ZISHU CAO

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Department of CEE, University of Cincinnati Cell: 513 356 3676

EDUCATION

Ph.D. Chemical Engineering 2015-2020

University of Cincinnati

Thesis Title: *MFI-Type Zeolite Nanosheets Laminated Membranes for Ion Separation in Aqueous Solutions*

Advisor: Prof. Junhang Dong

Master's Chemical Engineering 2011-2014

University of Cincinnati

Thesis Title: *Colloidal Zeolite Supported Ionic Liquid Membranes for CO_2/N_2 Separation*

Advisor: Prof. Junhang Dong

Bachelor's Environmental Science 2007-2011

Lanzhou University, China

RESEARCH INTERESTS

2D Materials, Membrane separation, Adsorption, Catalysis, Renewable energy, Bioresources, Carbon Capture

PROFESSIONAL EXPERIENCE

Aug 2020 to current **University of Cincinnati**, Post-Doctoral Fellow

Novel membrane system for lithium recovery from oil field brines

- Developed zeolite nanosheet laminated membranes on cheap polymer support
- Exceeded water flux goal through reduced substrate transport resistance

Coaxial cable sensor for in situ monitoring

- Developed materials with desired dielectric constants and high temperature stability
- Achieved metal conductors with superior electric conductivity, excellent thermal and chemical stability through electroplating
- Designed and built device for coaxial cable sensor test together with collaborators

Sep 2015 to Aug 2020 **University of Cincinnati**, Graduate Research Assistant

Zeolite nanosheet synthesis and chemistry control

- Synthesized organic structure directing agent
- Achieved hydrophilic ZSM-5 nanosheets for the first time

Nanosheet-based membrane for concentrated brine desalination

- Investigated ultrathin laminated zeolite nanosheet membrane fabrication
- Studied the transport mechanism of salts in the laminated membrane
- Achieved high-performance membrane for water reclamation from concentrated brine

Nanosheet/polymer composite membrane as ion separator for redox flow battery

- Developed methodology for nanosheet/polymer composite membrane fabrication
- Achieved excellent performance for redox flow battery applications

Sep 2012 to Aug 2014 **University of Cincinnati**, Graduate Research Assistant

Zeolite supported ionic liquid membrane for carbon capture from flue gas

- Developed protocols for colloidal zeolite coating and ionic liquid membrane fabrication
- Investigated materials physical and chemical properties and gas transport phenomena
- Achieved good CO_2/N_2 separation performance for simulated flue gas feed

Ceramic thin film for high temperature optical sensor application

- Explored thin film for coaxial fiber optic sensors for hydrogen detection

RESEARCH EXPERTISE

- Materials Synthesis: Organic synthesis, Crystallization, Chemistry and morphology control
- Membrane Fabrication: Zeolite, Metal-organic framework, Polymer
- Membrane Separation: Gas separation, Water treatment, Ion separation, Redox flow battery
- Adsorption: Adsorption isotherm, Breakthrough
- Instruments: GC-MS, HPLC, SEM, EDX, TEM, AFM, BET, ICP, IR, UV-Vis, XRD, TGA

HONORS AND AWARDS

2019 ChE Graduate Student Award, University of Cincinnati

2019 Graduate Student of the Month, University of Cincinnati

2011 Outstanding Graduates of Lanzhou University

TA EXPERIENCE

2013 Summer Transport II

2016 Spring Separations

2017 Spring Separations

2017 Fall Separations

2018 Fall Separation Processes

MENTORING EXPERIENCE

2015 Ruibo Qin (Master)

2016 Xinhui Sun (Ph.D.)

2018 Daniel Dong (Undergraduate), Nathan Estill (Undergraduate)

2019 Vignathi Karlapudi (Master)

2020 Hallie Grant (Undergraduate), Landysh Iskhakova (Ph.D.)

COMMUNITY SERVICE

- Volunteer Educator, Cincinnati Zoo
- Volunteer, Women in Engineering program in University of Cincinnati

JOURNAL PAPERS

1. **Z. Cao**, L. Iskhakova, X. Sun, J. Dong, Synthesis and molecule transport study of flower-like MFI-type zeolite, *drafting*.
2. **Z. Cao**, N. D. Anjikar, S. Yang, Small-pore zeolite membranes: synthesis and gas separation applications, *drafting*.
3. **Z. Cao**, L. Iskhakova, X. Sun, Z. Tang, J. Dong, ZSM-5 Zeolite Nanosheet-Based Membranes on Porous Polyvinylidene Fluoride for High-Flux Desalination, *ACS Appl. Nano Mater.* 2021, 4, 2895-2902.
4. J. Chai, A. Lashgari, **Z. Cao**, C. K. Williams, X. Wang, J. Dong, J. Jiang, PEGylation-Enabled Extended Cyclability of a Non-aqueous Redox Flow Battery, *ACS Appl. Mater. Interfaces* 2020, 12, 15262-15270.
5. **Z. Cao**, S. Zeng, Z. Xu, A. Arvanitis, S. Yang, X. Gu, J. Dong, Ultrathin ZSM-5 Zeolite Nanosheet Laminated Membrane for High-Flux Desalination of Concentrated Brines, *Science Advances*, 2018, 4: eaau8634.
6. I. Michos, **Z. Cao**, Z. Xu, W. Jing, J. Dong, Investigations on Mesoporous Glass Membrane as Ion Separator for Redox Flow Battery, *Batteries* 2019, 5, 6.
7. S. Zeng, A. Trontz, **Z. Cao**, H. Xiao, J. Dong, Characterizing the gas adsorption-dependent dielectric constant for silicalite nanoparticles at microwave frequencies by a coaxial cable Fabry-Pérot interferometric sensing method, *Madridge J. Nanotechn. Nanosci.* 2018, 3, 100-107.
8. Z. Zhang, M. Taylor, C. Collins, S. Haworth, Z. Shi, Z. Yuan, X. He, **Z. Cao**, Y. C. Park, Light-Activatable Theranostic Agents for Image-Monitored Controlled Drug Delivery, *ACS Appl. Mater. Interfaces* 2018, 10, 1534-1543.
9. S. Yang, A. Arvanitis, **Z. Cao**, X. Sun, J. Dong, Synthesis of Silicalite Membrane with an Aluminum-Containing Surface for Controlled Modification of Zeolitic Pore Entries for Enhanced Gas Separation, *Processes* 2018, 6, 13.
10. Z. Xu, I. Michos, **Z. Cao**, W. Jing, X. Gu, K.R. Kinkel, S. Murad, J. Dong, Proton-Selective Ion Transport in ZSM-5 Zeolite Membrane, *J. Phys. Chem. C.* 2016, 120, 26386-26392.
11. S. Yang, **Z. Cao**, A. Arvanitis, X. Sun, Z. Xu, J. Dong. DDR-type zeolite membrane synthesis, modification and gas permeation studies, *J. Membr. Sci.* 2016, 505, 194-204.
12. **Z. Cao**, S. Yang, X. Sun, A. Arvanitis, J. Dong, Colloidal Silicalite Coating for Improving Ionic Liquid Membrane Loading on Macroporous Ceramic Substrate for Gas Separation, *J.*

Membr. Sep. Techn. 2016, 5, 25-37.

13. R. Yang, **Z. Cao**, S. Yang, I. Michos, Z. Xu, J. Dong Colloidal Silicalite-Nafion Composite Ion Exchange Membrane for Vanadium Redox-Flow Battery, *J. Membr. Sci.* 2015, 484, 1-9.
14. H. Jiang, **Z. Cao**, R. Yang, L. Yuan, H. Xiao, J. Dong. Synthesis and study of $MgAl_2O_4$ spinel thin film as sapphire fiber cladding for high temperature applications, *Thin Solid Films* 2013, 539, 81-87.

PATENT

1. **Z. Cao**, L. Iskhakova, J. Dong, Self-Seeded Hydrothermal Growth of MFI Zeolite Nanosheets and Nanosheet Assemblies, *pending US patent application*.

CONFERENCE PRESENTATIONS

2. **Z. Cao**, L. Iskhakova, J. Dong, ZSM-5 Zeolite Nanosheet-Nafion Composite Membrane as an Ion Separator for Redox Flow Batteries, *AIChE Annual Meeting*, Virtual Online, 2020.
3. **Z. Cao**, J. Dong, MFI-Type Zeolite Nanosheets and Laminated Membranes for Ion Separation in Aqueous Solutions, *ChEE Seminar*, University of Cincinnati, 2020
4. **Z. Cao**, S. Zeng, Z. Xu, A. Arvanitis, J. Dong, MFI-Type Zeolite Nanosheets Coated Ceramic Membranes for Brine Pervaporation Desalination, *North American Membrane Society Annual Meeting*, Lexington, 2018.
5. S. Yang, **Z. Cao**, J. Dong, DDR-type zeolite membrane synthesis, modification, and gas permeation studies, *International Conference on Inorganic Membranes*, Atlanta, 2016.

2D Microporous Materials for Membranes, Adsorbents and Catalysts

<u>Overview</u>: My research stays at the interface of materials synthesis and separation science, with an emphasis on precisely controlling morphology and chemistry of nanostructured materials for membrane, adsorption and catalysis applications. It aims to address challenging issues faced by the energy, environment and sustainability sectors. In particular, I am focusing on three avenues: 1) Controlling morphology and chemistry of zeolite crystals through understanding of the interplays between different crystal facet growth and synthesis condition; 2) Fabricating ultrathin, even monolayer thick, nanosheet laminated membranes for transport phenomena study and unprecedented separation performance; 3) Evaluating and tailoring the adsorption and catalytic properties of 2D microporous materials for bulkier molecules and complex mixtures. The overall objective is nano-engineering of microporous materials with structural elucidation, growth mechanism perception, and industrial application exploration relevant to renewable energy and resources, chemical production, water quality, and the environment.

<u>Research Accomplishments</u>:

For my graduate and postdoctoral research, I have been working on zeolite-based materials and membranes for various applications. It has been summarized in Figure 1. Zeolite has uniform sub-nanometer pores. It demonstrates great potential for adsorption, membrane separation and catalysis applications with its molecular sieving capability. On the materials side, zeolites have been prepared with different morphologies and chemistry. Through the control of nucleation and crystallization rates, nanosheets, nano-size spheres and conventional coffin-shaped crystals were prepared. Molecule transport in zeolite nanosheets differs from conventional zeolites because it is over ten times thinner. When used as adsorbent, catalyst, molecules only need to diffuse a short distance for entering and exiting nanosheets. It could address the transport limitation for zeolite to be used in applications involving molecules approaching zeolite pore size. The synthesis of MFI zeolite nanosheets has been achieved by addressing the kinetics for the growth of different crystal facets. The chemistry control for MFI nanosheets was realized for the first time with new synthesis protocols. Ultrathin zeolite nanosheet laminated membranes with reduced transport resistance were successfully fabricated. Nanosheets were also used for composite membrane fabrication, the large aspect ratio

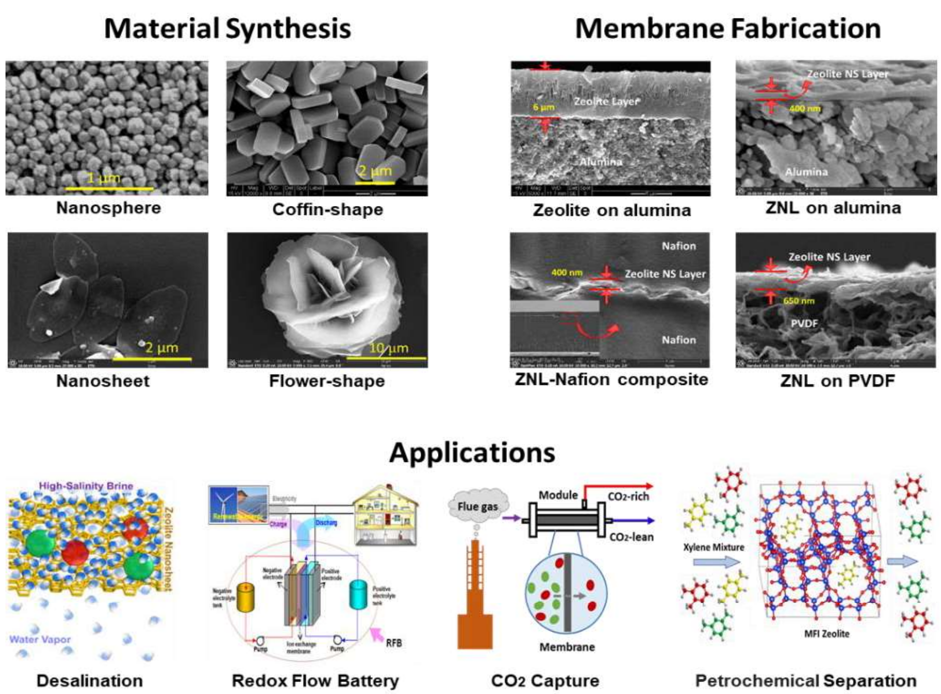

Figure 1 (a) Different MFI zeolite crystal morphologies achieved; (b) zeolite membranes fabricated on different substrates; (c) attempted membrane- and adsorption-based applications.

offers of the chance of highly selective separation because small molecules could directly pass through the nanosheets, but large molecules have to go through a tortuous diffusion path. The membranes have been used for desalination of high-salinity brine and as proton exchange membranes for redox flow batteries. The research is critical for achieving zero wastewater discharge and for developing a cheap energy storage technology. Other attempted applications include CO_2 capture from flue gas and separation of xylene isomers. I have published 12 papers in prestigious journals, such as *Science Advances* and *ACS Appl. Nano Mater*. Two more first-author papers are being drafted for publication.

Research Topics

As a faculty member, I will establish a research group to meet the growing demands in environmental and energy sectors. The development of 2D materials opens new opportunities to address the transport limits faced by different applications. The realization of more industrial application relies on the ability to fine-tuning materials structure and chemistry, and appropriate mass-production methodology. Following section lays out three specific application topics that my first 2-3 students will investigate. Zeolites are often given as the examples, but the research will be extended to frontier microporous materials, such as covalent-organic frameworks (COFs) and metal-organic frameworks (MOFs) in both 2D and 3D forms. The application backgrounds and fundamental mechanisms differs for those research topics, but they are all centered on 2D materials development and aims at addressing thermodynamic and transport limits faced by conventional materials. The success of proposed research relies on understanding of the synergistic effects of synthesis parameters' influence on crystal growth, such as chemical and physical properties of structure directing agent, growth kinetics of different crystal facets and seed properties. My group will narrow the knowledge gap and address the technical challenges preventing the synthesis of perfect nanosheets, delicate chemistry and structure control, mass-production of 2D porous micromaterials.

Topic 1. 2D Microporous Materials Derived Membranes

In theory, the thinnest membrane made from 2D materials is single layer thick, which is ranging from sub-nanometer to a few nanometers depending on the specific materials. The molecule transport in membrane is generally understood as adsorption of the molecule, followed by diffusion inside the materials and desorption. When the membrane is thin enough, such as monolayer thick, the diffusion process may not be the rate determining step anymore. Unprecedented transport phenomena are expected but have not been experimentally verified. Disruptive membrane separation performance will be achieved, particularly for the separations involving slow diffusing molecules. My group will work on the synthesis of perfect large-aspect-ratio nanosheets and unconventional monolayer-thick membrane fabrication methods. While working towards the ultimate goal of monolayer-thick membranes, we will also conduct research on the fabrication of ultrathin nanosheets laminated membranes and molecule transport in the membranes. Special interest is on the development of highly selectively and permeable proton exchange membranes for redox flow batteries, a cost-effective technology for addressing the intermittency issue for renewable energy. Current benchmark membranes, i.e. Nafion, have limited selectivity between proton and other cations, which causes significant crossover and comprised efficiency. It also limits the usage of cheap electrolyte, such as Fe/Cr, as the regeneration of the battery is more challenging with different metal ion pairs. My group will utilize the molecular sieving characteristics of zeolite or another type of microporous materials and the low transport resistance from nanosheet layer to develop highly competitive proton exchange membranes for energy storage batteries. Another interested area is biofuel or biochemical related separations, such as the separation of succinic acid or citric acid from a mixture of carboxylic acids among other similarly sized molecules, which is a significant industrial challenge in the biorefining sector. With the initiative of reducing carbon footprints, it is important to address those challenges faced by producing chemicals from renewable sources.

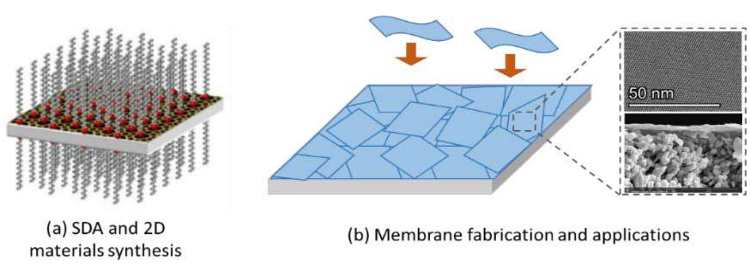

Figure 2. (a) SDA structure design and 2D materials synthesis; (b) Ultrathin 2D materials laminated membrane fabrication and separation applications.

Topic 2. Tailor-Designed Microporous Sorbents

Microporous materials are naturally good sorbents with large surface area and pore volume. Zeolite has found a lot of industrial applications as sorbents, such as Y-type zeolite for air separation in pressure swing adsorption process, NaA zeolite used for dehydration. Highly selective separation could be achieved through molecular sieving effect, for which only smaller molecules could be adsorbed. When the adsorbate size is smaller than the materials pore size but approaches it. The diffusivity decrease exponentially with their relative size. Moreover, for complex mixture, the slower diffusing molecules tend to block the passage of other molecules and slow down the adsorption/desorption processes. The slow kinetics limits the separation efficiency and industrial applications. 2D adsorbents have great potential for addressing the diffusion limits. Comparing to conventional adsorbents, the diffusion length to reach the internal pores for 2D adsorbents are minimal. Therefore, the diffusion influence would be minimal. Moreover, the large external surface area of 2D materials allows versatile surface functionalization opportunities to add new adsorption properties. 2D microporous adsorbents have potential for challenging separation and other applications. Examples include the separation of biofuel or biochemical from fermentation broth and recovery of rare-earth elements to address the emerging demands by renewable energy sector. There are two major challenges to be addressed before more industrial applications could be realized. The first challenge is the lack of thermodynamic and transport properties, particularly for complex mixtures or under bio-environment. The second challenge is lack of economical and scalable fabrication methods for 2D adsorbents. My group will work on 2D microporous materials synthesis, structure and chemistry control, adsorption and transport property studies. The research will benefit better understanding of 2D microporous materials and their adsorption applications.

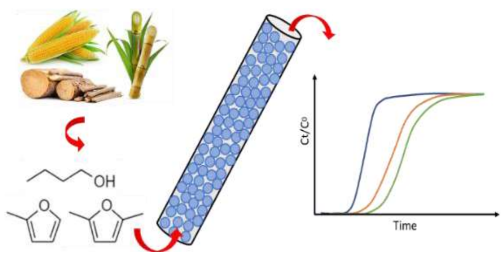

Figure 3. An application example: separating biochemicals/biofuel from fermentation broth with 2D adsorbents

Topic 3. 2D Catalysts

Zeolite has found applications as catalysts for a range of reactions, such as cracking, aromatic alkylation, Beckmann rearrangement and selective oxidations. The uniform pore opening and unique cavity structure for each type of zeolite allow molecular sieving and steric controlled catalytic behaviors. Moreover, active catalytic sites (Brønsted or Lewis acid) and concentration could be tailored through the replacement of framework atoms (such as Al, Ga, Ti) and balancing cations. There have been strong interest in increasing the accessibility of active site in zeolites so that they can be used for bulkier components. A practical approach is shortening the effective length of diffusional pathway to reach active sites through the utilization of nanosized, hierarchical or 2D zeolites. The shortened diffusion path contributes to enhanced reaction rates for reactions under diffusion control. Likewise, products formed within zeolitic pores diffuse out more rapidly, limiting side reactions and bringing improved selectivity and less coking. The two main challenges for more applications with 2D catalysts are (1) the difficulty of chemistry and fine structure control; (2) limited amount of catalysis study with more practical applications. The structure directing agent for 2D zeolites needs to promote the nucleation and crystallization but prevents or limits growth in one direction to achieve nanosheet structure. Such features limit its ability for directing nucleation and crystal growth. The condensation reaction with non-Si tetrahedron atoms has significantly different enthalpy and entropy for the growth of different crystal facets comparing to Si. My group will work on 2D zeolite synthesis with interested chemistry and use them for catalysis involving bulky molecules or complex mixtures, such as cracking of large molecule hydrocarbon and biochemical processing. We will also seek collaboration opportunities with other research groups for elucidating crystal growth and catalysis mechanisms through molecular simulation and/or other advanced techniques.

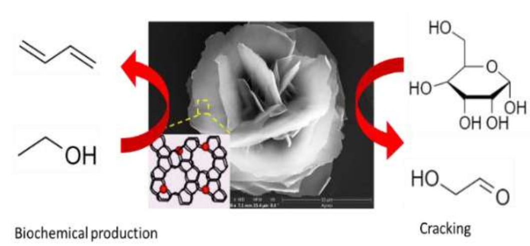

Figure 4. 2D materials used as catalysts for biochemical production and large-molecule cracking

Teaching Statement

Teaching Philosophy

My main objective as a teacher or mentor is to help students realize and maximize their personal and technical skills, and become a motivated life-long learners. To achieve this goal, my overall teaching philosophy is that teaching through active participation in their coursework or lab work. Studies have shown that active and evidence-based instructional methods benefit not only higher grades but also senses of self-improvement and belongingness. Such outcomes are particularly important for underrepresented groups and first-generation college students, and thus help increase retention and promote overall diversity.

College courses could be boring, particularly those courses piled with physical definitions and mathematical formulas, such as thermodynamics. It is hard for the students to picture those concepts and their importance. Questioning the students with common observations relevant to chemical engineering principles is a good way of triggering curiosity and critical thinking. With more and more resources and content creating tools available nowadays. Relevant images and videos are more accessible. The implementation of more visually informative and attractive contents will greatly enrich the courses. I believe that an interactive, group-based classroom is a good way to enhance participation and self-learning. Small projects with appropriate difficulty level and application background will be planned. Routine meetings will be held with them to promote healthy teamworking environment and keep them on track. I am dedicated to keep a vibrant classroom and improve my teaching skills through effective communication with the students.

Outside of the classroom, I will design sets of small research projects great for undergraduate students to practice their course learnings and learn state of art materials and technologies. For outreach activities involving middle or high school students, more intuitive demonstration modules will be adopted. An example could be purification wastewater contaminated with dyes, for which students see drastic difference from the treatment. It is a great introduction for younger students to have a fun, hands-on experience in STEM with a link to the university. The students will also be encouraged to participate in interested research topics in my lab. Engaging high school students as well as their teachers into a research laboratory has been shown to increase enrollment and retention of underrepresented groups in STEM fields. Such opportunities make research feel more accessible to the younger generations and trigger interests.

Undergraduate and Graduate Courses

I am well educated for the chemical engineering fundamentals despite a bachelor's degree in Environmental Science. I have solid background on Chemical Engineering Thermodynamics, Transport Phenomena, Unit Operations, Fluid Mechanics etc. through my undergraduate and graduate studies. I would be very comfortable teaching most fundamental courses offered by the chemical engineering program for both undergraduate and graduate level. Depending on the elective course demands by the department, I plan to develop a dual-level elective course on Membranes for Energy & Environment Applications. The purpose of this course is to give students a general idea of membrane separation and trending applications, particularly applications relevant to renewable energy and wastewater reclamation. The course will focus on materials chemistry, pore structure, surface science and discuss the influence of those parameters on membrane performance from microscopic understandings. Another elective course option is Porous Materials. Porous materials have found a lot of applications, such as battery, catalysis, adsorption and membrane. It will cover broad range of materials, such as zeolite, metal-organic frameworks, activated carbon and 2D materials. The course will discuss the synthesis, characterization and the performance structure relationships from engineering perspective. The elective courses will contribute to the education of next-generation engineers with interdisciplinary background and prepare them for careers in emerging areas, such as renewable energy, carbon capture and sequestration.

List of 3 References:

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