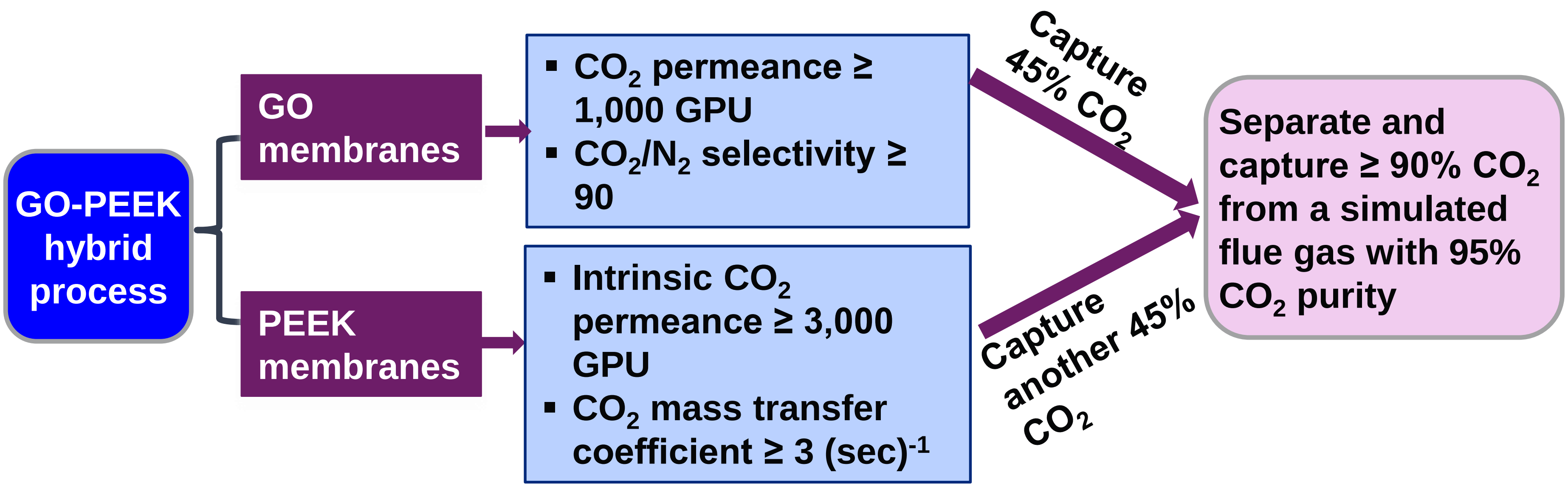
NCCC testing results indicate DOE's technical target can be achieved

- **CO_2 removal rate:**



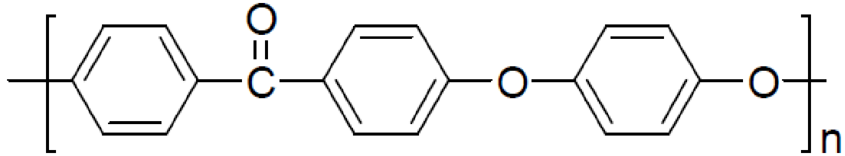
- **CO_2 purity: > 98.6% CO_2**

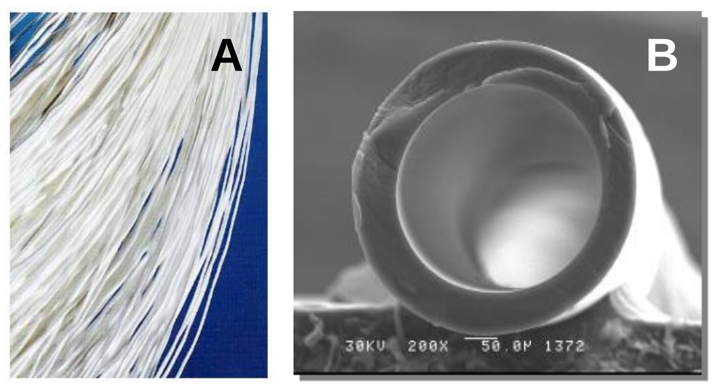
GO-PEEK technical goals



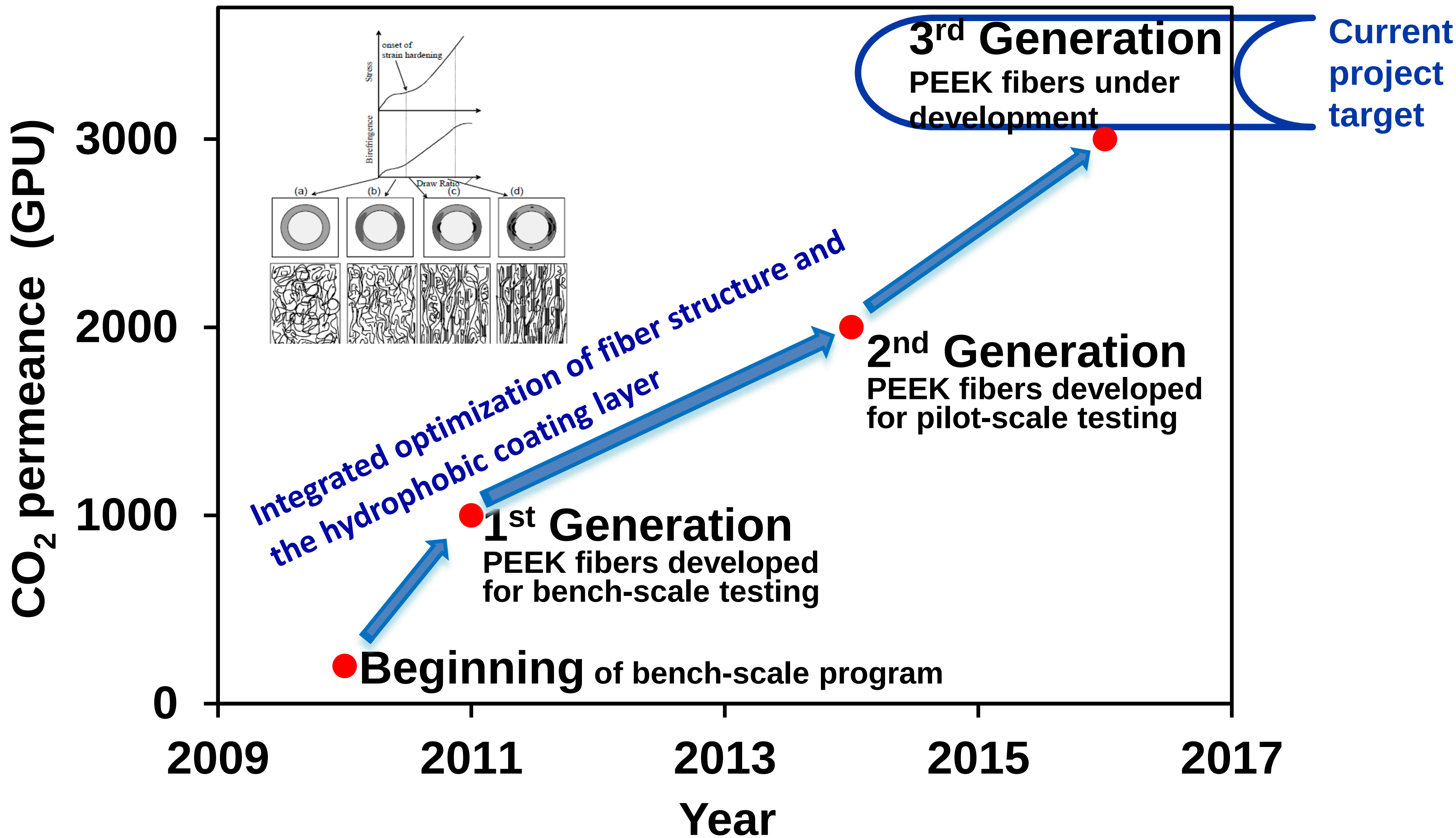
GPU= **G**as **P**ermeation **U**nit

Progress on PEEK Membranes





Under the current program, we are developing PEEK fibers with intrinsic CO_2 permeance of 3,000 GPU



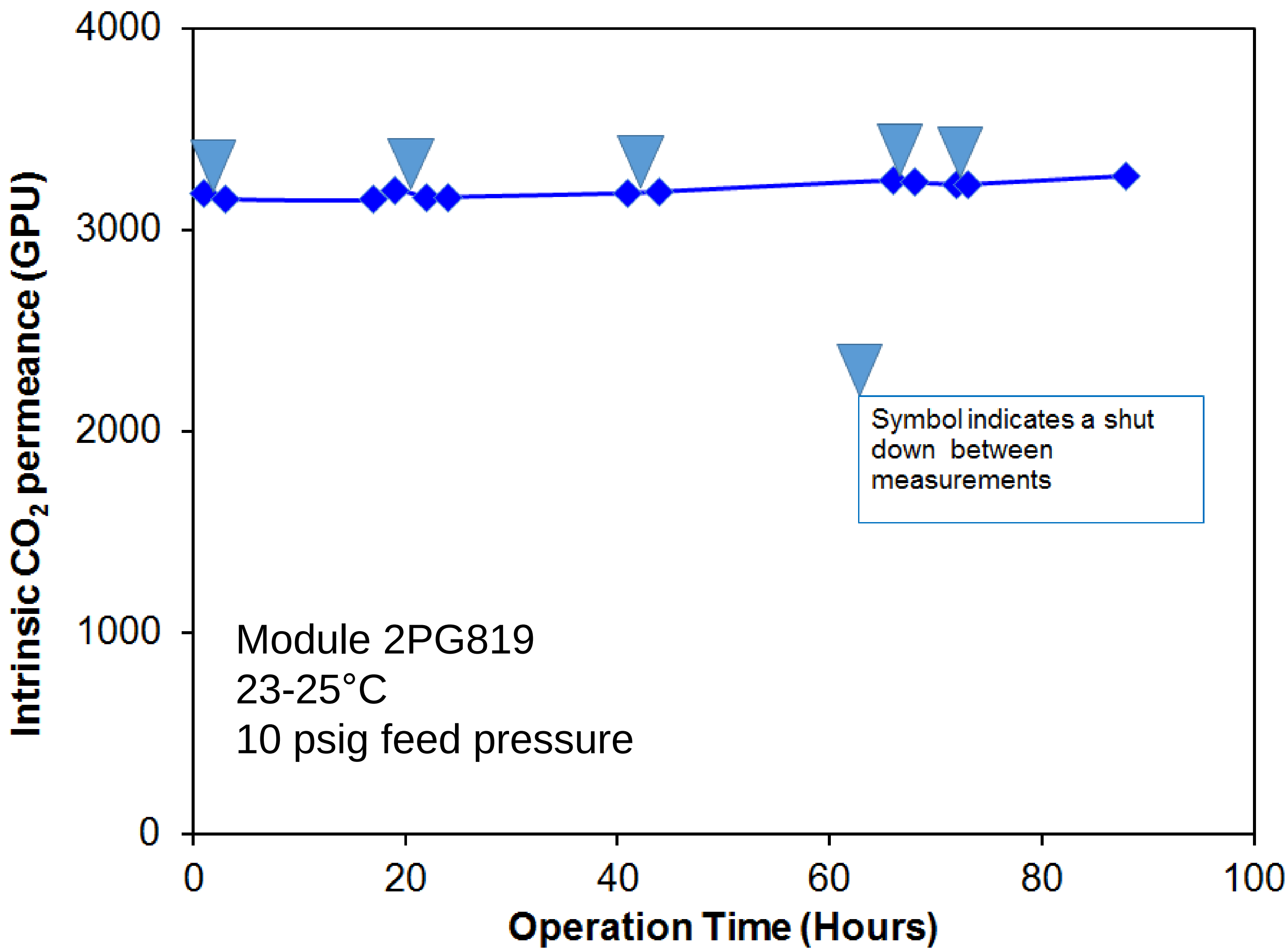
1 GPU = 1 x 10^6 cm^3 (STP)/cm^2 • s • cmHg

Eight types of fibers were investigated

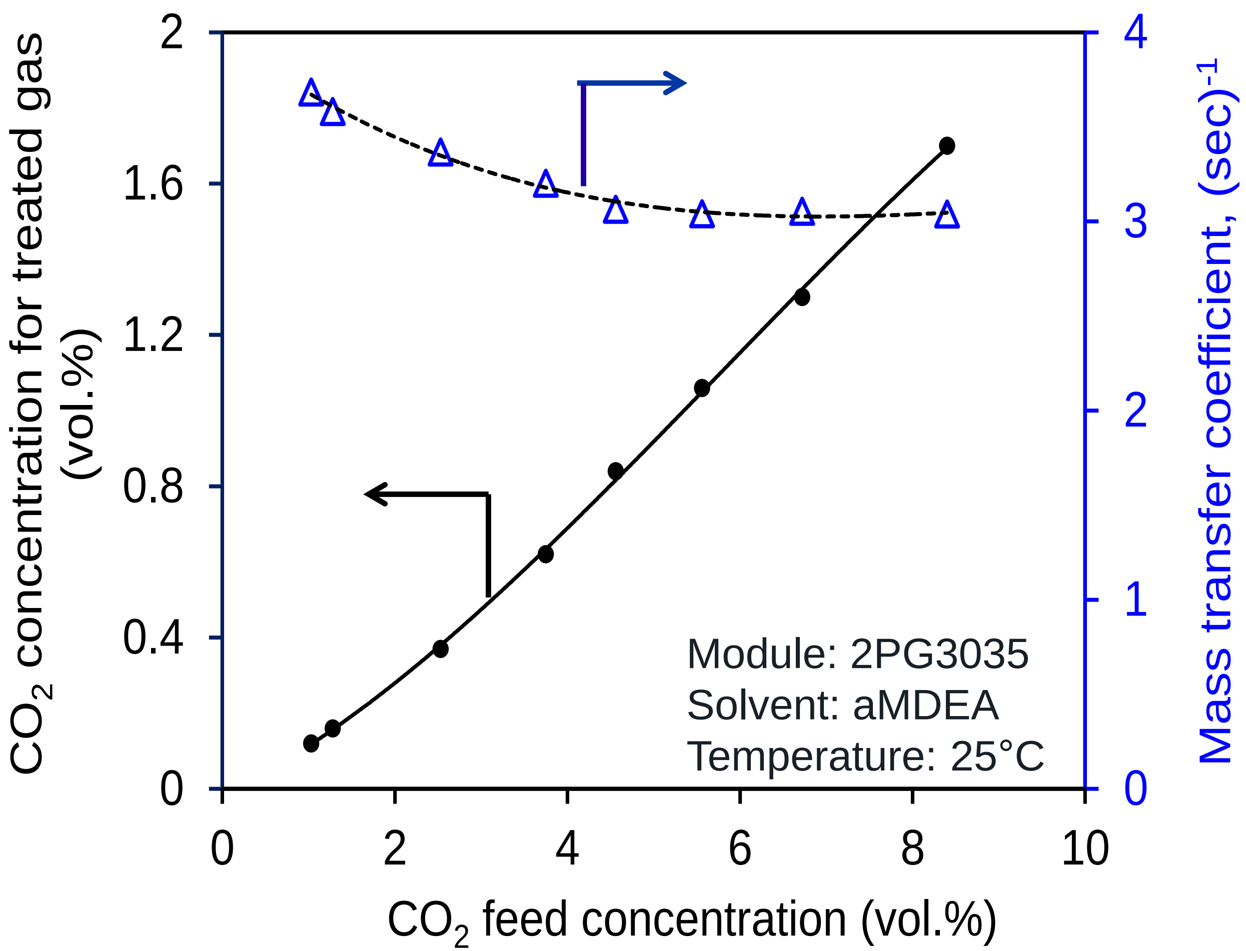
Sample No.	Fiber OD (Micron)	Fiber ID (Micron)	CO_2 permeance* (GPU)
78-33-3A	582	350	2,300
78-33-3B	582	350	2,500
78-118-3A	569	358	2,300
78-118-3B	569	358	2,800
78-117-5A	569	353	3,400
78-117-5B	569	353	3,400
78-117-5C	569	353	3,700
78-117-5D	569	353	3,800

Temperature: 25°C, feed pressure: ~ 5 psig

2-inch module 2PG819 containing 78-117-5C fibers (CO_2 permeance of 3,700 GPU)

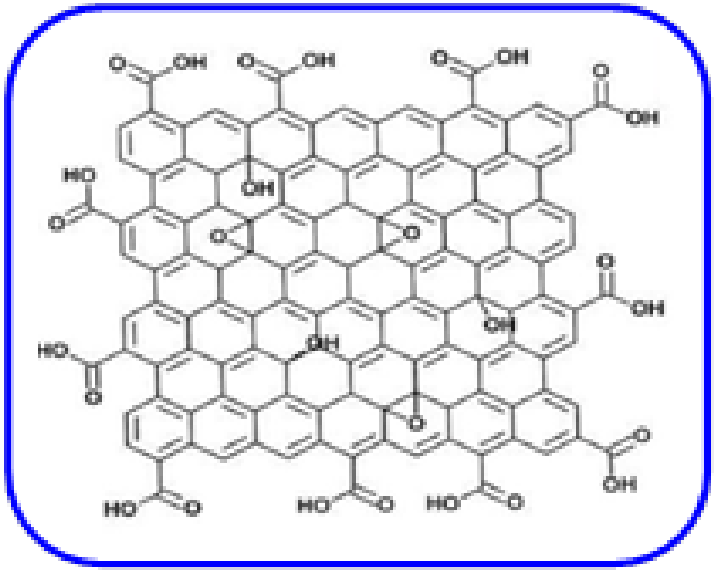


PEEK membrane module effective in capturing CO_2 from low CO_2-concentration feeds in membrane contactor



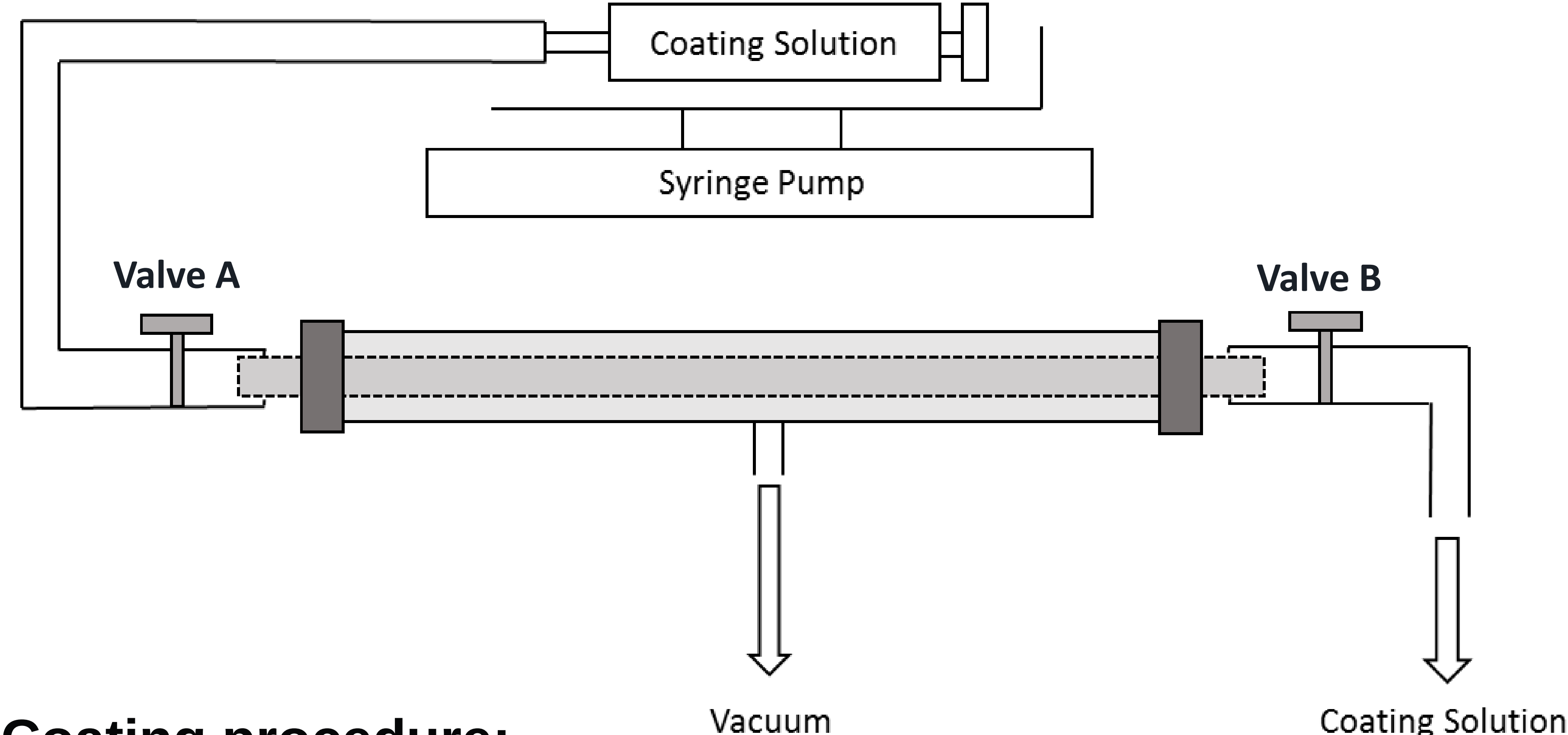
Goal of mass transfer coefficient > 3 $(sec)^{-1}$ achieved

Progress on GO Membranes



<u>GO</u>: single-atomic layered, oxidized graphene

Procedure developed for coating GO-based membrane on hollow fiber (HF) support

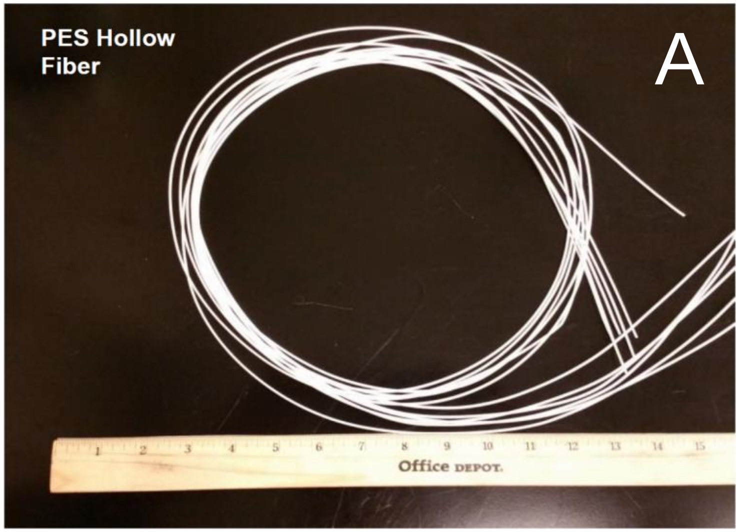


Coating procedure:

1. Valves A and B are open, GO dispersion flows continuously in hollow fiber
2. Vacuum filtration is conducted for a controlled time; and
3. Valves A and B are closed; coated fiber stays under vacuum for a controlled time

GO membrane (thickness: ~9 nm) supported on polyethersulfone (PES) hollow fiber

PES fiber



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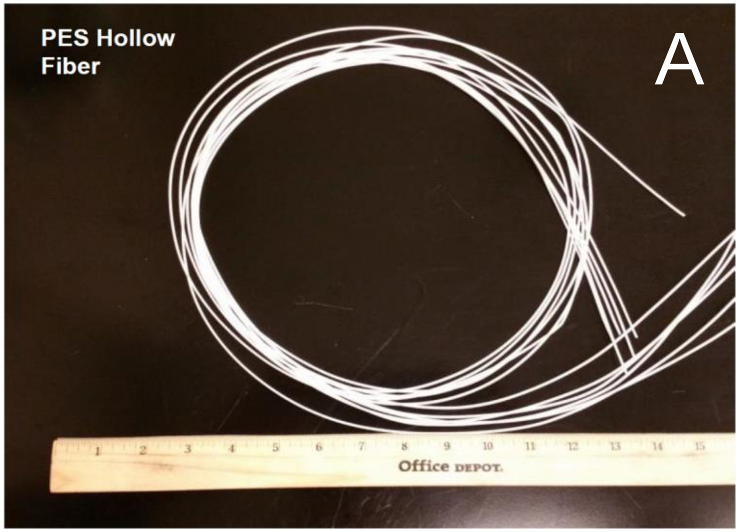

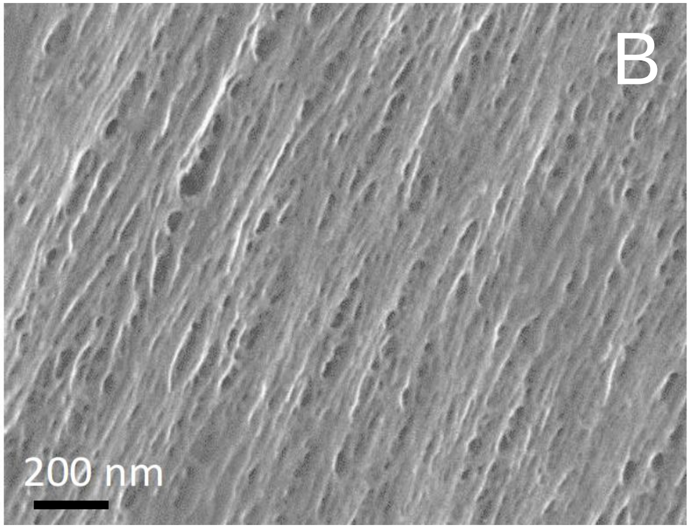

Uncoated fiber surface

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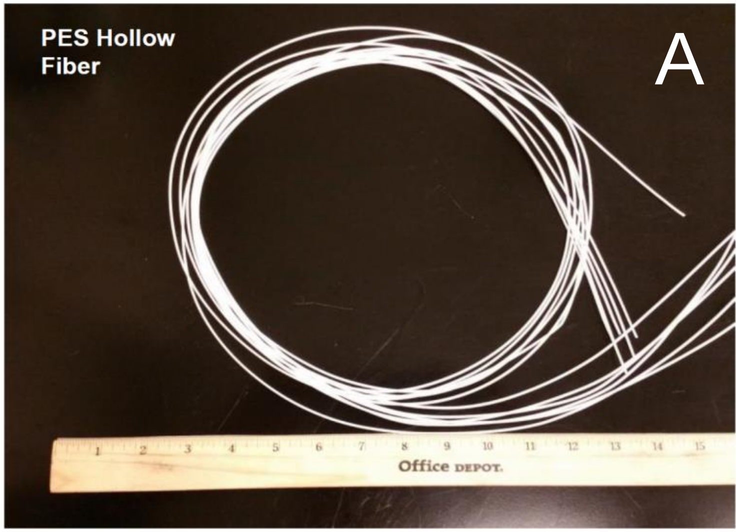
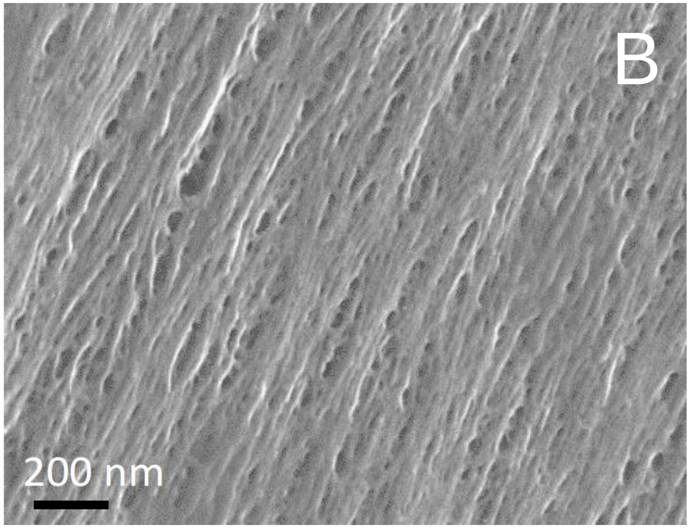
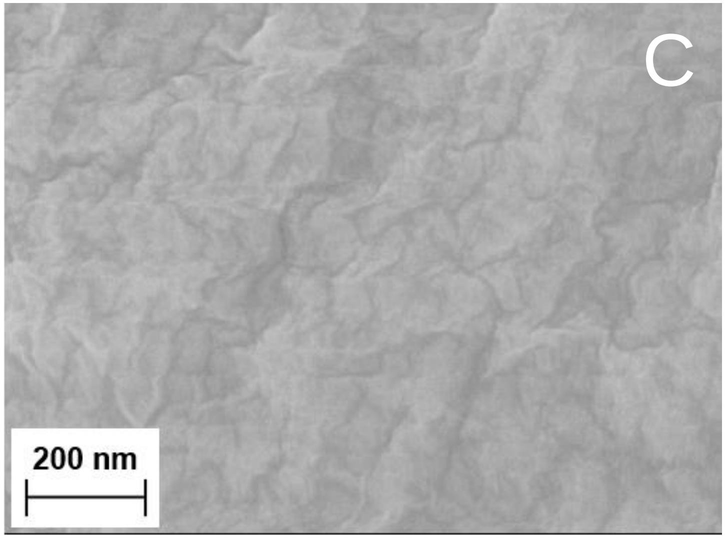




Uncoated fiber surface

Coated fiber surface



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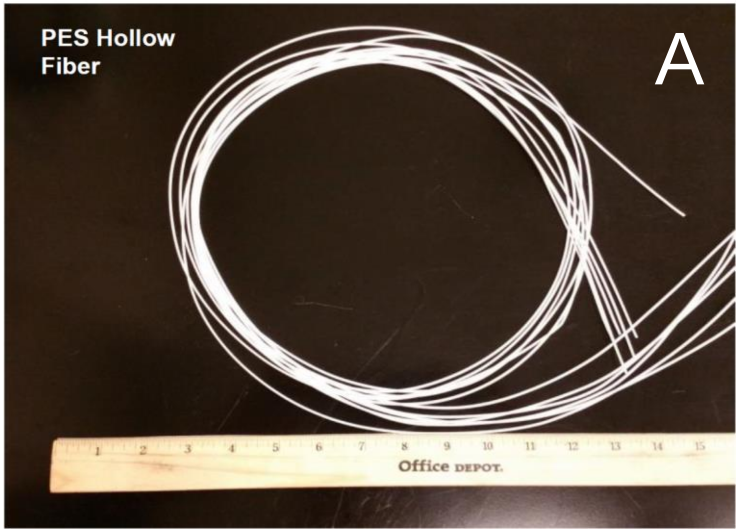

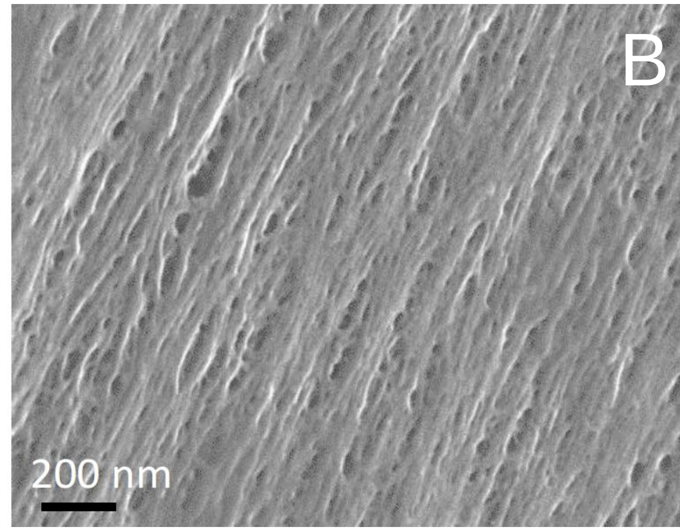

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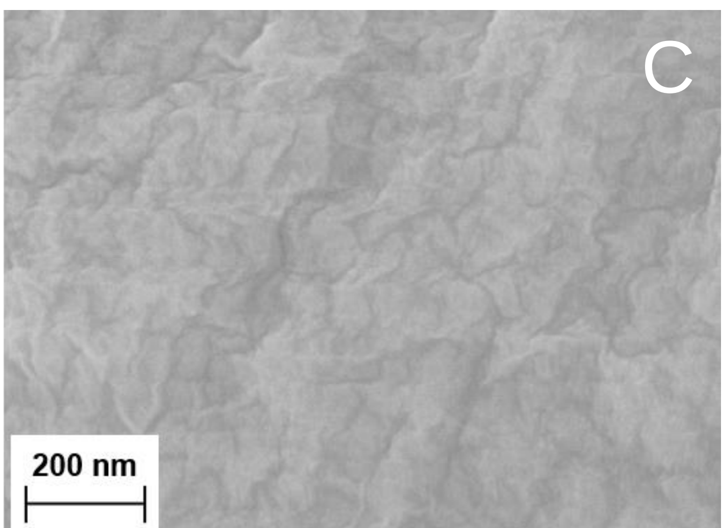
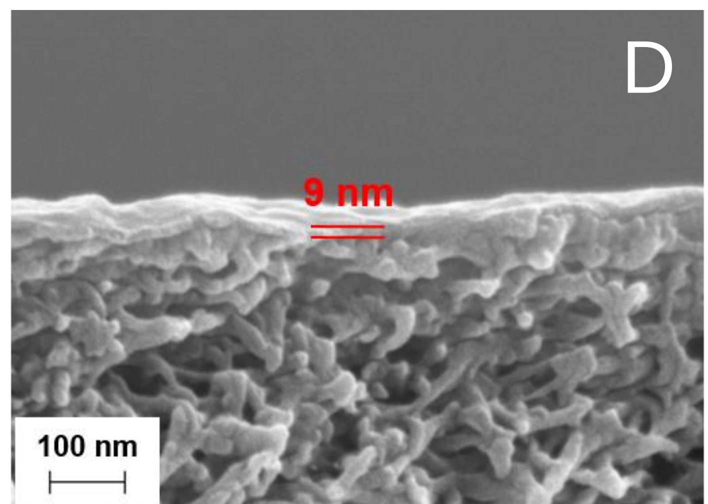
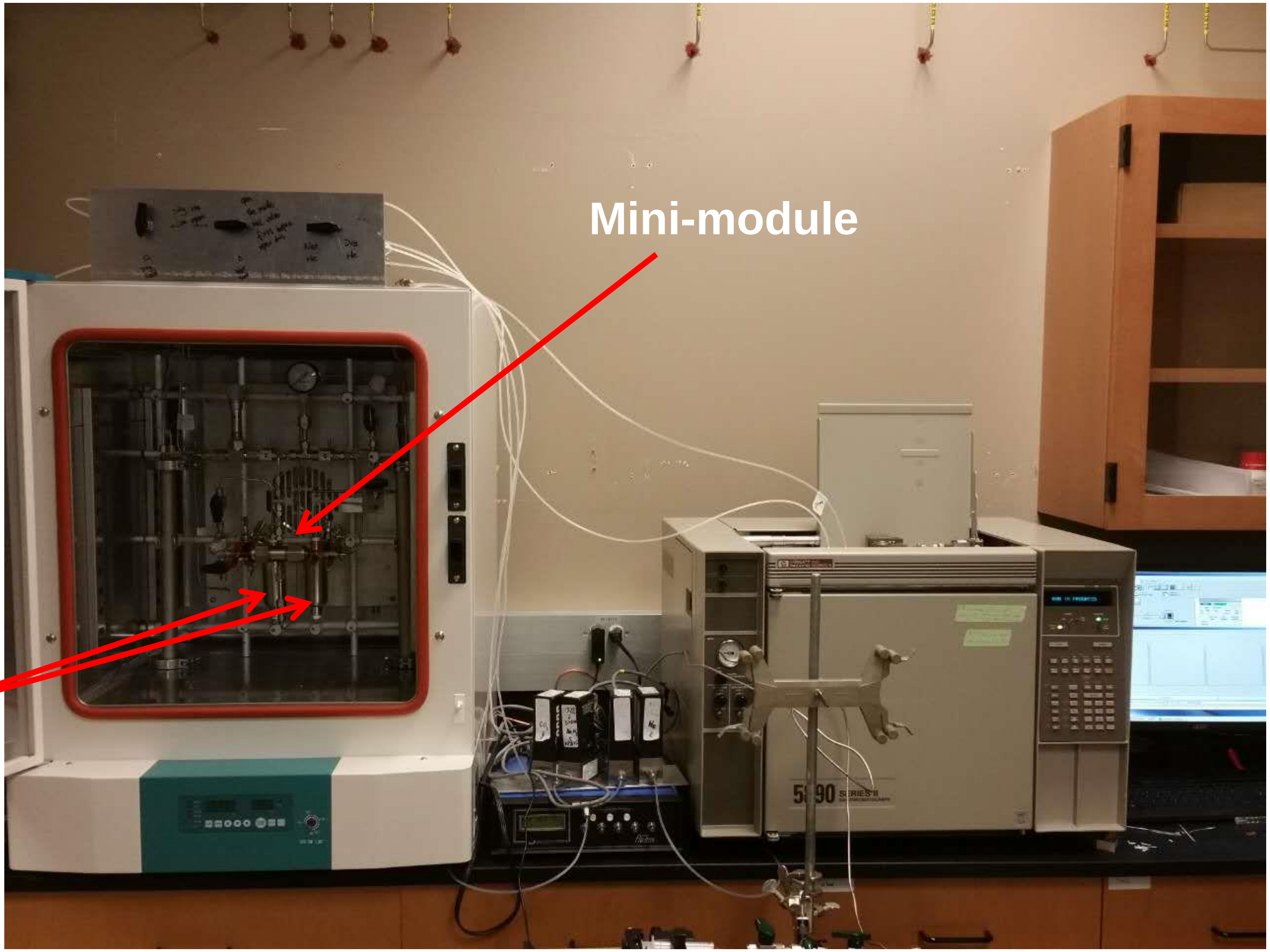




Coated fiber cross section

Coated fiber sealed in a mini-module for gas permeation testing

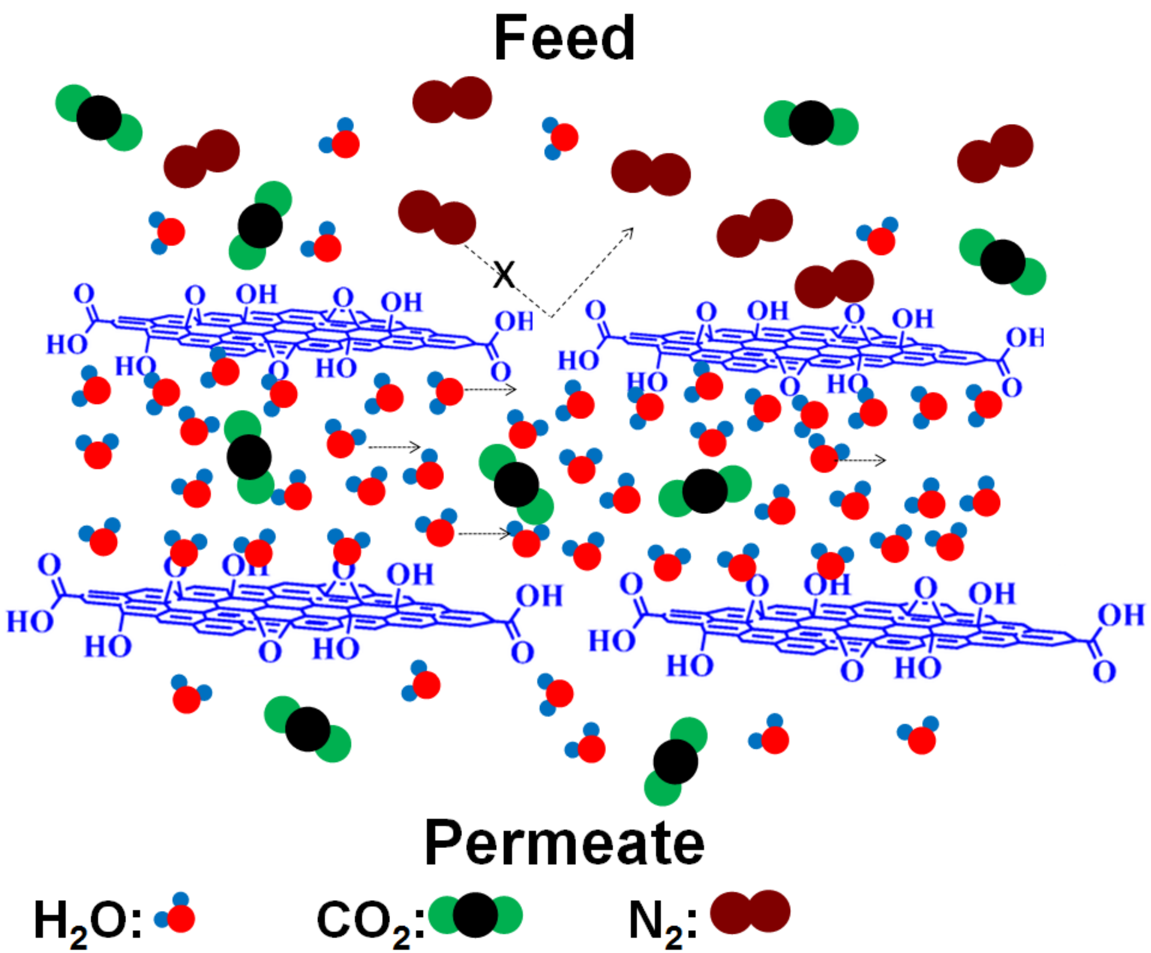
Permeation testing unit



Water bubbler and knockout vessel

Initial GO membrane performance under simulated flue gas condition

- CO_2 permeance of 100 GPU and selectivity of 49 obtained for a humidified 15%/85% CO_2/N_2 mixture



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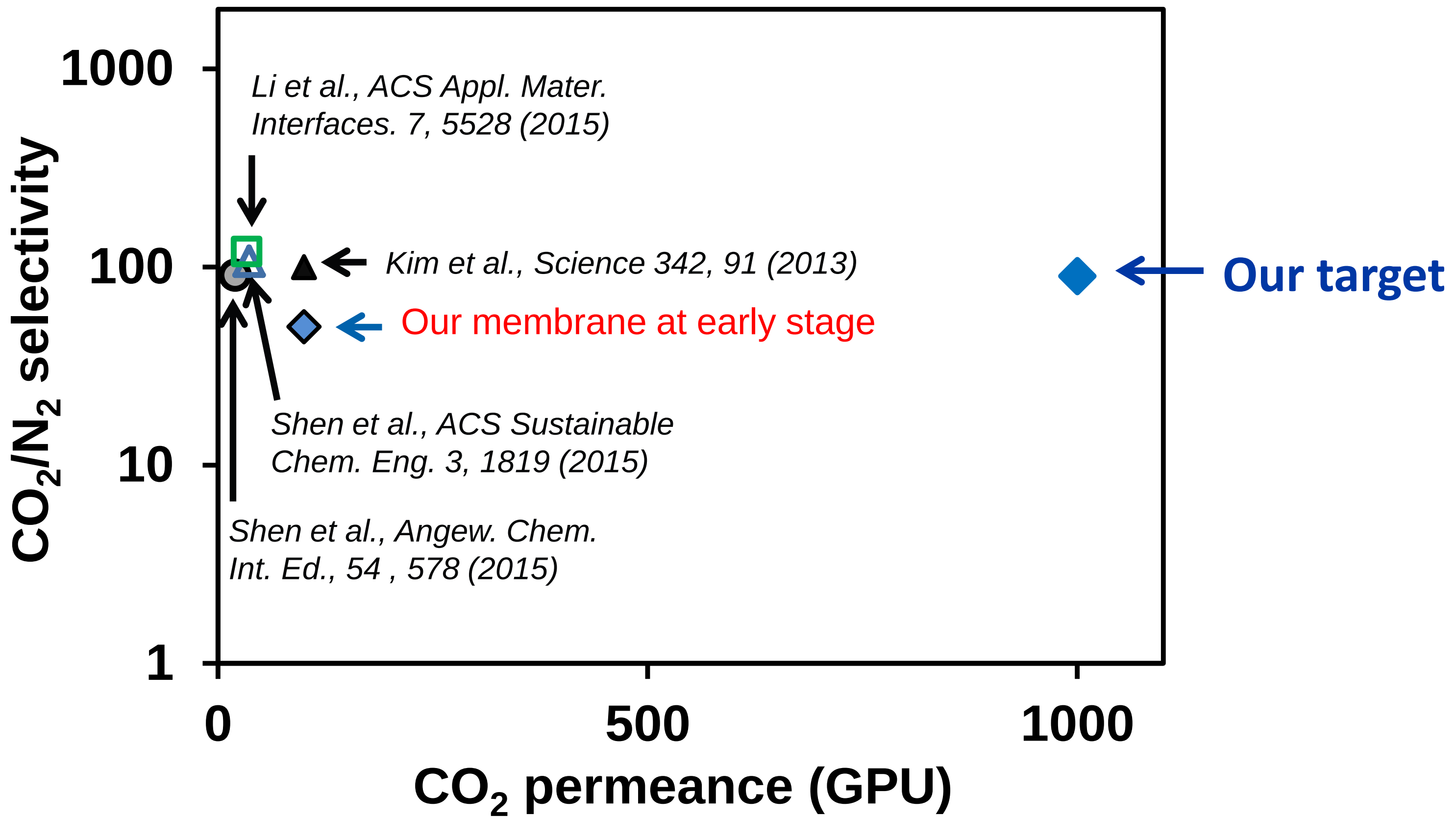
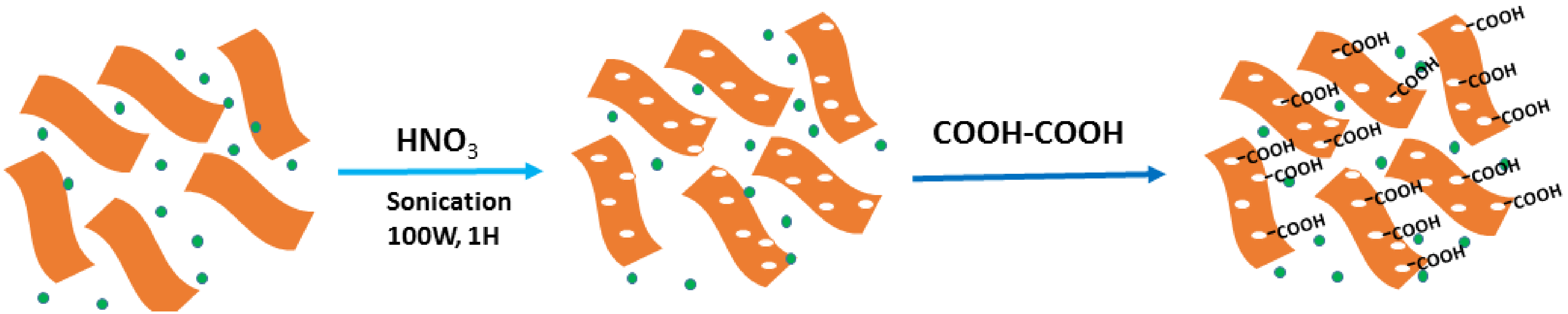
Challenge: GO membrane performance needs significant improvement



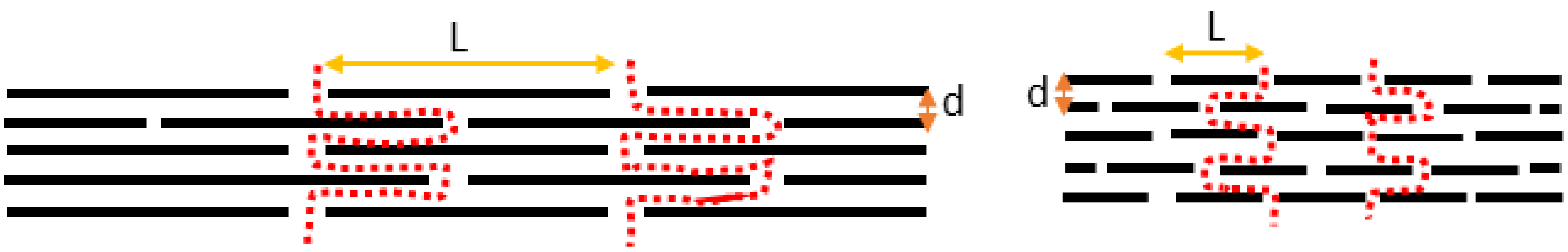
Approaches to improve CO_2 permeance

- Create more structural defects on GO flake by HNO_3 etching



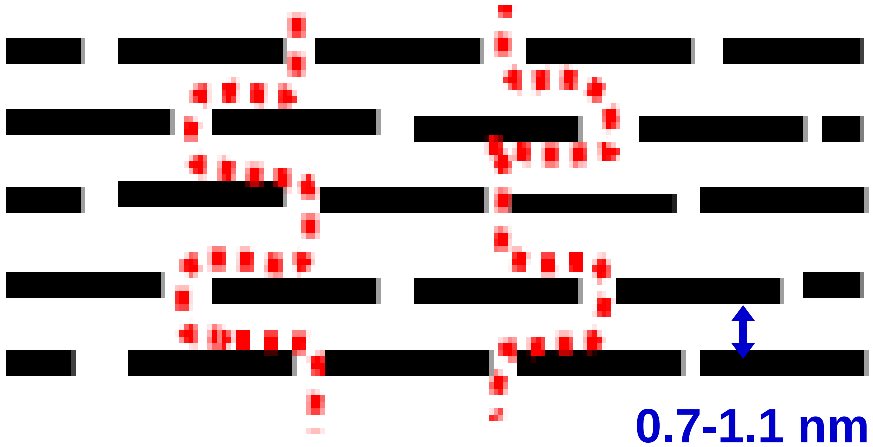
- Reduce GO flake lateral size by ultra-sonication

W/O ultra-sonication **W/ ultra-sonication**



Approach to improve CO_2/N_2 selectivity: fill the space between GO layers with CO_2-philic agent

- CO_2-philic agent enables facilitated transport mechanism to separate CO_2 from N_2



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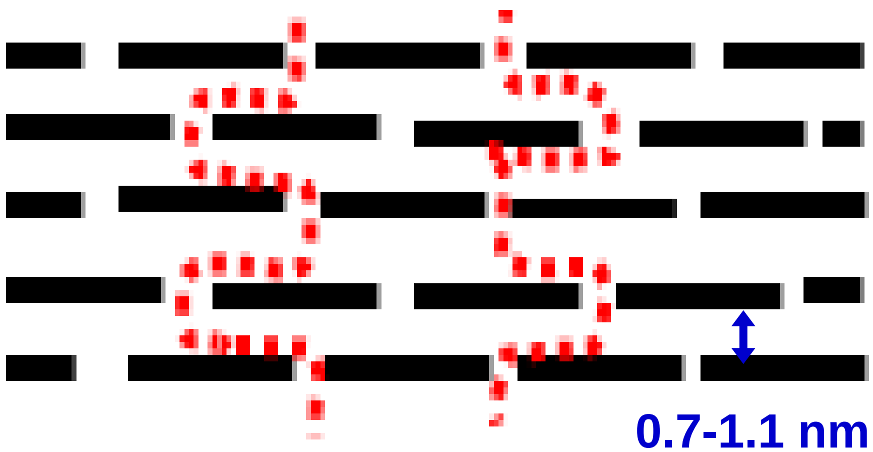
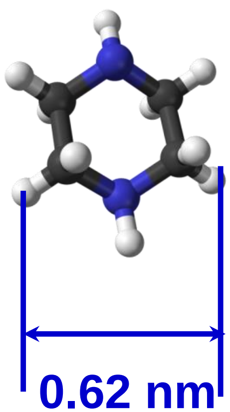
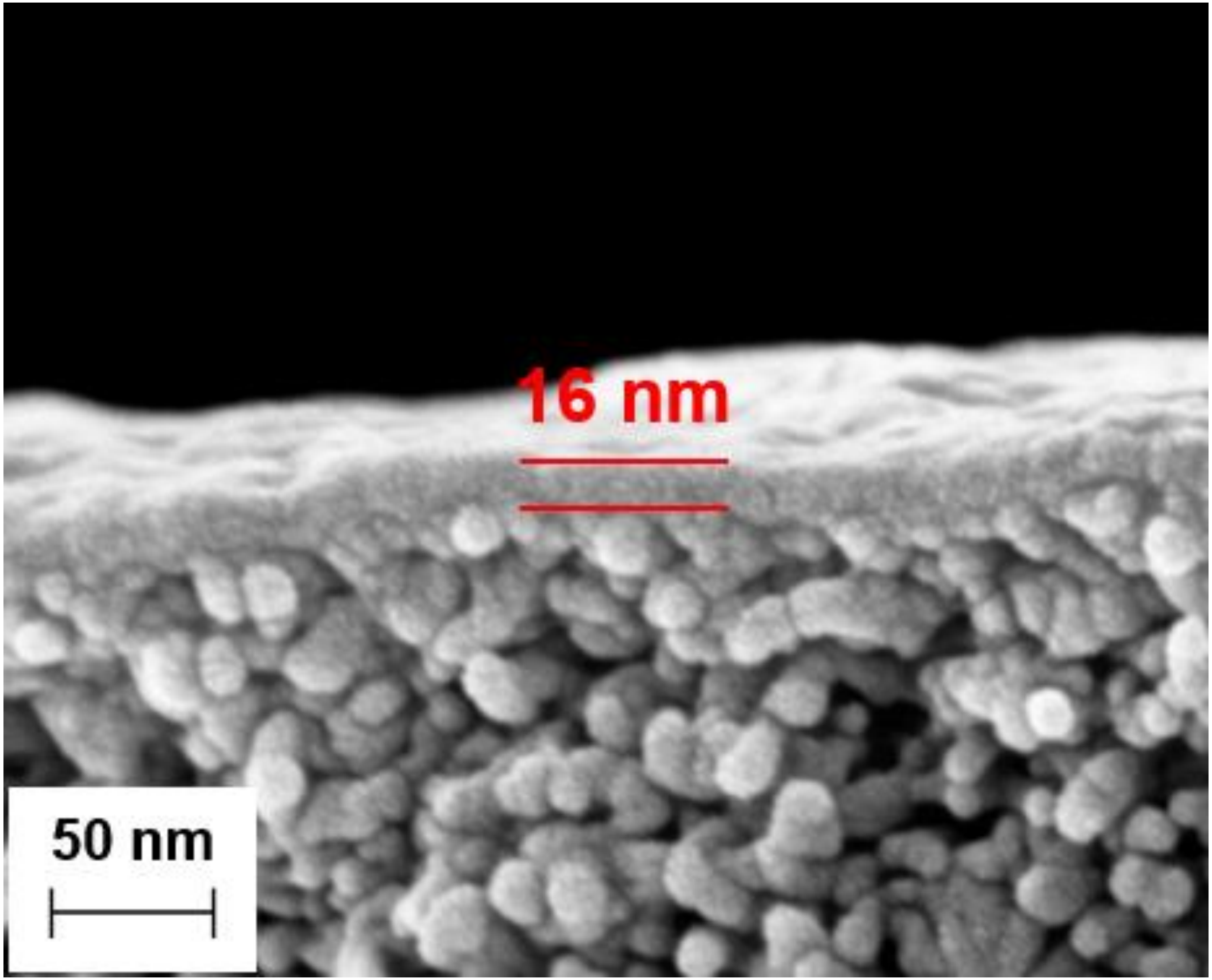


CO_2-philic agent example: piperazine (PZ)

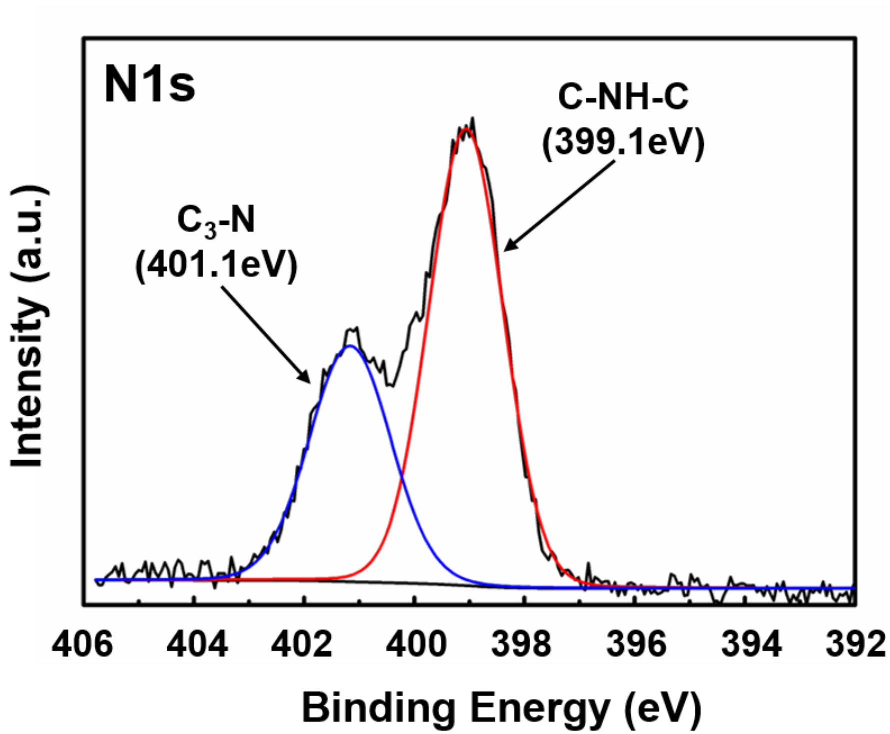


Cross-sectional SEM of the PZ filled GO membrane

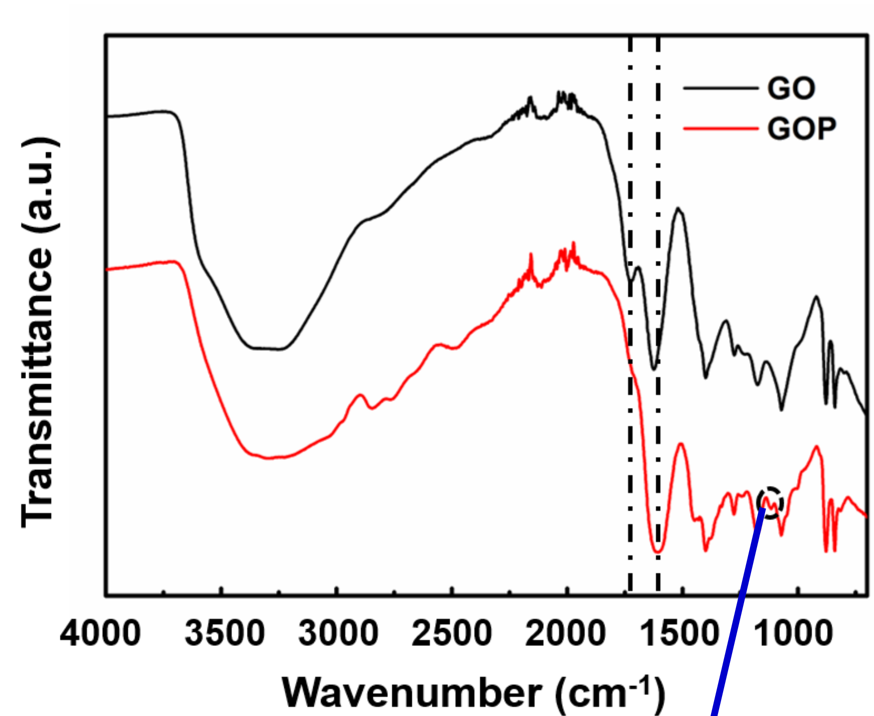


XPS and FTIR analysis confirmed the crosslinking of PZ with GO sheets

XPS



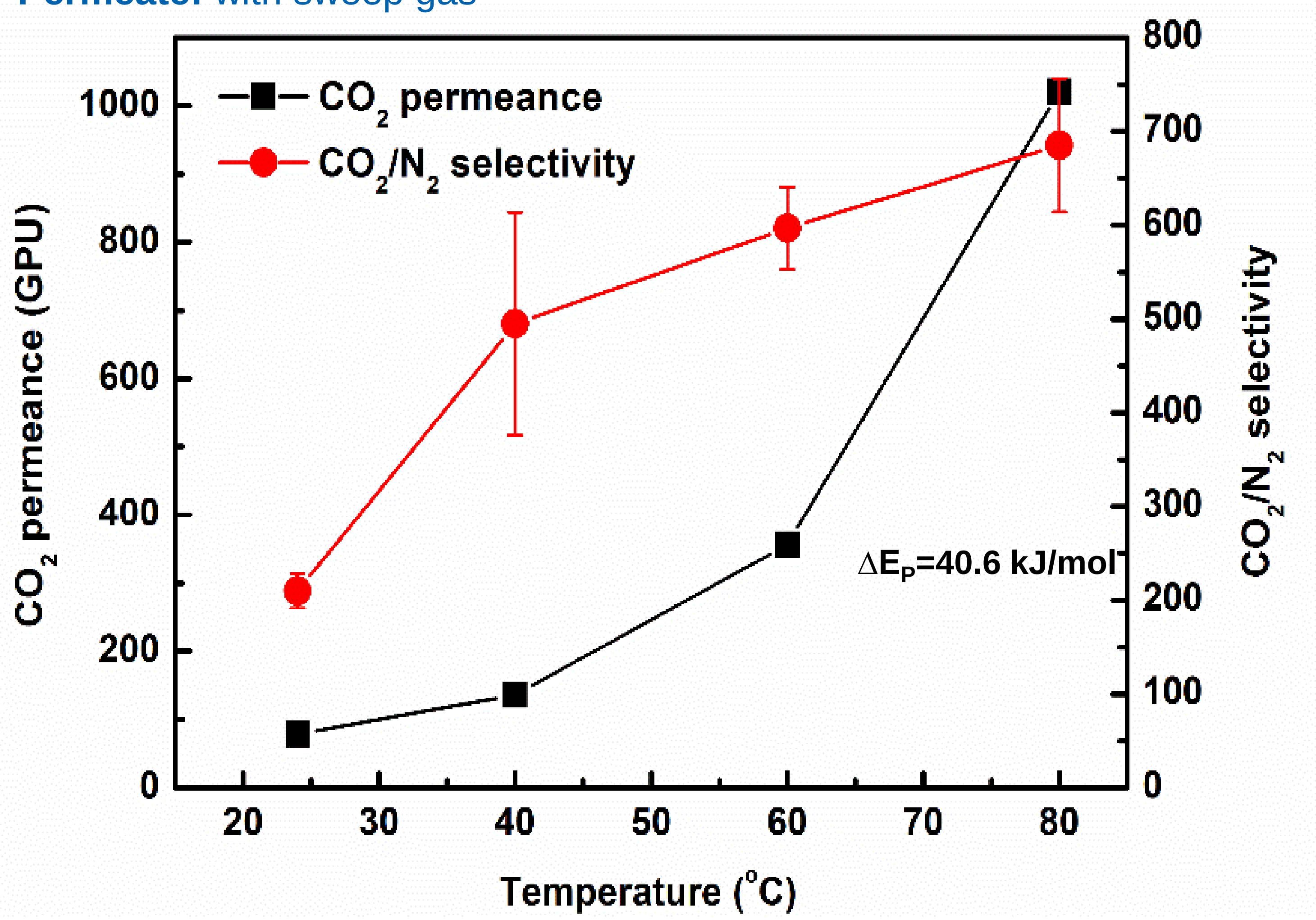
FTIR



C-N bonds

GO-based membranes separation performance

Feed: 15% CO_2/85%N_2 with saturated water vapor
Permeate: with sweep gas



Facilitated transport mechanism

–

0.7-1.1 nm

Facilitated transport mechanism

$$2CO_2 + 2RR'NH + H_2O \rightleftharpoons RR'NCOOH + RR'NH_2^+ + HCO_3^-$$

$$CO_2 + RR'R''N + H_2O \rightleftharpoons RR'R''NH^+ + HCO_3^-$$

–

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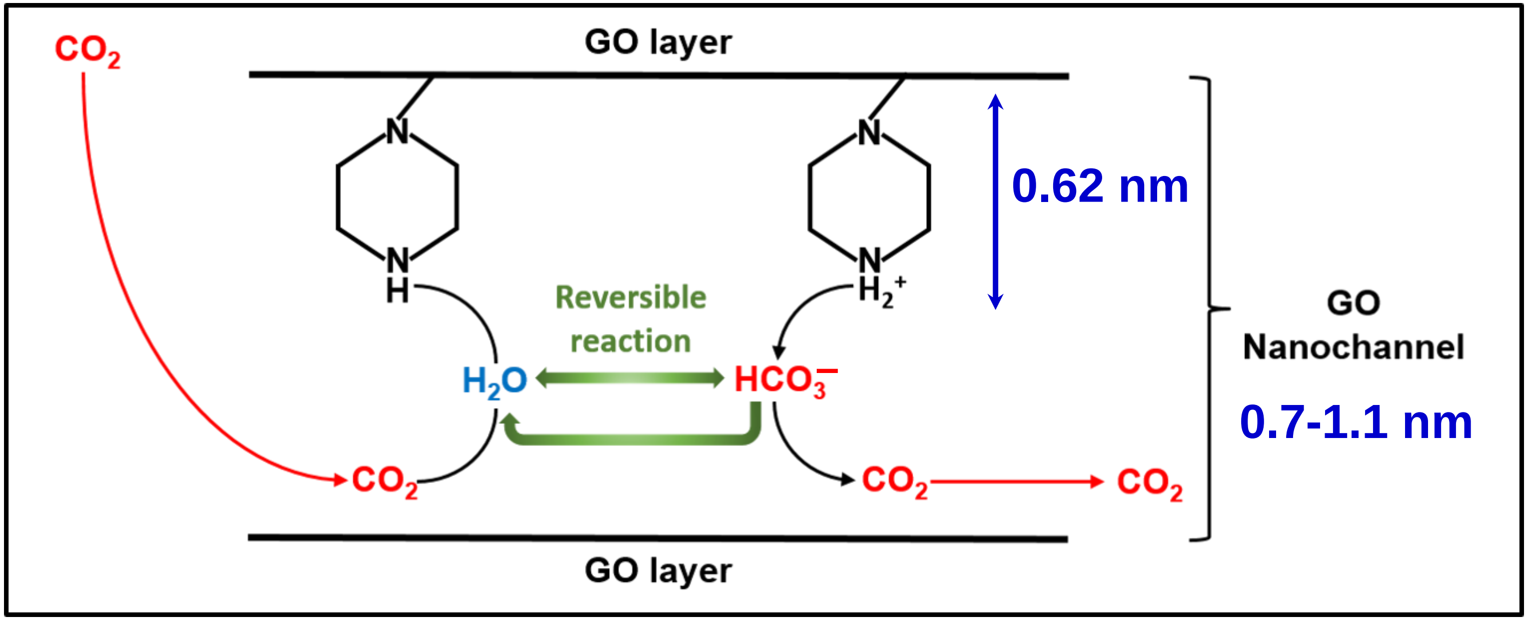
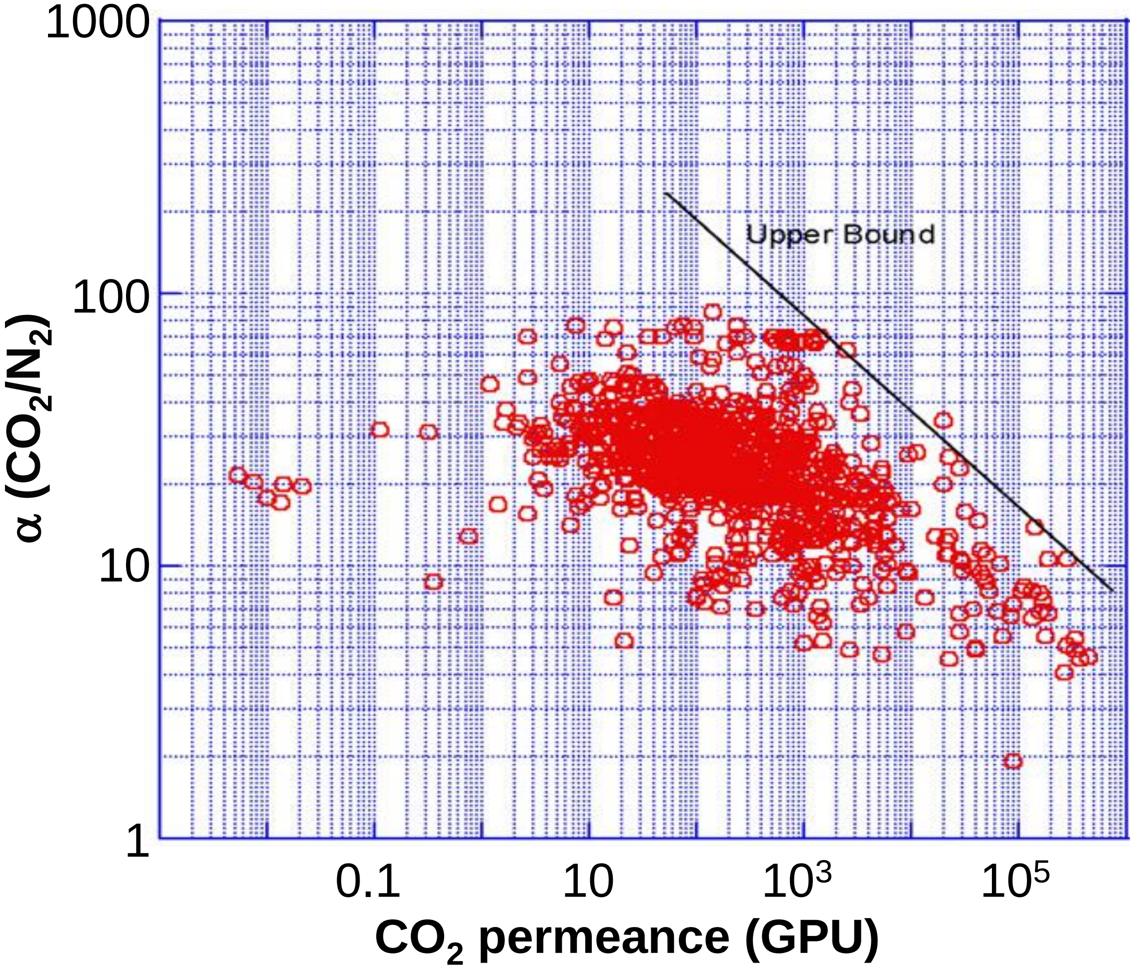


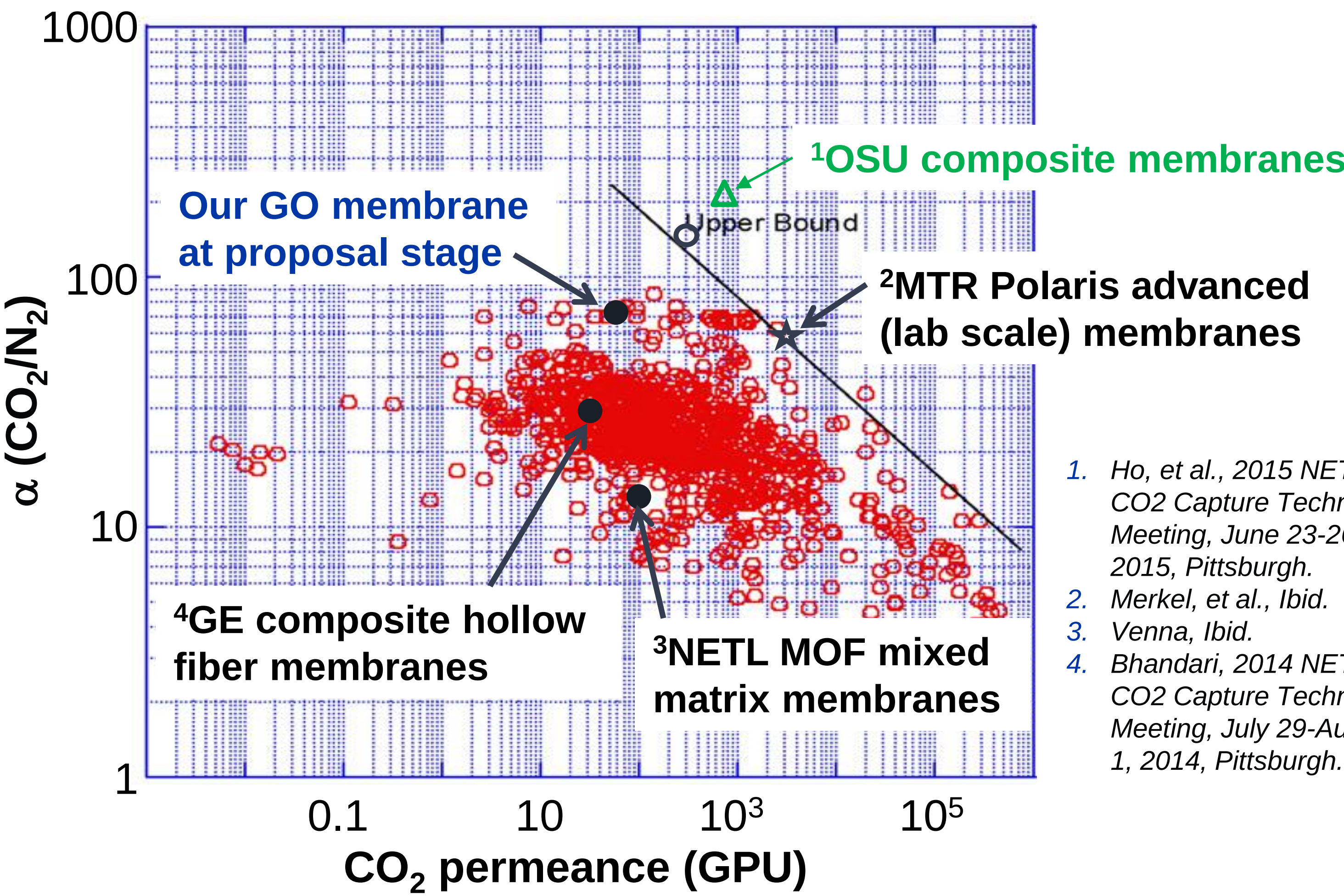
Comparison to other CO_2/N_2 separation membranes



Robeson, J. Membrane Sci. ***2008****, Vol. 320, p390*

Note: Polymer data points (red): 100 nm membrane thickness assumed

Comparison to other CO_2/N_2 separation membranes



1. *Ho, et al., 2015 NETL CO2 Capture Technology Meeting, June 23-26, 2015, Pittsburgh.*
2. *Merkel, et al., Ibid.*
3. *Venna, Ibid.*
4. *Bhandari, 2014 NETL CO2 Capture Technology Meeting, July 29-August 1, 2014, Pittsburgh.*

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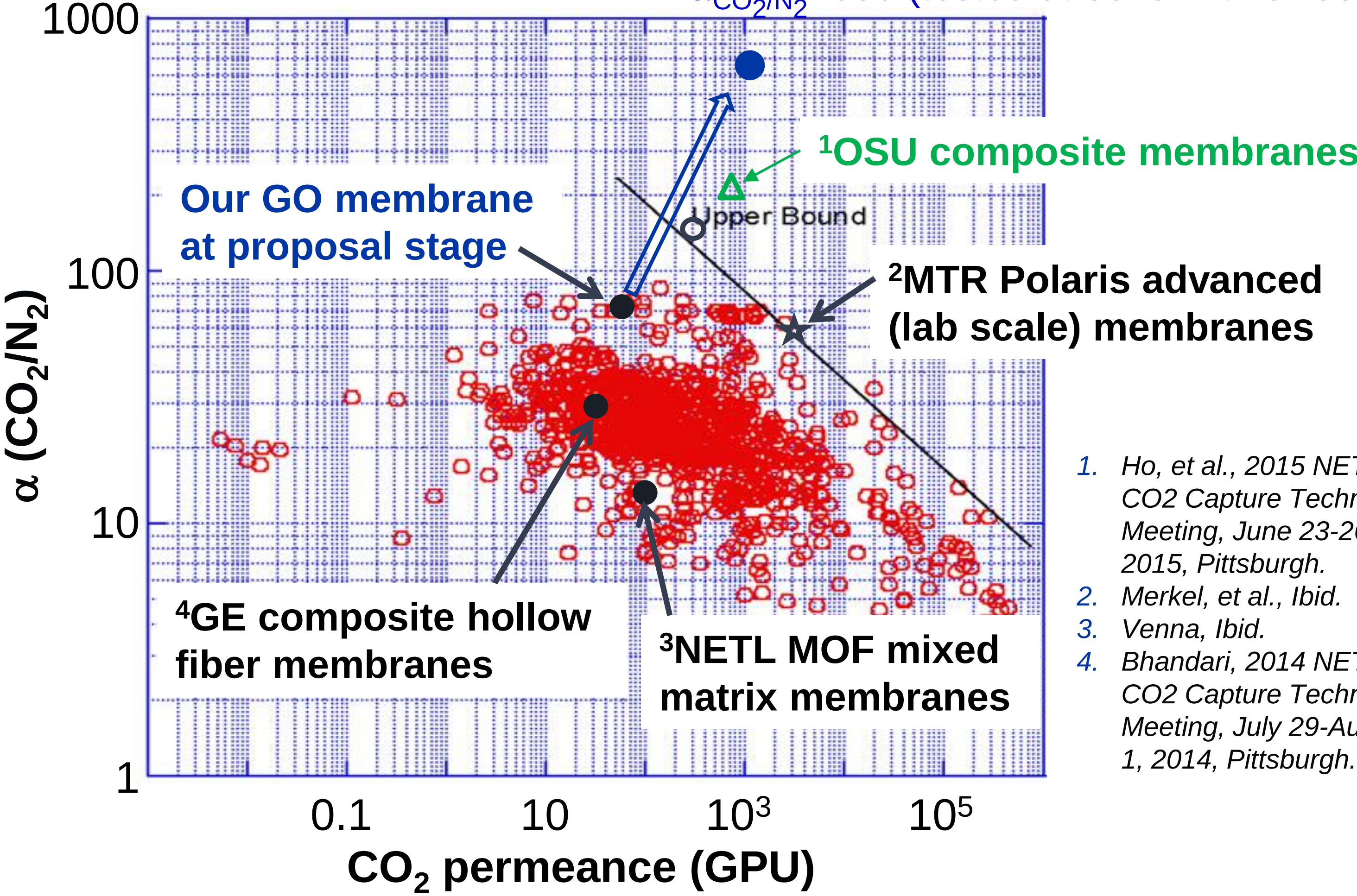
Note: Polymer data points (red): 100 nm membrane thickness assumed

Comparison to other CO_2/N_2 separation membranes

Our GO membranes: P_{CO2}: 1000 GPU, α_{CO_2/N_2}: 680 (tested at 80°C with sweep gas)



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Future work overview/roadmap

GO Membrane Development

PEEK Membrane Development

Task 6.0 (RPI) – Further GO optimization

Task 7.0 (GTI) – Performance stability testing of GO membranes using simulated flue gases

Integrated GO-PEEK Hybrid System

Task 9.1 (RPI) – GO membrane support for integrated testing

Task 8.0 (GTI)– Modification of an existing HFMC apparatus to GO-PEEK system

Task 9.2 (ALaS) – PEEK membrane support for integrated testing

Task 10.0 (GTI) – CO_2 capture testing using integrated GO-PEEK hybrid system

Task 11.0 (Trimeric)– High-level techno-economic feasibility study

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After the current project, steps can be taken to further reduce cost for GO-based membranes

- New process design
- Increase CO_2 permeance for GO membrane
- Advanced manufacture process to lower membrane costs

Hollow fiber configuration

module can be used in bench scale

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Hollow fiber configuration

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Flat sheet membranes to be used in spiral wound configuration

Summary

- We are developing a transformational hybrid process for CO_2 capture combining a conventional gas membrane unit and a HFMC unit
- **The 3rd Generation PEEK fiber** developed to date
  - Fibers with intrinsic CO_2 permeance >3,000 GPU at 25°C
  - Membrane module effective in capturing CO_2 from low CO_2-concentration feeds with aMDEA solvent
- **GO membrane** developed to date
  - CO_2 permeance > 1,000 GPU and α_{CO_2/N_2} > 600 obtained at 80°C for a humidified CO_2/N_2 mixture
  - Superior performance to GO-based membranes reported in the literature
- Future work will focused on further GO membrane development, integrated testing and TEA

Acknowledgements

- **Financial and technical support**

DE-FE0026383

- **DOE NETL José Figueroa and Lynn Brickett**
- **Dr. Yu Group**
  - **Fanglei Zhou**
  - **Huynh Ngoc Tien**
  - **Jarvis Chen**
  - **Mahdi Fathizadeh**

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