Direct Air Capture Using Trapped Small Amines in Hierarchical Nanoporous Capsules on Porous Electrospun Fibers

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Project Overview

Funding: $800,000 from DOE; $200,000 Cost Share

Overall Project Performance Dates: 2/1/2021-7/31/2022

Project Participants:

University at Buffalo
The State University of New York

ASU

gti®

Overall Project Objectives:

Develop an innovative sorbent structure of trapped small amines in hierarchical nanoporous capsules (HNC) embedded in porous electrospun fibers (PEF) for direct air capture (DAC). This involves the tailoring of both sorbent and PEF materials to achieve a compact system for DAC with high capacities for CO_2 at concentrations typically available in air and at near ambient conditions.

Technology Background

Transformational Adsorbent Utilizing Small Trapped Amines

Dry condition: 0.5 mol CO_2 per mole of N

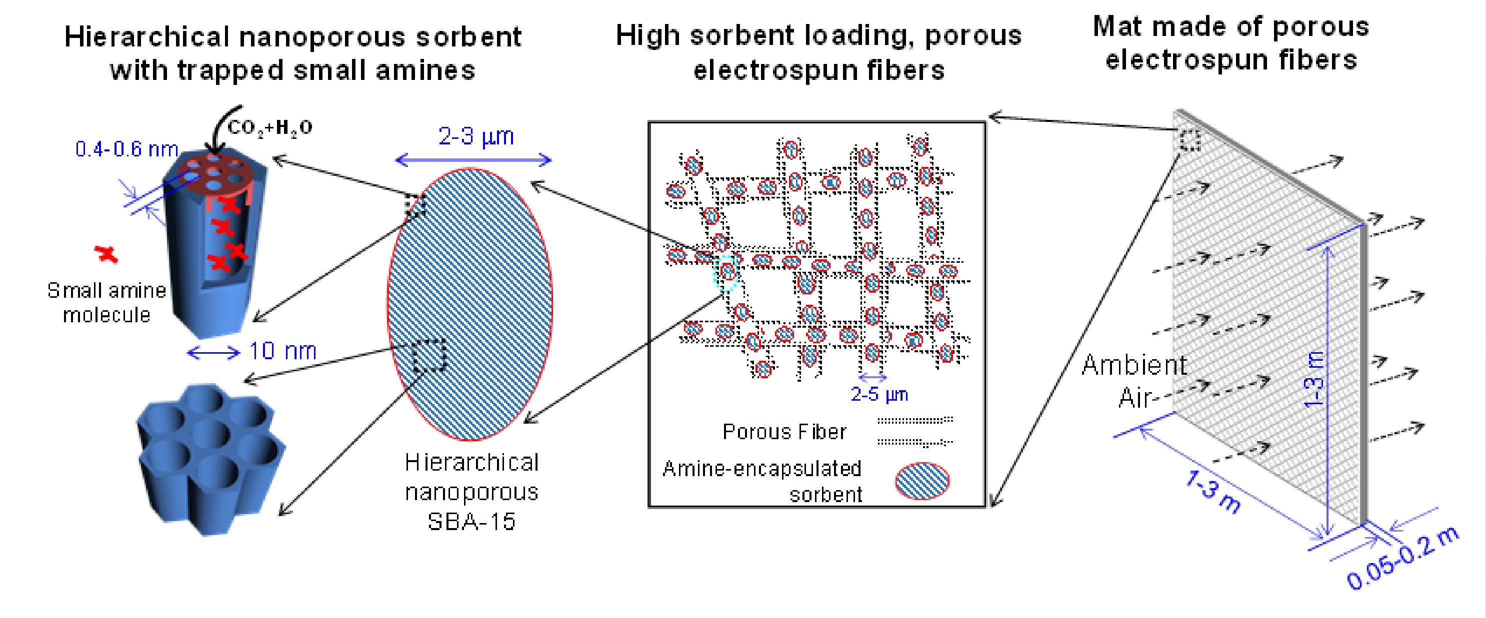
$$CO_2 + 2RNH_2 \leftrightarrow RNH_3^+ + RNHCOO^-$$

$$CO_2 + 2R_1R_2NH \leftrightarrow R_1R_2NH_2^+ + R_1R_2NHCOO^-$$

Moisture condition: 1 mol CO_2 per mole of N

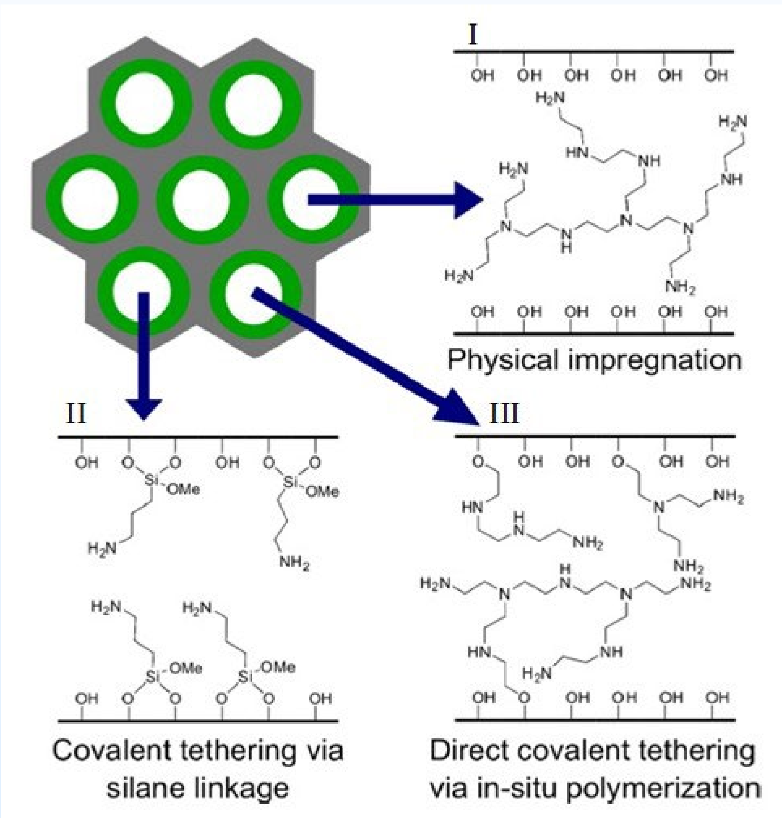
$$CO_2 + R_1R_2NH + H_2O \leftrightarrow \underset{\text{bicarbonate}}{\underline{R_1R_2NH_2{}^+HCO_3{}^-}} \leftrightarrow \underset{\text{carbonate}}{\underline{R_1R_2NH_2{}^+CO_3{}^{2-}}}$$

$$CO_2 + R_1R_2R_3N + H_2O \leftrightarrow R_1R_2R_3NH^+HCO_3{}^- \leftrightarrow R_1R_2R_3NH^+CO_3{}^{2-}$$

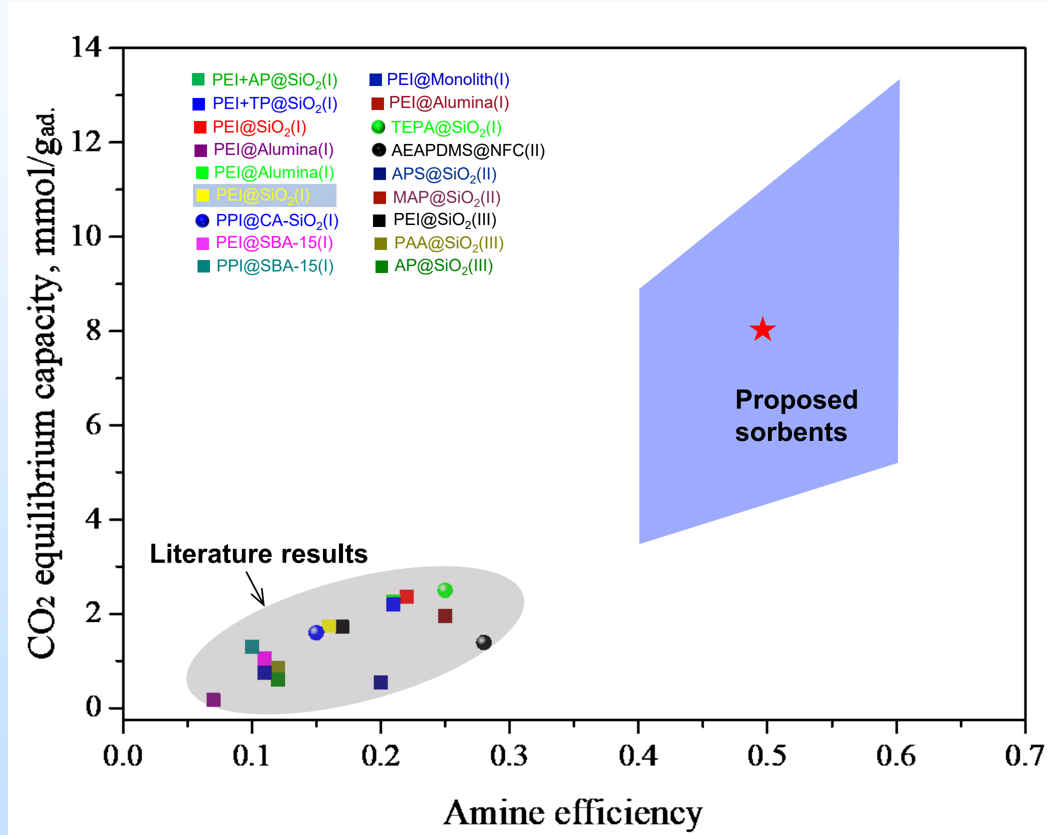


Comparison with amine-based sorbents reported in the literature

Amine-based sorbents reported in the literature

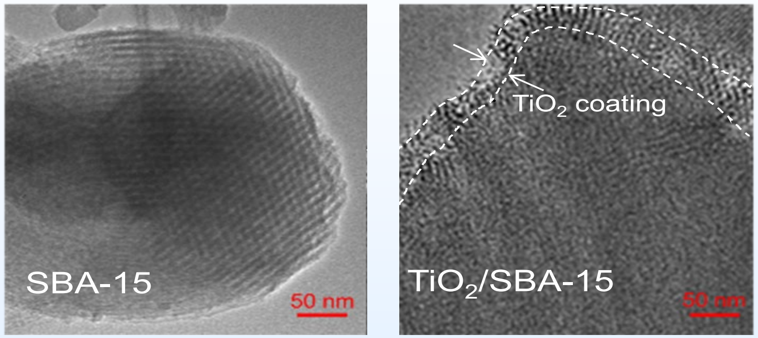


Superior projected performance of the proposed sorbent

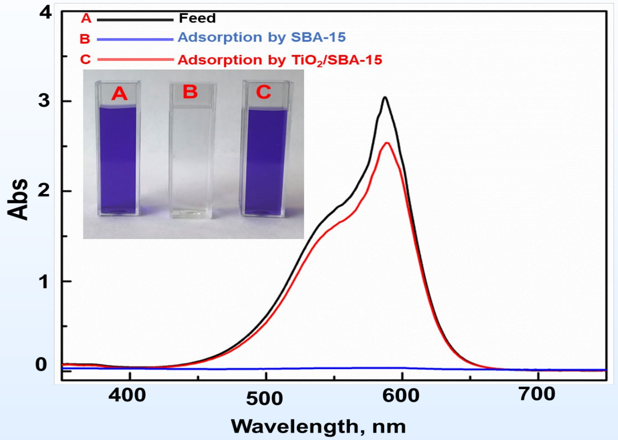


Uniform microporous coating with micropores

TEM images



Dye rejection



Technical and economic advantages

- Fast reaction kinetics and high amine efficiency
- High CO_2 adsorption capacity and good stability
- High sorbent loading on PEFs and fast exposure of sorbent material to air;
- Low energy penalty from the low support fraction/high sorbent loading;

Challenges of our technology

- Precise control of the surface coating pores to prevent amine loss
- High loading of sorbent particles in PEFs

Technical Approach/Project Scope

Experimental design and work plan

Sorbent Development

Task 2 – Development of hierarchical nanoporous capsules with trapped small amines

Porous electrospun fiber Development

Task 3 – Development of porous electrospun fiber macroscopic scaffold with loaded hierarchical nanoporous capsules

Task 4 – Direct air capture of CO_2 testing

Task 5 – High-level process design/analysis

Member	Specific project roles/responsibility
University at Buffalo, The State University of New York	• Project management and planning • Sorbent material development • PEF embedded sorbent direct air capture of CO_2 tests • Supporting high-level process design and analysis
ASU	• PEF development • Supporting high-level process design and analysis
gti	• High-level process design and analysis

Project schedule

- **Month 6:** Achieve microporous coating pore size <0.7 nm and amine loss <5% after 10 heating-cooling cycles (M2.1)
- **Month 13:** Achieve >75% sorbent loading in PEF and CO_2 capacity loss <10% relative to powder sorbents (M3.2)
- **Month 15:** Achieve CO_2 equilibrium capacity >8 mmol/g sorbent at ambient temperatures and pressures (M2.3)
- **Month 15:** Achieve CO_2 working capacity >4.5 mmol/g fiber sorbent material and $t_{1/2}$ <30 min (M4.1)

Project success criteria

- Achieve CO_2 working capacity of 3.5-5 mmol/g fiber sorbent material and $t_{1/2}$ <30 min
- CO_2 working capacity loss <10% and $t_{1/2}$ increase <10% after cyclic testing
- Issue high-level process design/analysis topical report
- Submit Final Technical Report

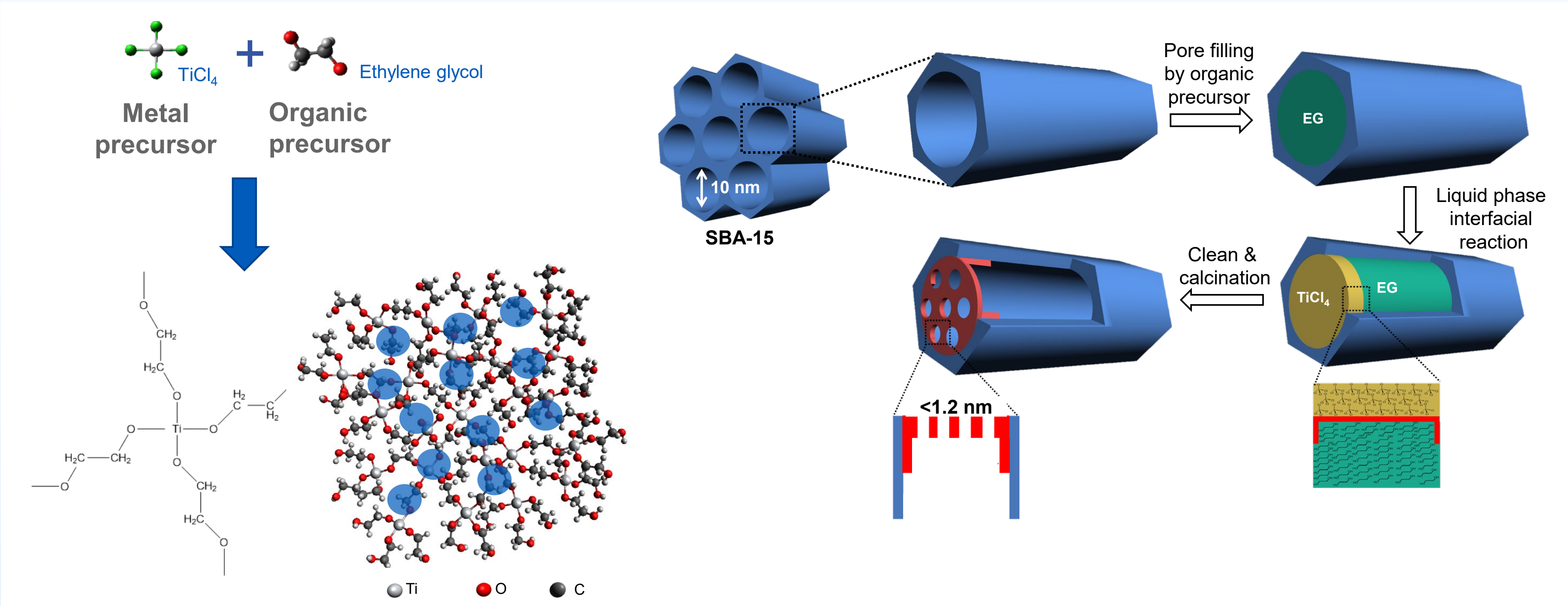
Technical Approach/Project Scope

Risks and mitigation strategies

Perceived Risk	Risk Rating			Mitigation/Response Strategy
	Probability	Impact	Overall	
	Low, Moderate (Mod), High			
Technical/Scope Risks:				
Potential amine loss during regeneration	Low	High	Low	1) Optimize microporous coating pore size before amine loading; select amines with larger size 2) Increase ALD cycles during sealing process to reduce pore mouth size 3) Optimize liquid precursor composition for liquid interfacial reaction to better control coating pore size
Sorbent CO_2 adsorption capacity not sufficiently high or kinetics not sufficiently fast	Low	High	Low	1) Increase amine loading to increase amine group density, especially primary amine group density; 2) Optimize coating pore size to allow faster diffusion;
Air flow pressure drop not sufficiently low in the sorbent DAC process	Low	Mod	Low	1) Optimize fiber sorbent packing density to balance air flow and CO_2 capacity per volume; 2) Optimize sorbent bed configuration
Cost/Schedule Risks:				
Delay of tasks	Low	Low	Low	Early and frequent meetings will be held to avoid delay of tasks. The project team will monitor the staffing/equipment needs closely
Financial Risks:				
The shortfall of cost share	Low	Low	Low	UB is committed to providing the required cost share
Management, Planning, and Oversight Risks: Minimal – UB, ASU and GTI are implementing project management systems to minimize management risks.				

Progress and Current Status of Project

Liquid-liquid interfacial reaction to form microporous coating

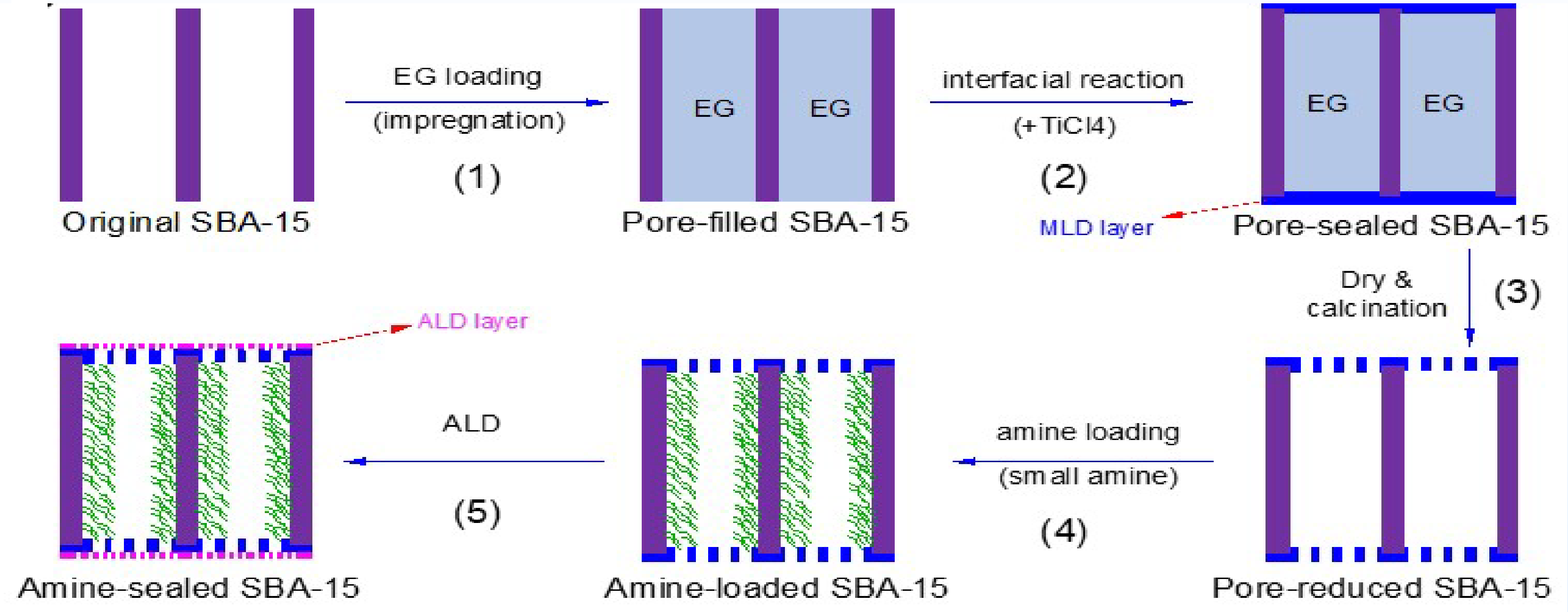


Factors influencing coating pore size:

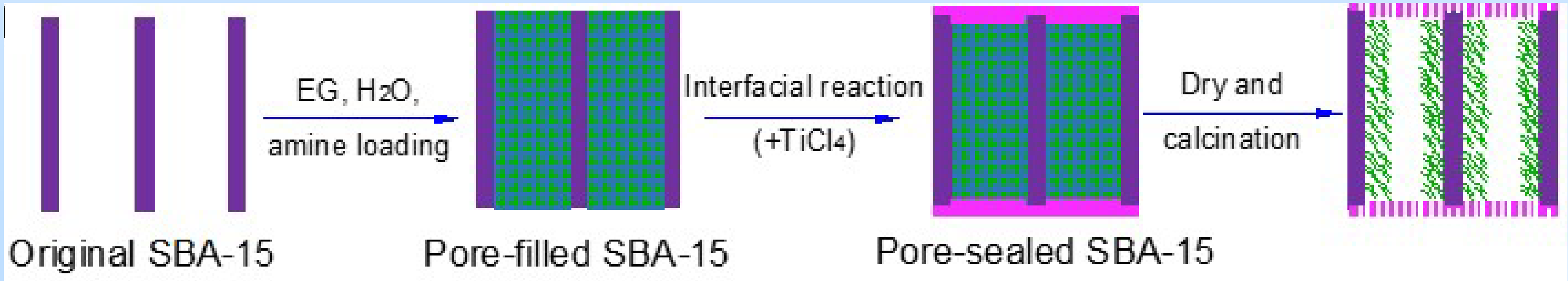
i) Organic precursor composition (different glycols, water percentage in glycols, etc.)
ii) Calcination conditions (temperature, gas environment, etc.)

Deposition of microporous coating by liquid phase interfacial reaction

1. Amine loading followed by coating pore narrowing



2. Direct encapsulation



Coated SBA-15 prepared by precursor loading via ***vapor condensation***

Percentage of H_2O in ethylene glycol

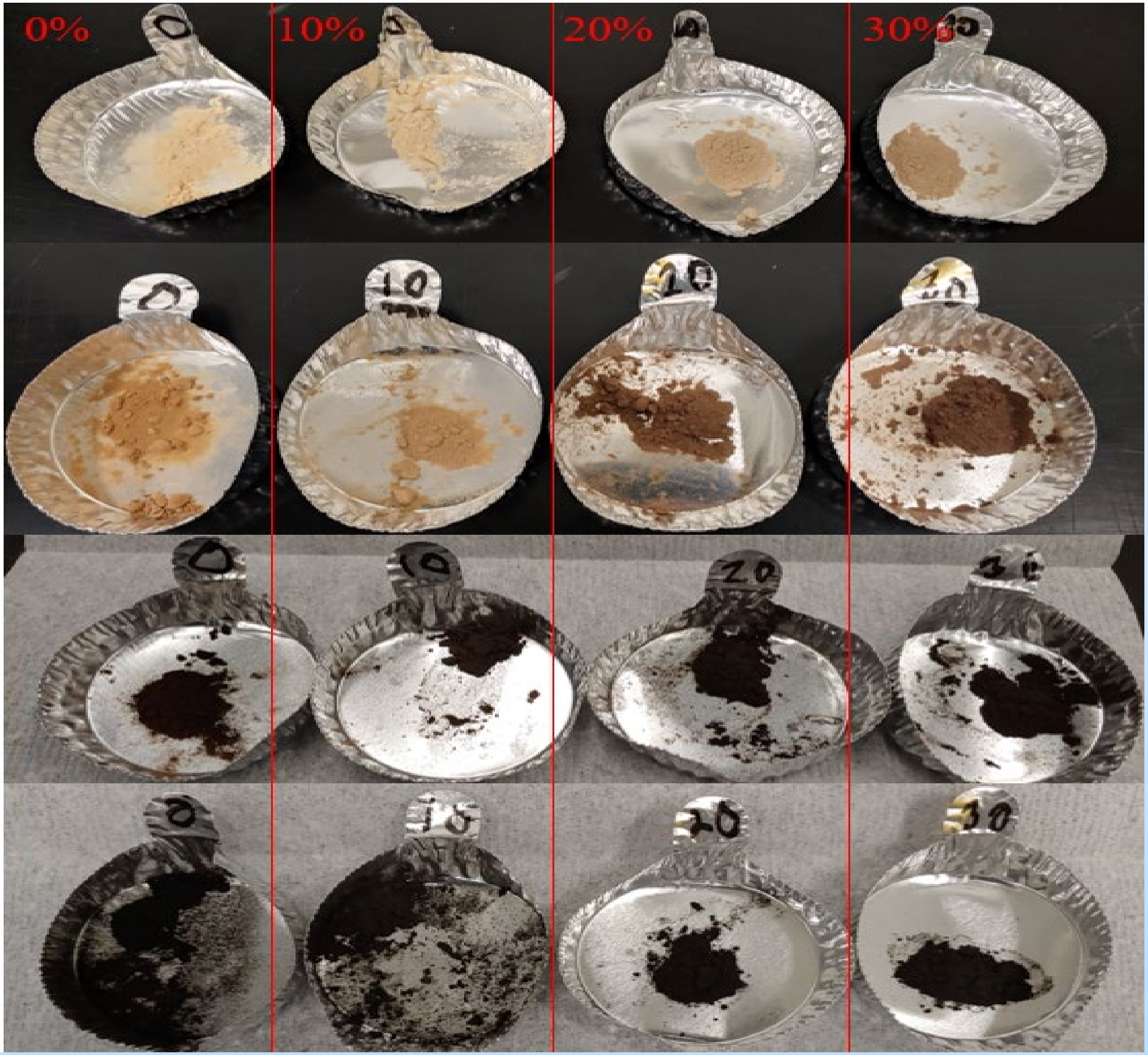
Calcination temperature in N_2

250 ^oC

280 ^oC

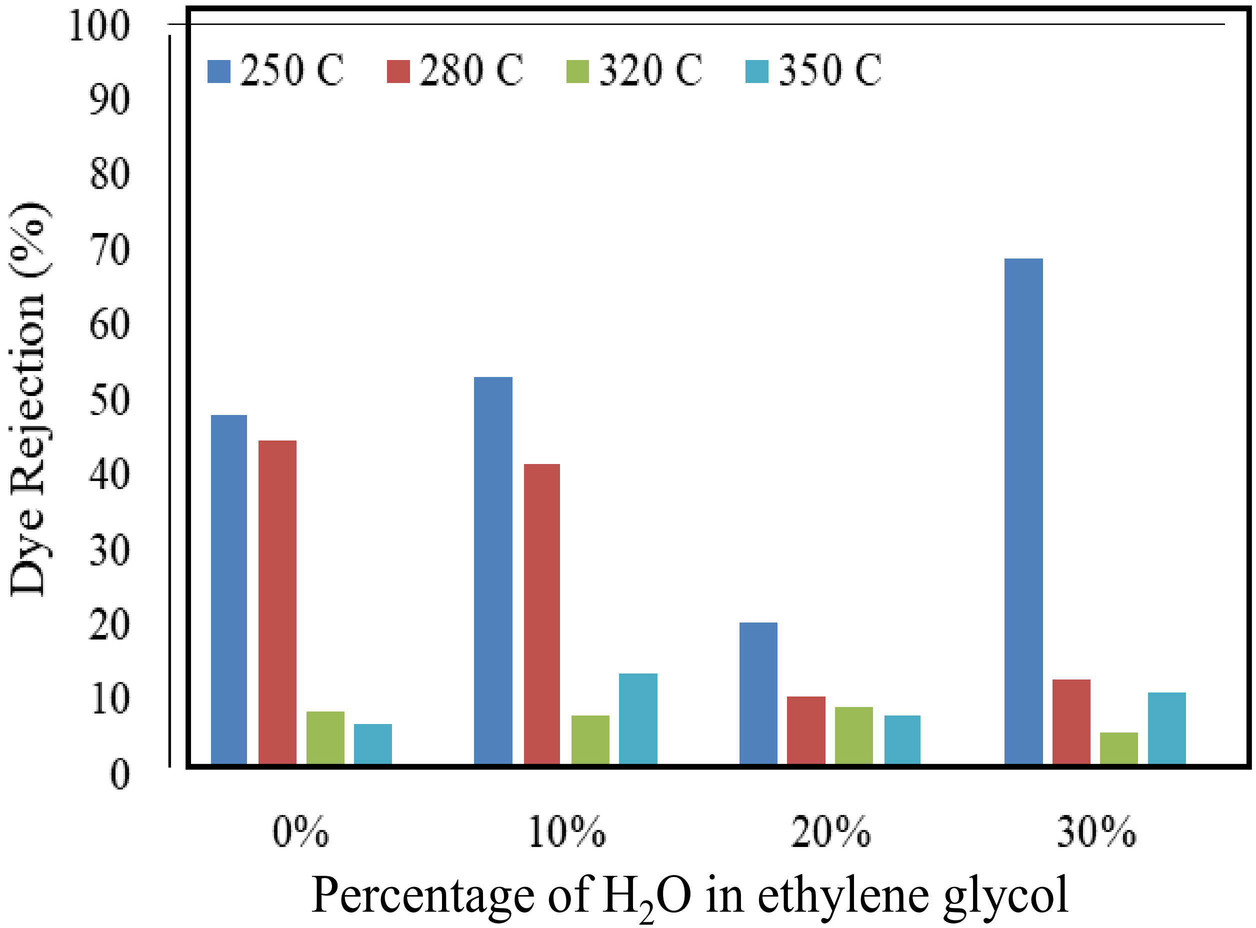
320 ^oC

350 ^oC

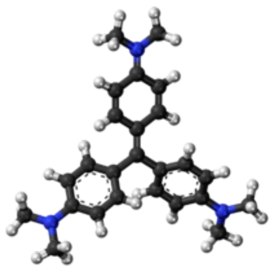


Coated SBA-15 prepared by pore filling via ***vapor condensation***

$$Dye\ Rejection = \frac{Supernatant\ Absorbance}{Stock\ Solution\ Absorbance} \times 100\%$$



Crystal Violet (CV)
(1.3 nm × 1.4 nm)



Note: CV rejection by pristine SBA-15 is 5%.

Coated SBA-15 prepared by precursor loading via ***liquid phase***

Sample #	H_2O Concentration in Ethylene Glycol (wt.%)	Liquid to Pore Ratio (LPR)	CV (~1.3 nm) Rejection (%)	O-xylene (0.69 nm) uptake (wt.%)
SBA-15	-	-	5	100
1	0	0.8	55	-
2		1	61	11
3		1.2	75	7
4		1.5	64	1
5	10	0.8	30	-
6		1	65	11
7		1.2	70	11
8		1.5	80	4
9	20	0.8	42	-
10		1	45	3
11		1.2	47	19
12		1.5	40	2
13	30	0.8	37	-
14		1	48	-
15		1.2	68	-
16		1.5	45	-

Plans for future testing/development

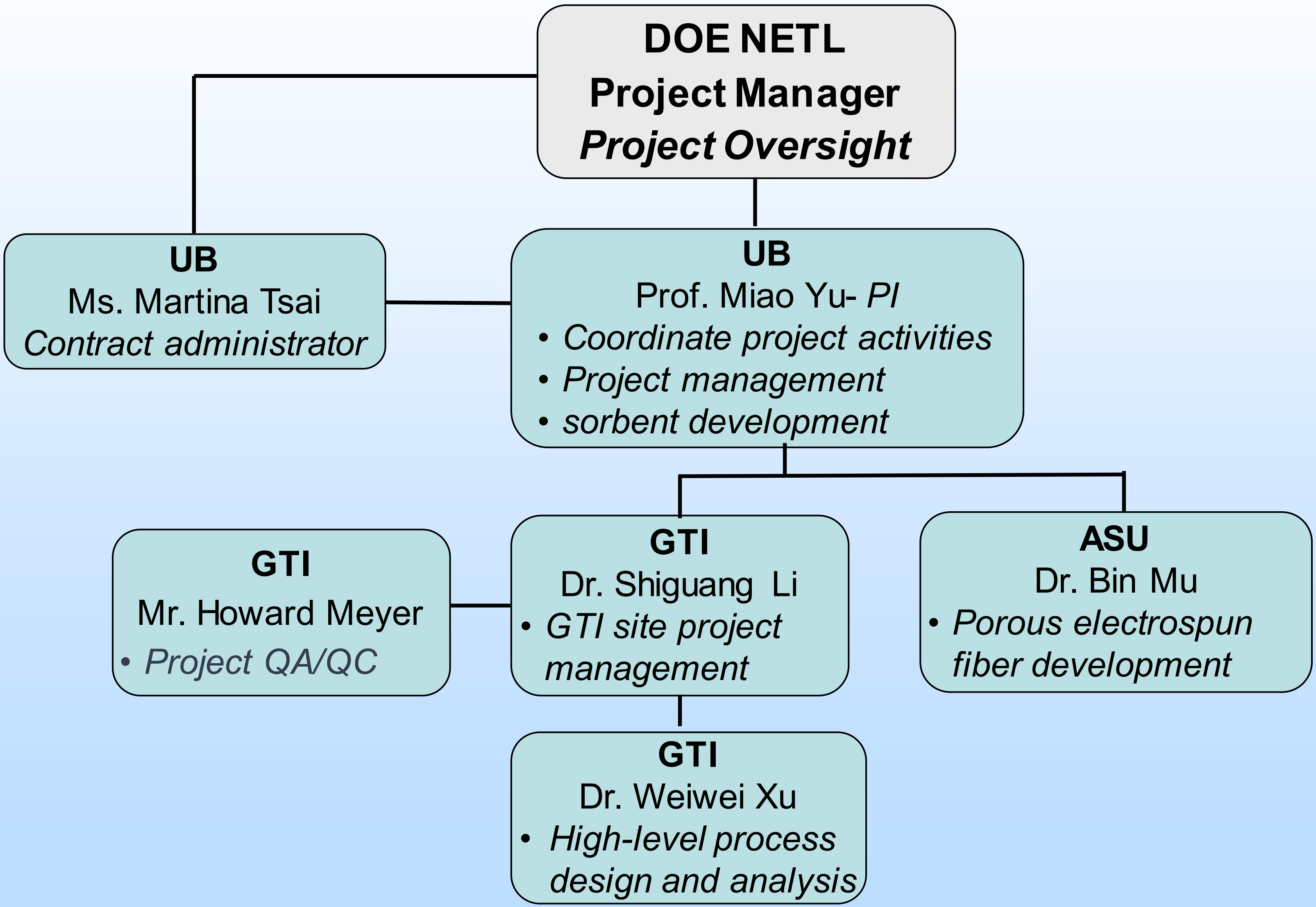
- Microporous coating: Further modify samples with microporous coating by molecular layer deposition in order to fine tune the coating pore size; detailed characterization of the coating pore size and sorbent pore volume and composition;
- Amine loading and sealing: Develop effective amine loading and sealing processes on samples with microporous coating; conduct amine loss evaluation;
- Porous electrospun fibers (PEF) loaded with sorbent: Optimize electrospinning conditions to incorporate sorbent materials and characterize composite sorbent structure;
- CO_2 sorption performance evaluation: Measure CO_2 adsorption capacity and kinetics for both powder form and fiber form; measure CO_2 working capacity under cyclic operation conditions and evaluate stability of the PEF sorbent.

Summary

- Microporous coating deposition processes based on both vapor condensation and liquid filling were developed;
- CV rejection suggested microporous coatings with pore size smaller than 1.3 nm were successfully deposited;
- O-xylene uptake indicated <0.7 nm coating pores were formed under optimized coating preparation condition

Appendix

Organization Chart



Gantt Chart

ID	Task No	MS No	Task Name	Start	Finish
1	1		Project Management and Planning	2/1/2021	10/31/2022
2		M1.5	Submit Final Technical Report	1/31/2023	1/31/2023
3	1.1		Project Management Plan	2/1/2021	7/31/2022
4		M1.1	Submit Updated Project Management Plan to DOE	3/31/2021	3/31/2021
5		M1.2	Complete Kickoff Meeting	4/30/2021	4/30/2021
6		M1.3	Submit Environmental, Health, and Safety Risk Assessemnt to DOE	4/30/2021	4/30/2021
7	1.2		Technology Maturation Plan	2/1/2021	4/30/2021
8		M1.4	Submit Technology Maturation Plan to DOE	4/30/2021	4/30/2021
9	2		Development of HNC with trapped small amines	2/1/2021	10/31/2022
10		M2.1	Achieve microporous coating pore size <0.7nm and amine loss <10-20% after heating-cooling cycles	10/31/2021	10/31/2021
11		M2.2	Achieve CO_2 equilibrium capacity >3 mmol/g sorbent at ambient temperature and pressure	1/31/2022	1/31/2022
12		M2.3	Achieve CO_2 equilibrium capacity of 5-8 mmol/g sorbent at ambient temperature and pressure	7/31/2022	7/31/2022
13	3		Development of PEF macroscopic scaffold embedded with HNC	8/1/2021	10/31/2022
14		M3.1	Achieve >50% sorbent loading in PEF and CO_2 equilibrium capacity loss <20%	12/31/2021	12/31/2021
15		M3.2	Achieve 70-80% sorbent loading in PEF and CO_2 equilibrium capacity loss <10-15%	7/31/2022	7/31/2022
16	4		PEF with embedded sorbent direct air capture of CO2 testing	1/1/2022	10/31/2022
17		M4.1	Establish effective CO_2 desorption process conditions; achieve CO2 working capacity 0f 3.5-5 mmol/g fiber sorbent material and $t_{1/2}$ (time to reach 50% of equilibrium capacity) <30 min	7/31/2022	7/31/2022
18		M4.2	Working capacity determined based on cyclic testing: CO_2 working capacity loss <10% and $t_{1/2}$ increase <10%	10/31/2022	10/31/2022
19	5		High-level process design/analysis	5/1/2022	10/31/2022
20		M5.1	Issue High-level process design/analysis topical report	10/31/2022	10/31/2022