DOE Contract No. DE-FE0031598

Bench-scale Development of a Transformational Graphene Oxide-based Membrane Process for Post-combustion CO_2 Capture

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2019 Carbon Capture, Utilization, Storage, and Oil and Gas Technologies Integrated Review Meeting

August 26 - 30, 2019, Pittsburgh, PA

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Project overview

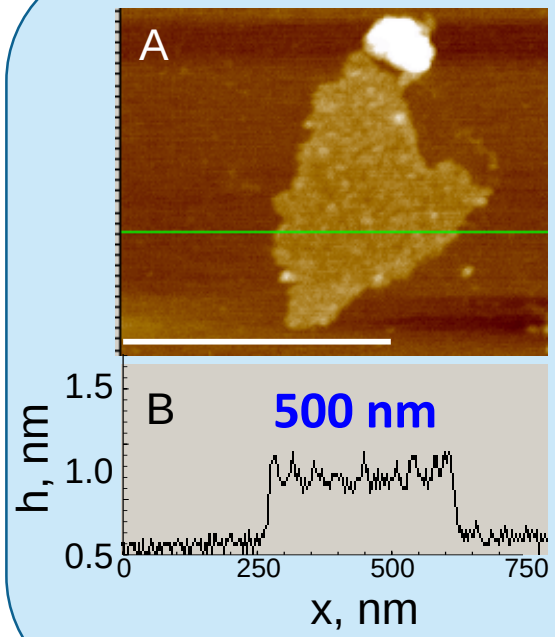
- **Performance period**: June 1, 2018 – Sep. 30, 2021
- **Funding**: $2,914,074 from DOE; $728,738 cost share
- **Objective**: Develop a transformational graphene oxide (GO)-based membrane process (**GO²**) for CO_2 capture with 95% CO_2 purity and a cost of electricity (COE) at least 30% lower than DOE amine reference baseline SC PC plant case
- **Team:**

Member	Roles
gti	• Project management and planning • Quality control • CO_2 capture performance tests
Rensselaer	• GO membrane development and scale-up
The Ohio State University	• Scale-up of flat sheet GO membrane modules • Process design and optimization
National Carbon Capture Center	• Site host
Trimeric Corporation	▪ Technical & economic study

GO membrane technology based on our work published in *Science, Nature Communications, and Journal of Membrane Science*

Science
AAAS

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



- **Contribution**:
  - Single-layered GO flake prepared as thin as 1 nm
  - Structural defects on GO flakes can be controlled as transport pathway for selective gas separations

nature COMMUNICATIONS

ARTICLE

DOI: 10.1038/s41467-017-02318-1 OPEN

Ultrathin graphene oxide-based hollow fiber membranes with brush-like CO_2-philic agent for highly efficient CO_2 capture

ELSEVIER

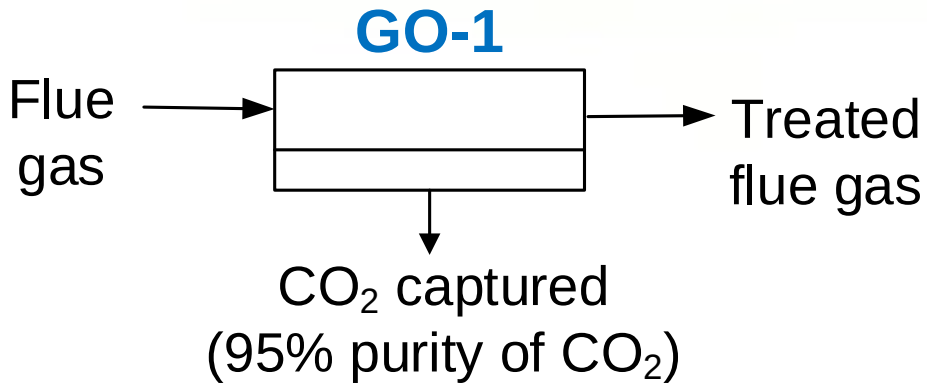
Journal of Membrane Science
Volume 573, 1 March 2019, Pages 184-191

Ultrathin, ethylenediamine-functionalized graphene oxide membranes on hollow fibers for CO_2 capture

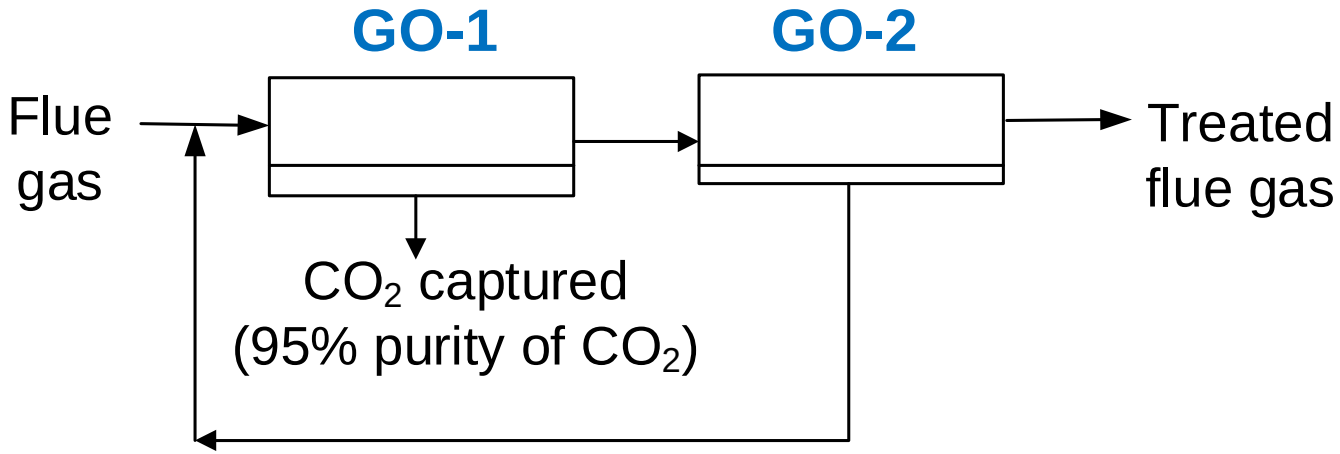
gti

Process description

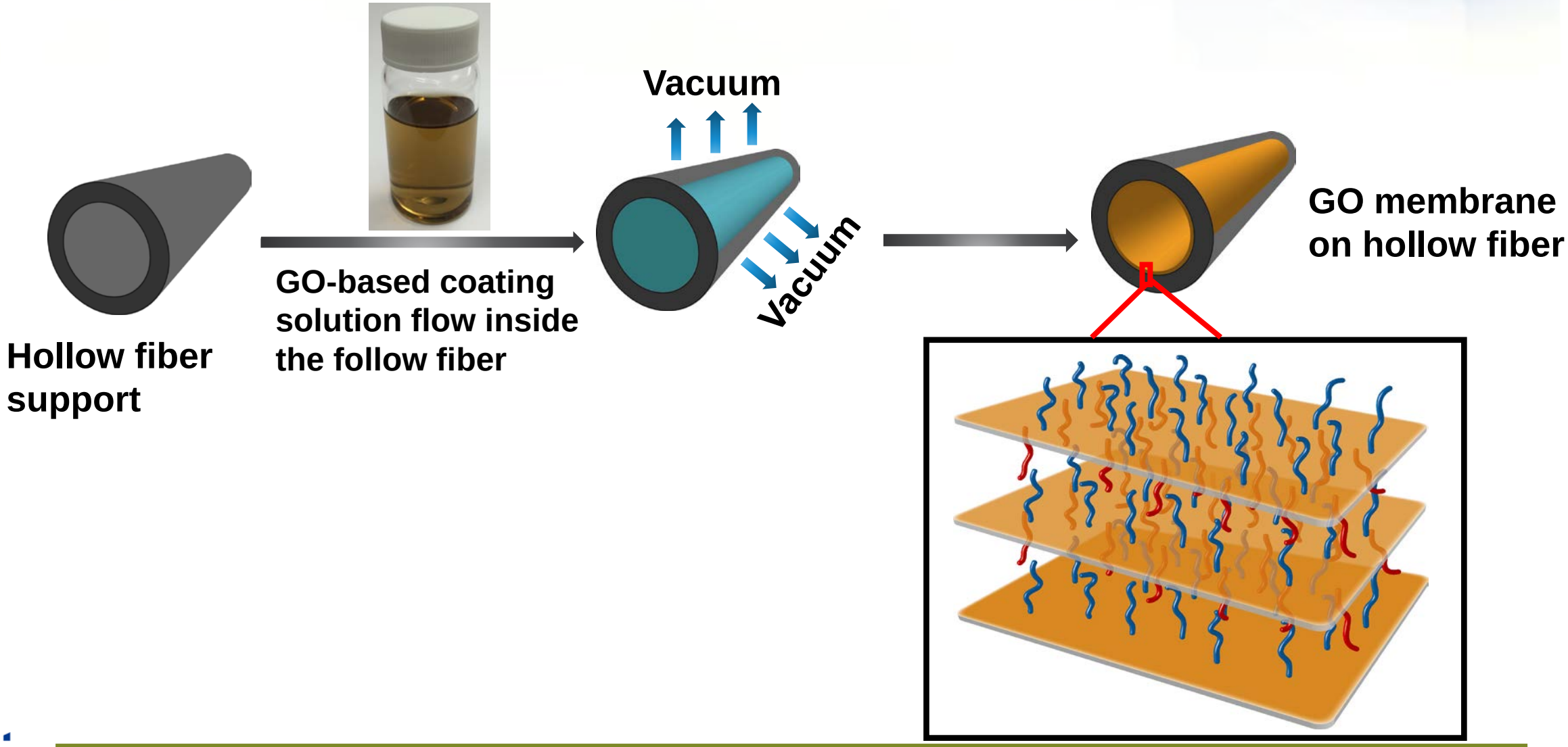
- 70% removal from coal flue gas: **single stage**



- 90% removal from coal or natural gas flue gases: a proprietary **GO^2 process** integrates a high-selectivity GO-1 membrane and a high-flux GO-2 membrane for optimal performance

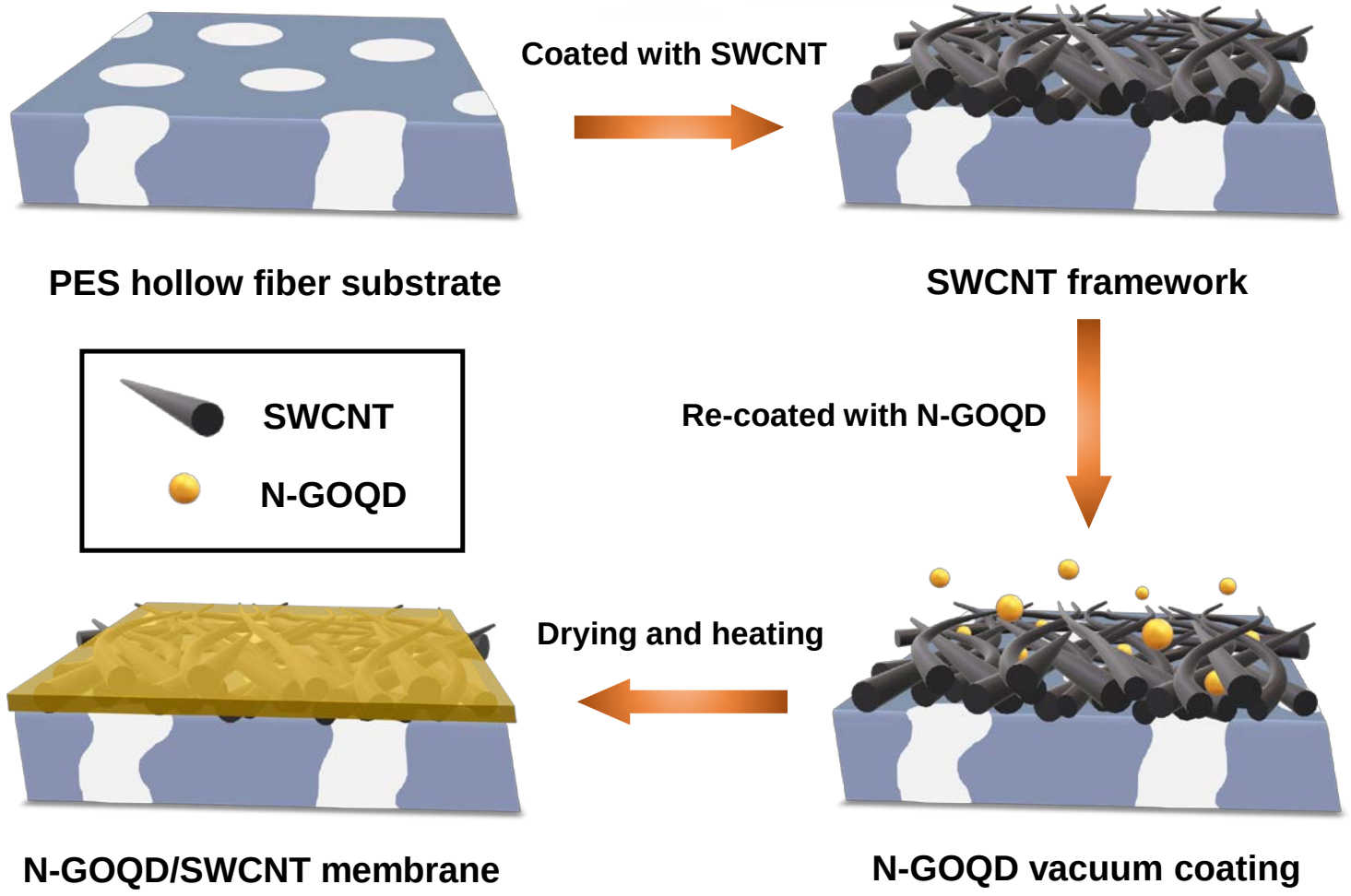


An scalable procedure developed for fabrication of GO membranes on hollow fibers



An innovative membrane structure: GO nanochannels intercalated by single-walled carbon nanotube (SWCNT)

- What does this structure look like?

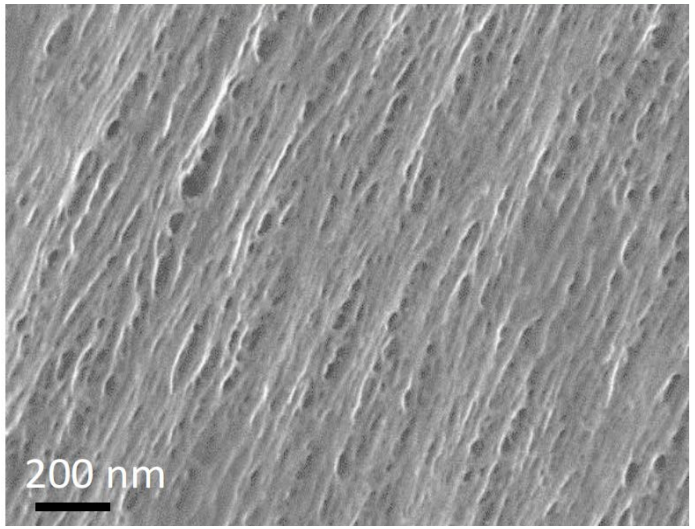


- Why this structure?
  - SWCNTs narrow surface pore size below GOQD size
  - Infiltrated GOQDs pack densely with SWCNTs to form a carbon-based hybrid membrane

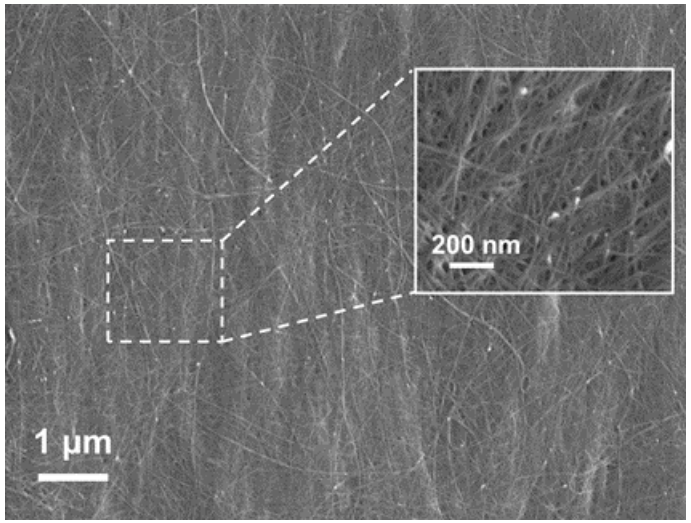
SWCNT: single-walled carbon nanotube
N-GOQD: nitrogen-doped graphene oxide quantum dot

SWCNT successfully prepared on PES hollow fiber

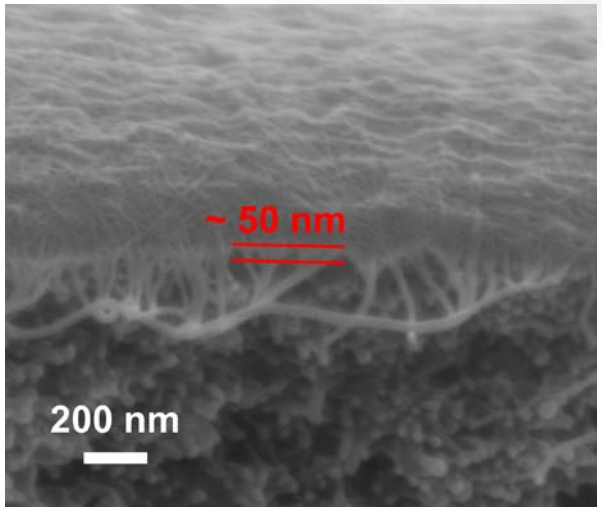
PES fiber surface

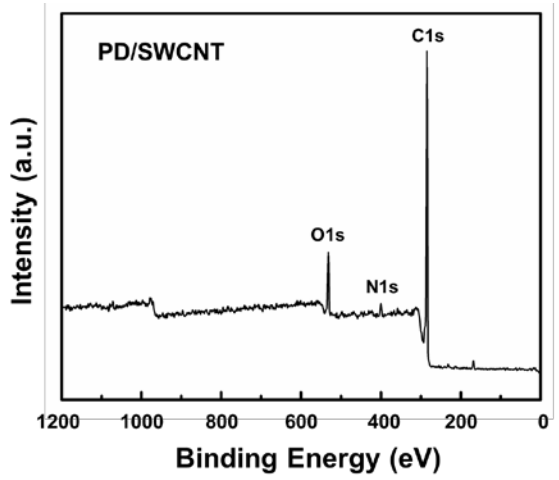


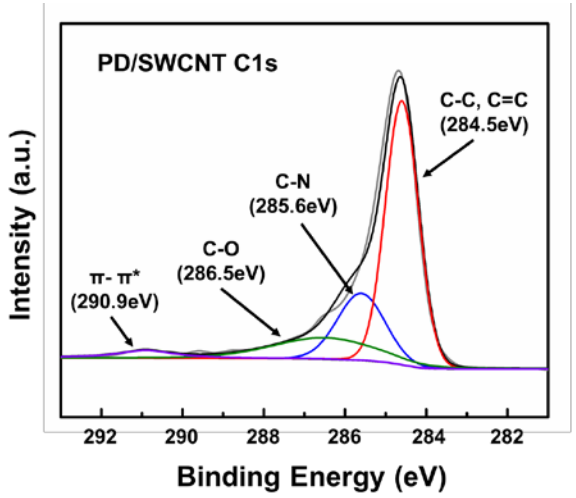
SWCNT-PES surface

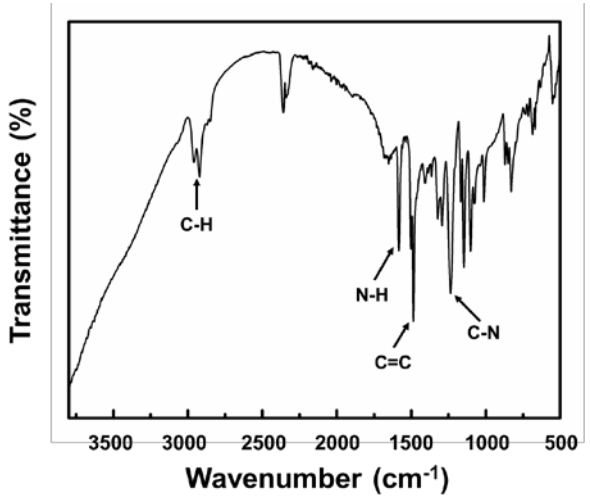


SWCNT-PES cross section



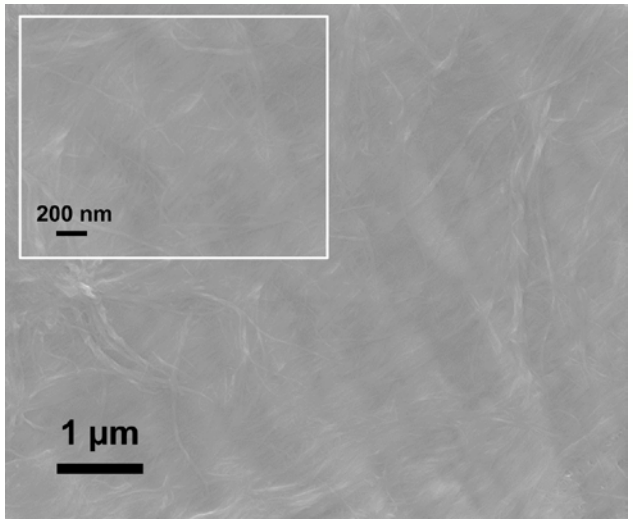


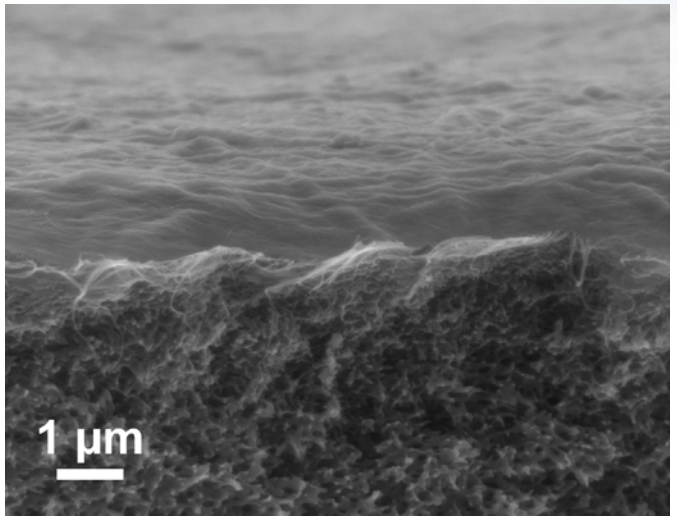


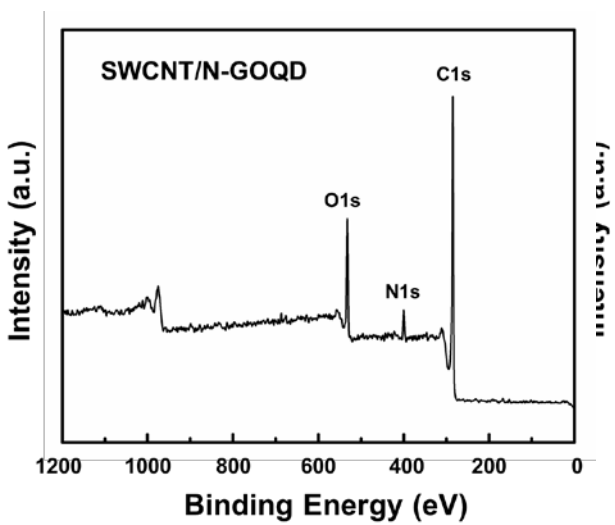


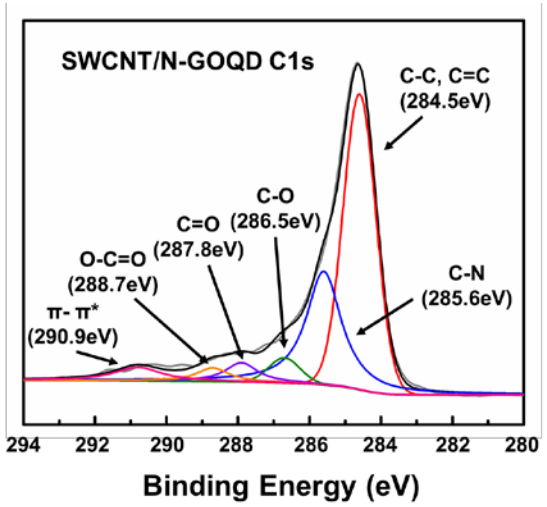
SWCNT: single-walled carbon nanotube
PES: polyether sulfone

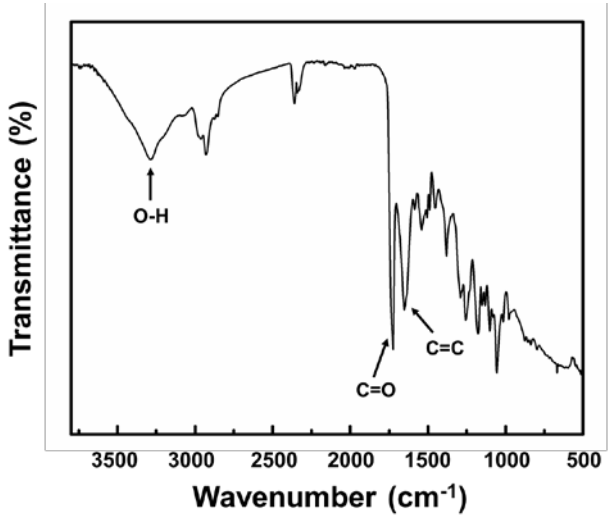
N-GOQD/SWCNT/PES membranes: SEM, XPS, and FTIR



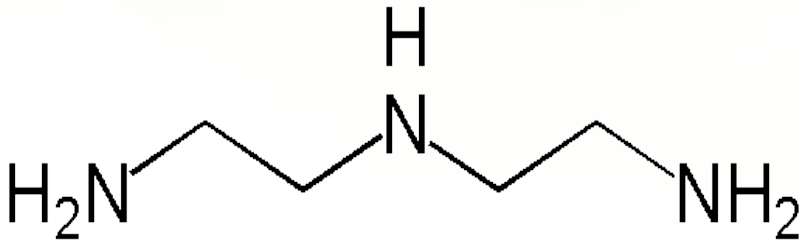




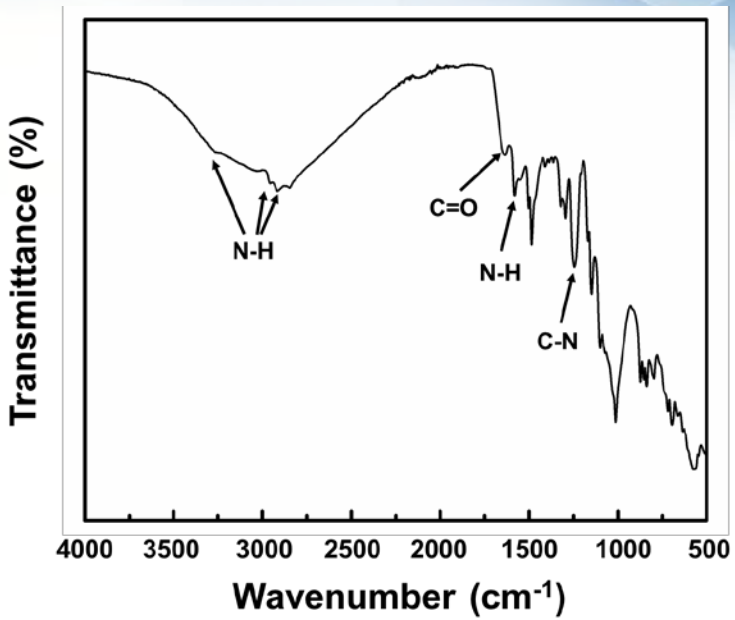




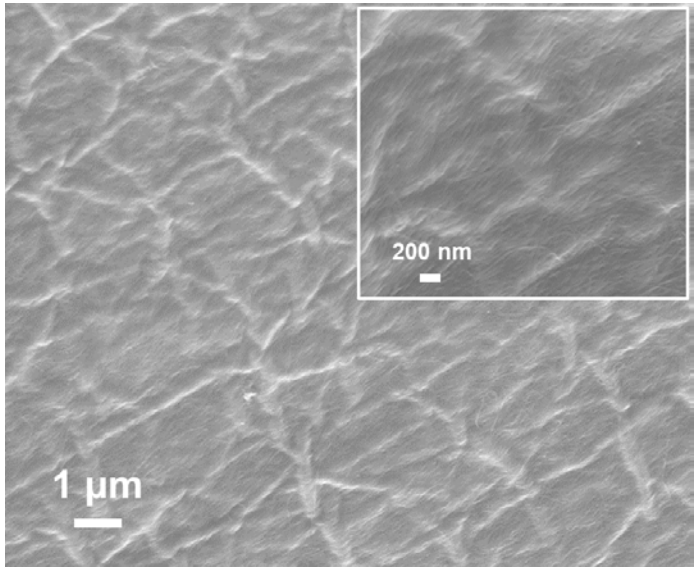
DETA functionalized N-GOQD/SWCNT/PES membrane



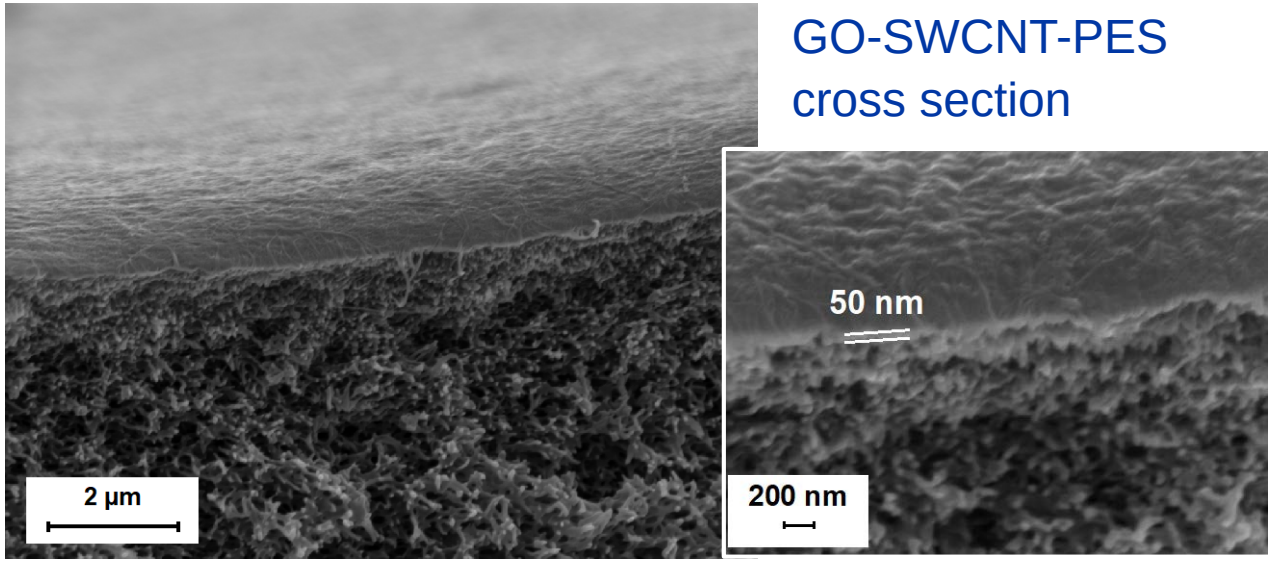
- Cyclic capacity
- Significant lower heat of absorption



GO-SWCNT-PES surface



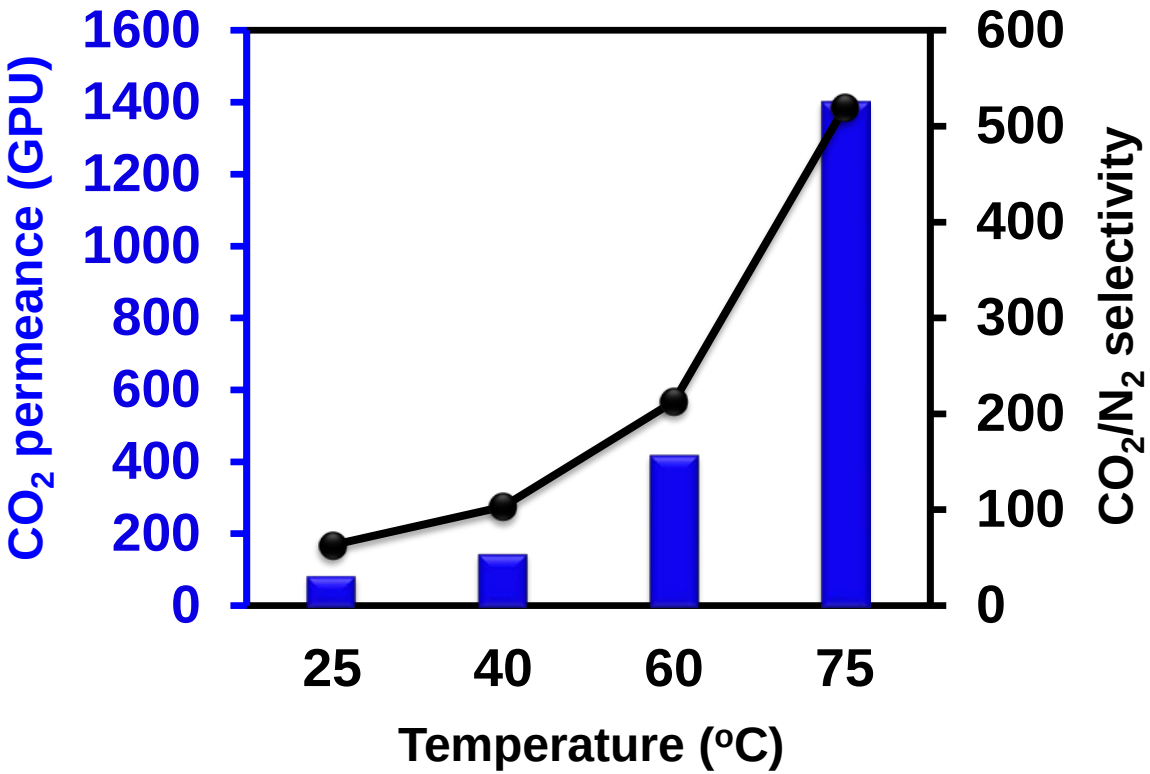
GO-SWCNT-PES cross section

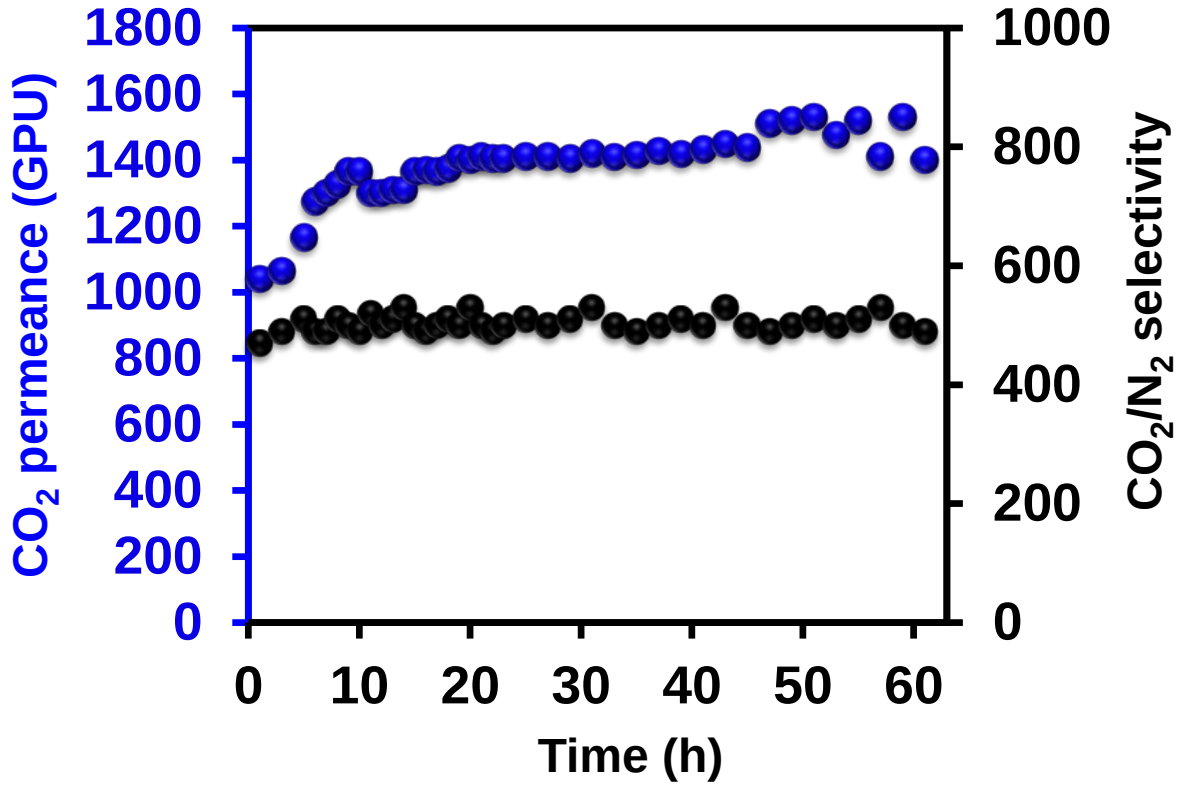


DETA: diethylenetriamine

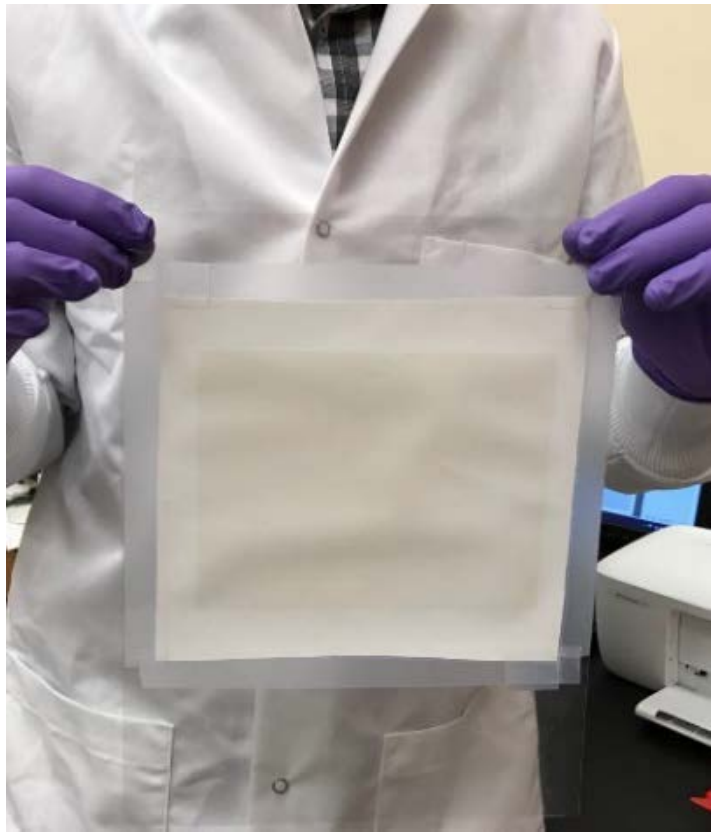
DETA functionalized N-GOQD/SWCNT/PES membrane showed high CO_2/N_2 separation performance and good stability

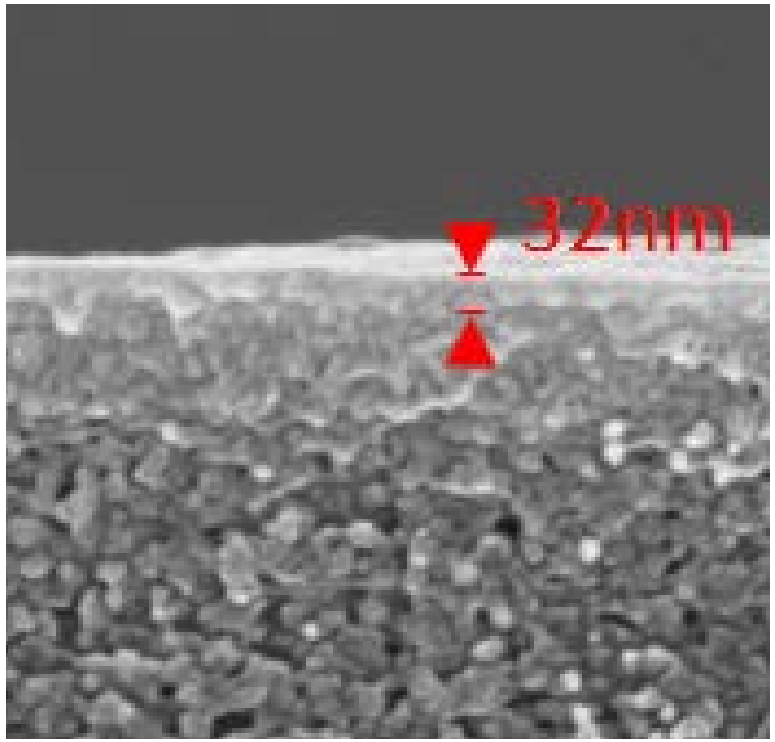
- 75 °C, 2 psig, sweep gas mode, 100% humidity in feed

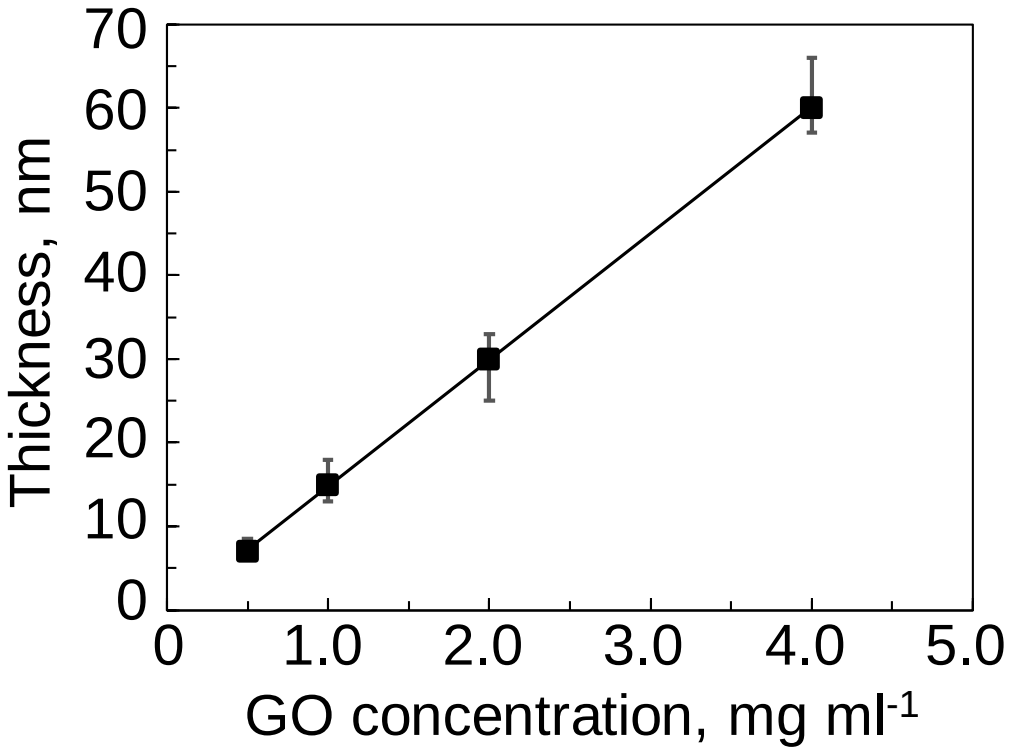




In addition to hollow fiber membranes, flat sheet membranes were successfully prepared by printing



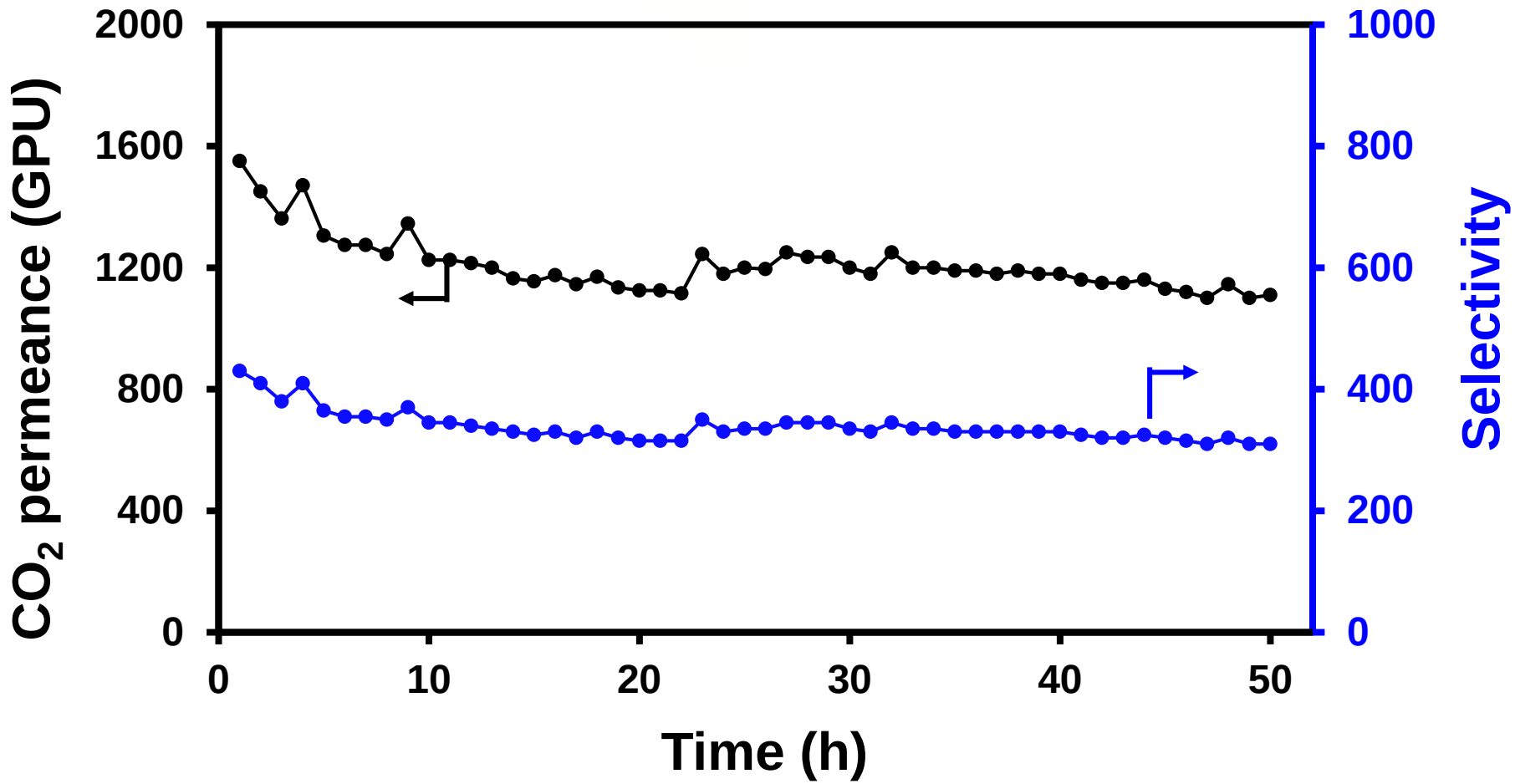




Fathizadeh et al., ***Journal of Materials Chemistry A****, 5, 20860 (2017)*

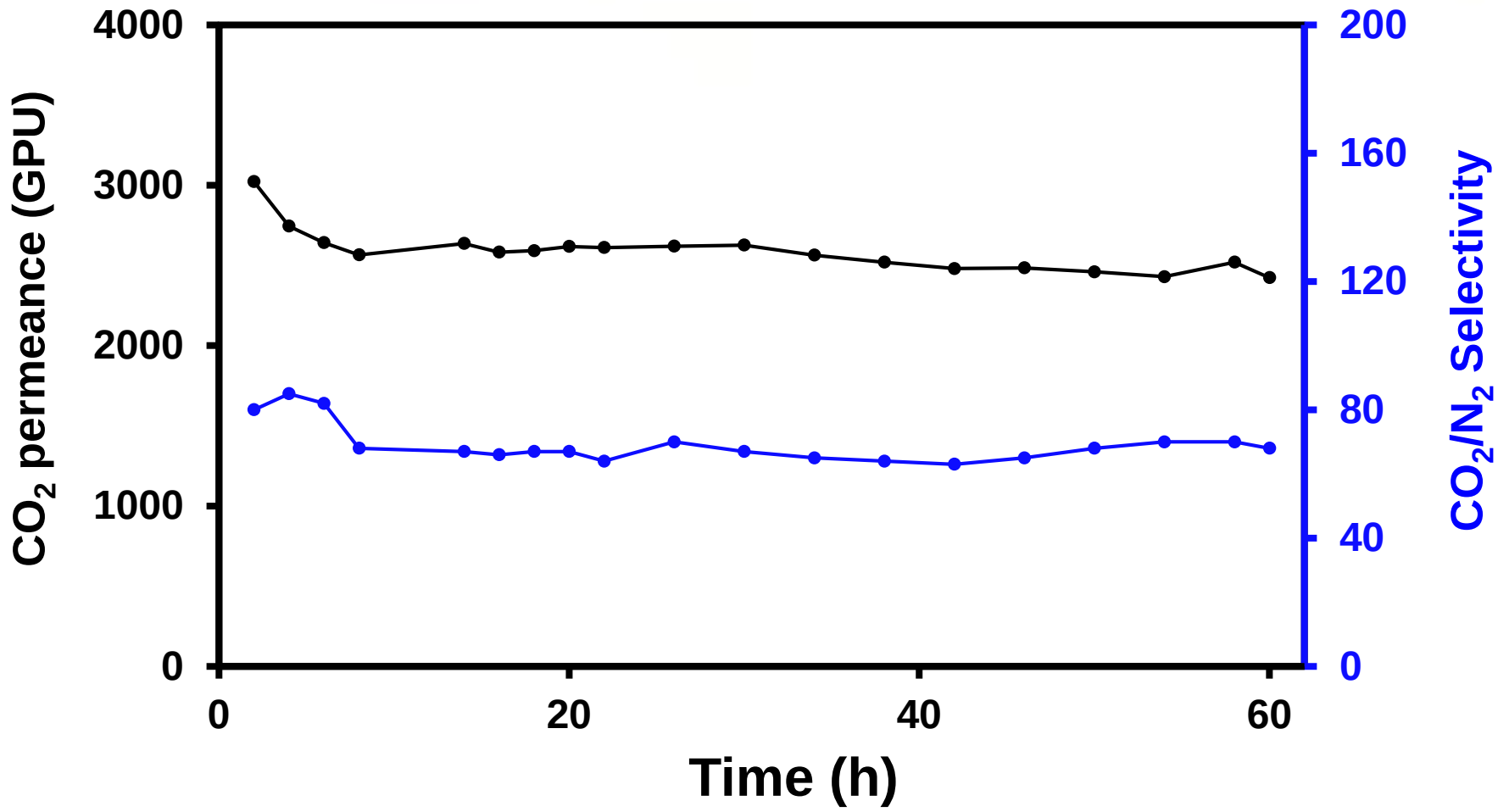
Printed GO-1 membrane showed CO_2/N_2 selectivity as high as 300 with CO_2 permeance of 1,100 at 80°C

80°C, wet condition, vacuum permeation system (permeate side pressure: 0.4 bara)

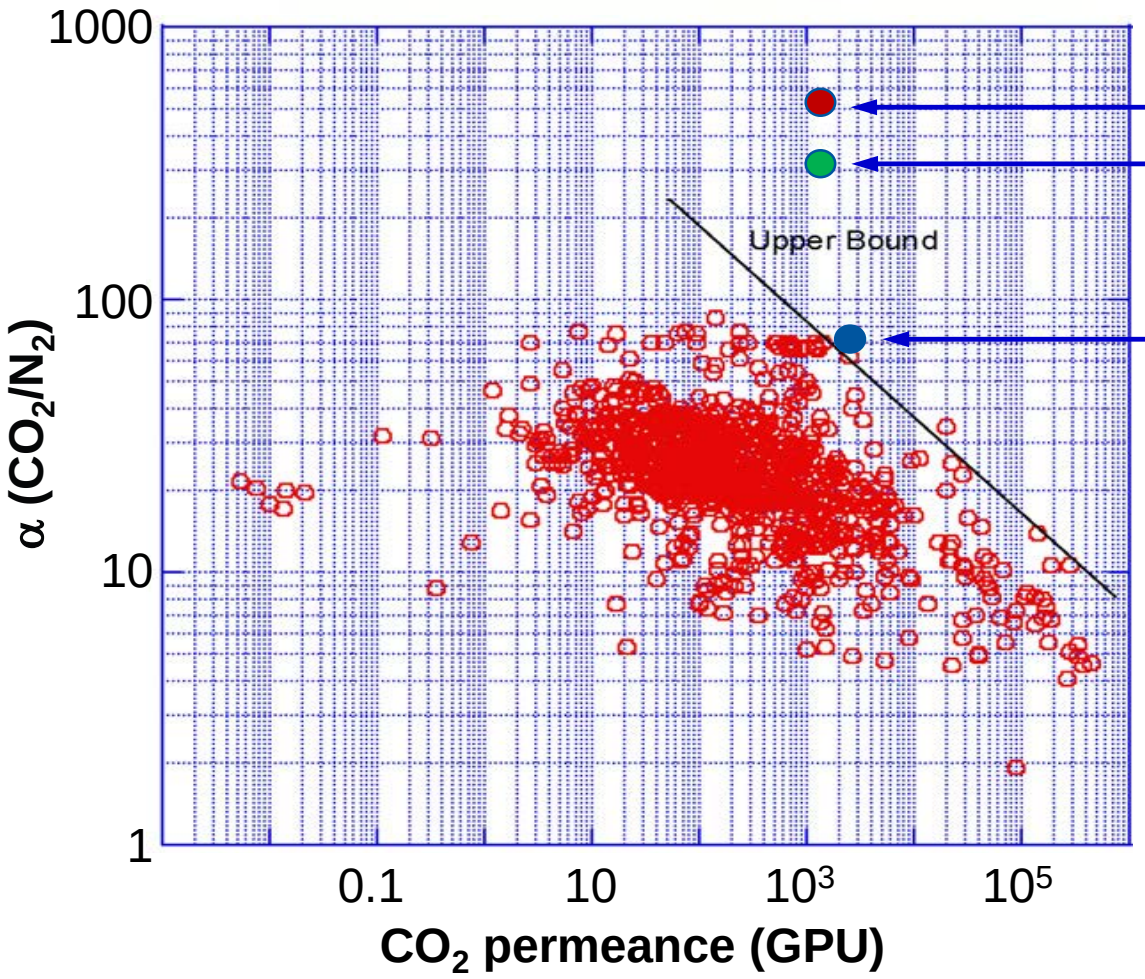


Printed GO-2 membrane showed CO_2 permeance as high as 2,520 with CO_2/N_2 selectivity of 70 at 85°C

85°C, wet condition, vacuum permeation system (permeate side pressure: 0.4 bara)



Where do our membranes fall on the Robeson plots?



Vacuum filtration prepared GO-1 at 75°C

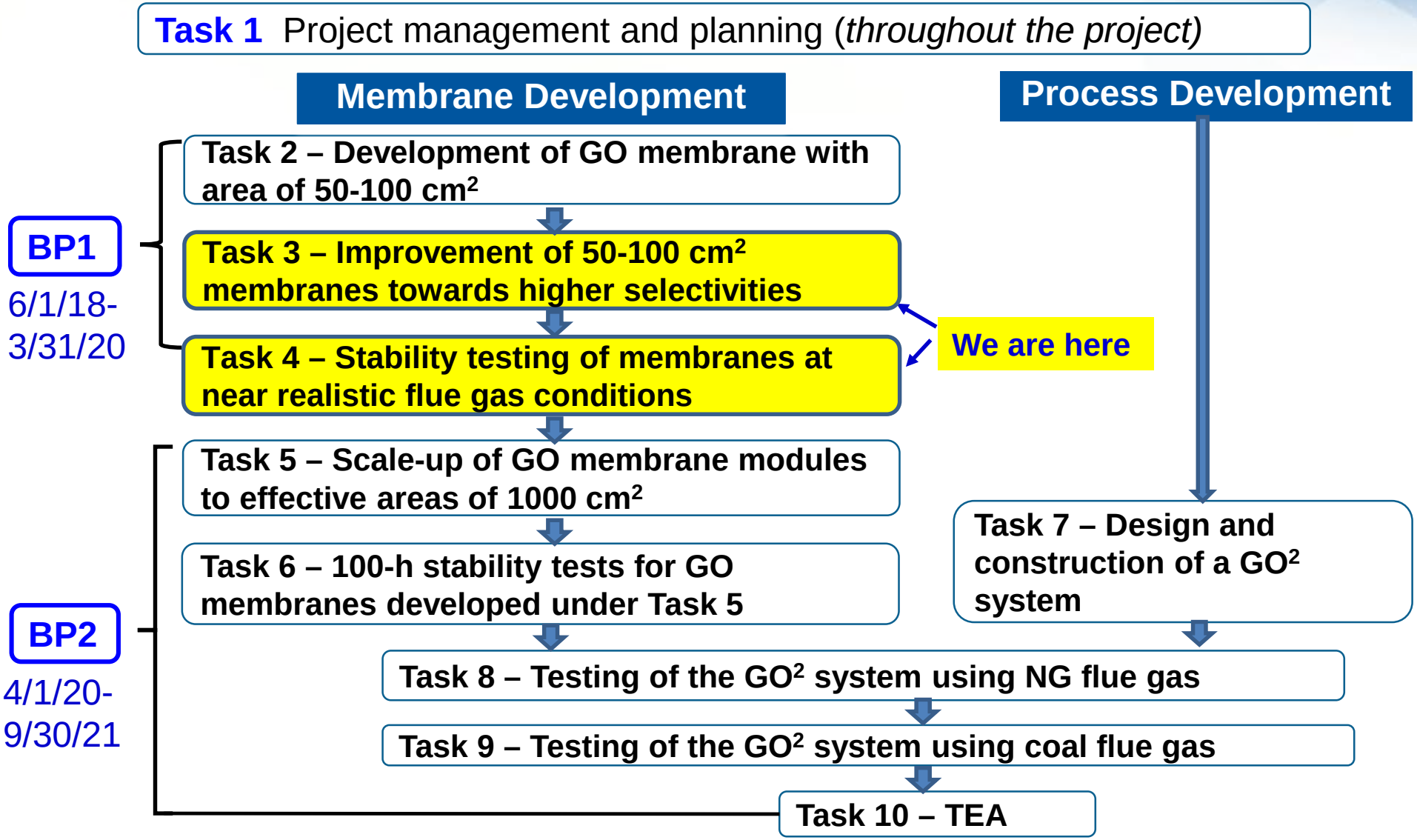
Printed GO-1 membranes at 80°C

Printed GO-2 membranes at 85°C

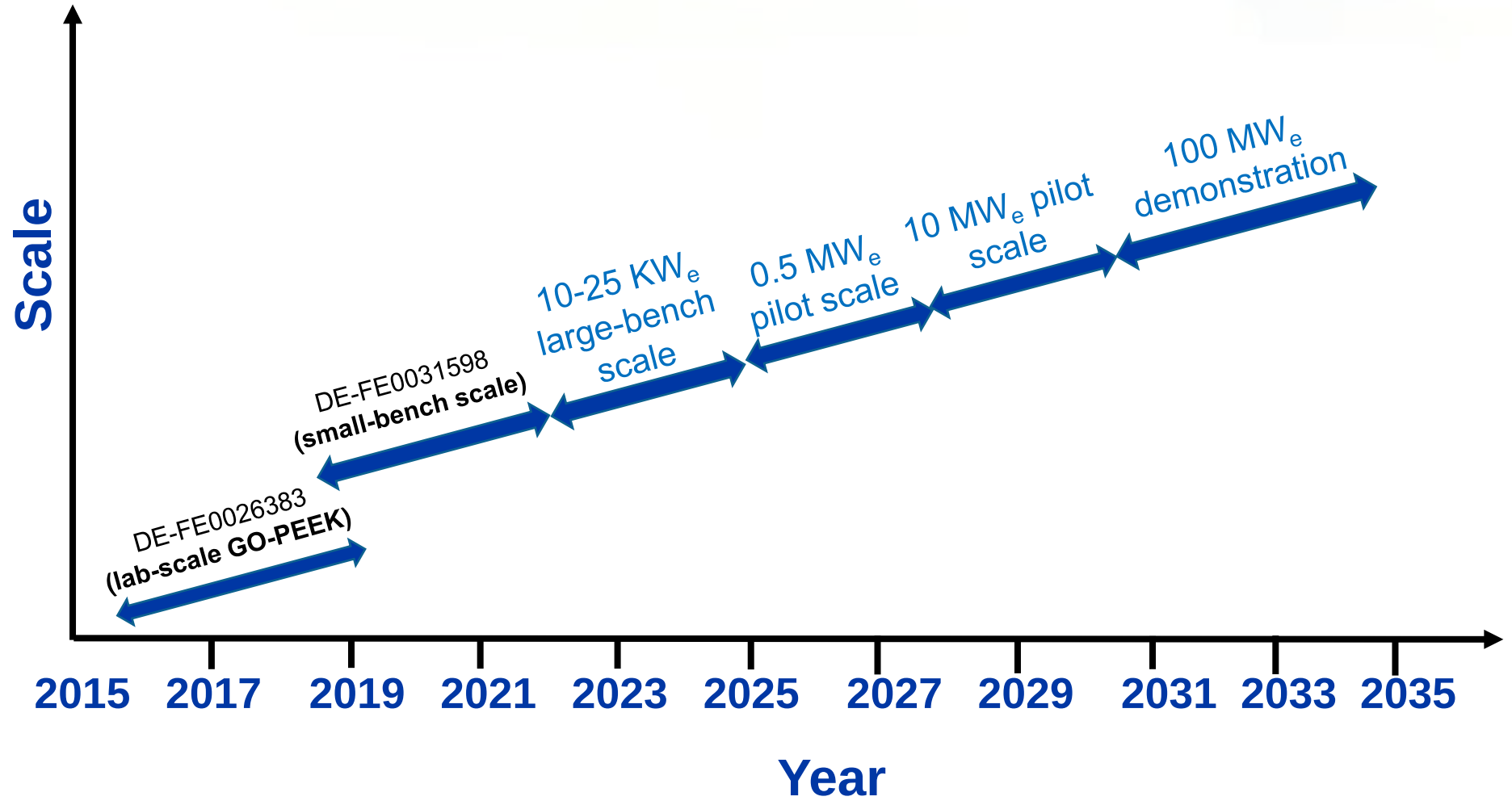
Robeson, J. Membrane Sci. ***2008****, Vol. 320, p390*

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

Future work overview/roadmap (in this project)



Envisioned technology development path



Summary

- We are developing a transformational graphene oxide-based membrane process for post-combustion CO_2 capture
  - **Single stage** for 70% removal from coal flue gas
  - **GO² process** integrating a high-selectivity GO-1 membrane and a high-flux GO-2 membrane for 90% removal from coal or natural gas flue gases
- GO-based membranes developed to date
  - **GO-1 membranes** (hollow fibers): CO_2 permeance of 1,400 GPU, and CO_2/N_2 selectivity of 520
  - **GO-2 membranes** (flat sheet fabricated by printing): CO_2 permeance of 2,520 GPU, and CO_2/N_2 selectivity of 70
- Future work
  - Scale up membranes
  - Design GO^2 process and testing at the NCCC with actual flue gas

Acknowledgements

- Financial and technical support

DE-FE0031598

- DOE NETL: Andrew O'Palko, Steven Mascaro, José Figueroa and Lynn Brickett

- CO_2 Capture Project - Phase 4
- The CCP4: Betty Pun and Mark Crombie

- The National Carbon Capture Center (NCCC): Frank Morton and Tony Wu

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