Abstracts by speakers

Day 1: 19/01/2022
Theme: Gas Separation

1. Chemistry and engineering of graphene at Å scale for energy-efficient gas separation

Kumar Varoon Agrawal, GAZNAT Chair of Advanced Separations, EPFL, Switzerland.

High-performance molecular-sieving membranes are expected to play a crucial role in improving the energy efficiency of the gas separation processes reducing the related carbon emission. Toward this goal, our laboratory at EPFL (http://las.epfl.ch) is engaged in chemistry and engineering of two-dimensional materials at the angstrom length scale to address the challenges in the scalable synthesis of membranes hosting atom-thick selective layer separating molecules based on their relative diffusivities through the custom-designed nanopores.

In this seminar, I will present the work on the synthesis of nanoporous graphene membranes by the top-down and the bottom-up synthetic strategies. I will discuss key challenges in the design of such membranes followed by strategies that permit the incorporation of vacancy defects (nanopores) at a high density but also with a narrow pore-size-distribution with a molecular differentiation resolution below 0.3 Å, leading to the realization of record-high performance in post-combustion carbon capture [1-6]. I will discuss the fabrication of graphene membranes based mechanical reinforcement strategy that allows one to scale-up membranes for gas separation [4, 7]. Finally, I will describe the ongoing pilot plant demonstrator project for the postcombustion capture.

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2. Intrinsically Porous Polymers for Gas Separations

Zachery P. Smith, Professor of Chemical Engineering, MIT, USA.

Gas separation membranes present an opportunity to replace centuries-old separation technologies and to help achieve a low-carbon future. However, there are various challenges in designing materials with high flux, high selectivity, and stability to relevant process conditions. In this presentation, two opportunities will be discussed for designing the next generation of gas separation membranes. First, the use of sorption-selective functional groups and the concept of free volume manipulation will be presented to demonstrate a method to control chemistry and microstructure at a sub-nanometer length scale. Second, an approach of using bottlebrush polymers with pre-designed side chains will be presented to demonstrate the role of side-chain structure for targeted separation applications. In addition to these studies, a short introduction to theory and applications of gas separation membranes will be discussed to highlight the exciting and interdisciplinary opportunities to leverage chemistry, chemical engineering, and materials science to address important societal and technological challenges needed for a clean-energy and low-carbon future.

3. Novel Mixed Matrix Polymer Membranes for Critical Gas Separations

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Polymeric membranes, which present an efficient solution for emergent technologies, such as CO_2 capture and natural gas purification, are effective at the selective and efficient transport of gases. The field of polymer membrane design is primarily based on empirical observation, which limits the discovery of new, advanced materials most appropriate for separating a given gas pair. Instead of relying on exhaustive experimental investigations, we apply machine learning on a limited set of experimental gas permeability data for six different gases in ~700 polymeric constructs that have been measured to date to predict the behavior of over 10,000 homopolymer architectures that are currently known. This machine learning technique, which only uses a small body of experimental data (and no simulation data) to accurately predict the behavior of large classes of polymers, evidently represents a novel means of exploring the vast phase space available for polymer membrane design in a manner that is orders of magnitude more efficient than typical empirical observations. However this approach suggests that the current polymers used in membrane applications represent the best that this template can provide – thus new platforms are required to improve performance. We thus propose novel membranes based on polymers mixed with nanoparticles (GNPs). The issues raised by these methods and ways to use and leverage them to systematically improve performance is the second major focus of my tutorial.

4. Affordable clean water using advanced materials

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Sustainable nanotechnology has made substantial contributions in providing contaminant-free water to humanity. In this talk, I will present the compelling need for providing access to clean water through nanotechnology-enabled solutions and the large disparities in ensuring their implementation. I will discuss the current nanotechnology frontiers in diverse areas of the clean water space with an emphasis on applications in the field and provide suggestions for future research. Extending the vision of sustainable and affordable clean water to environment in general, I note that cities can live and breathe well by adopting such technologies. By understanding the global environmental challenges and exploring remedies from emerging nanotechnologies, sustainability in clean water can be realized. I will suggest specific pointers and quantify the impact of such technologies.

5. Biomimetic Ideas for Sustainable Membrane Separations

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Keywords: Separations, reverse osmosis, biomimetic membranes, artificial channels

Abstract: Membranes are rapidly becoming the fastest growing platform for water purification, wastewater reuse, and desalination. They are also emerging in importance for carbon capture, hydrocarbon separations, and are being considered for applications involving catalysis and sensing. All synthetic membranes have selectivity-permeablility tradeoffs, i.e if a membrane has high permeability, it will have a lower selectivity between two solutes or between a dissolved solute and a solvent. This is due to the mechanism of solution-diffusion through a wide distribution of free volume elements in non-porous membranes such as reverse osmosis membranes used for desalination and reuse, and a wide pore size distribution in porous membranes. I will illustrate this for a case of reverse osmosis membrane with some recent work on membrane structure. A simple solution to the trade-off, in concept, to such a challenge is to do what nature does – design precise angstrom to micron scale pores with no polydispersity. However, so far such an ideal has not been realized in synthetic membranes and in particular for angstrom scale separations. We will discuss bioinspired ideas, and its realization in our lab, that could lead to an achievement of such an ideal membrane based on biological protein channels and artificial channels that mimic their structure.

6. The influence of temperature on nanofiltration selectivity

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Nanofiltration (NF) is a pressure-driven membrane-based solution treatment technology, similar to reverse osmosis (RO). Nanofiltration is typically used in water purification for cases requiring selectivity between monovalent ions and multivalent ions. Incoming streams to be treated by can occur over a wide range of temperature, usually between 20-100oC. The advantage of operating NF at higher temperatures is increased water recovery, while the key drawback is diminished salt retention. Although the change of these performance metrics is widely reported in literature, few sources explain the causative mechanisms. The first part of the talk elucidates the effect of individual membrane properties and mobilities on NF permeate quality. The changes in membrane structural and charge-based properties with temperature, and the resulting effect on permeate quality are discussed. A comparison of sets of parameters on the extent to which they explain the change in NF selectivity with temperature change are shown. Although solvent viscosity and solute diffusivity are typically used to explain membrane selectivity changes with temperature, modeling results in this work show that membrane parameter changes, including charge, play a significant role in explaining changes in NF performance with temperature. The second part of the talk discusses an industrially important application of NF for monovalent-multivalent ion separations i.e. in the 'fractionation' of sodium-chloride and sodium-sulfate. The work introduces an analytical framework to aid an industrial operator to improve inter-species selectivity with changes in temperature and other operating conditions. Methods to mitigate unfavorable selectivity changes with changing operating conditions are discussed. The final segment of the work shows that commercial reverse osmosis membranes although commonly considered non-porous do exhibit solute-solvent transport coupling, especially at higher pressures, which indicates the presence of free volume large enough to support such species transport-coupling in these membranes.

7. How Grain Boundaries and Interfacial Electrostatic Interactions Modulate Water Desalination Via Nanoporous Hexagonal Boron Nitride

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ABSTRACT

To fulfil the increasing demand for drinking water, researchers are currently exploring nanoporous two-dimensional materials, such as hexagonal boron nitride (hBN), as potential desalination membranes. A prominent, yet unsolved challenge is to understand how such membranes will perform in the presence of defects or surface charge in the membrane material. In this work, we study the effect of grain boundaries (GBs) and interfacial electrostatic interactions on the desalination performance of bicrystalline nanoporous hBN, using classical molecular dynamics simulations supported by quantum-mechanical density functional theory (DFT) calculations. We investigate three different nanoporous bicrystalline hBN configurations, with symmetric tilt GBs having misorientation angles of 13.2°, 21.8°, and 32.2°. Using lattice dynamics calculations, we find that grain boundaries alter the areas and shapes of nanopores in bicrystalline hBN, as compared to the nanopores in monocrystalline hBN. We observe that, although bicrystalline nanoporous hBN with a misorientation angle of 13.2° shows improved water flow rate by ~30%, it demonstrates reduced Na+ ion rejection by ~6%, as compared to monocrystalline hBN. We also uncover the role of the nanopore shape in water desalination, finding that more elongated pores with smaller sizes (in 21.8°- and 32.2°-misoriented bicrystalline hBN) can match the water permeation through less elongated pores of slightly larger sizes, with a concomitant ~3-4% drop in Na+ rejection. Simulations also

predict that the water flow rate is significantly affected by interfacial electrostatic interactions. Indeed, the water flow rate is the highest when altered partial charges on B and N atoms were determined using DFT calculations, as compared to when no partial charges or bulk partial charges (i.e., charged hBN) were considered. Overall, our work on water/ion transport through nanopores in bicrystalline hBN indicates that the presence of GBs and surface charge can lead, respectively, to a drop in the ion rejection and water permeation performance of hBN membranes.

8. Understanding the Structure-Property Relationships in Metal Organic Frameworks for Gas Separations and Storage

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ABSTRACT

Metal-organic frameworks (MOFs) are highly porous materials with exceptional surface areas (as high as 6000 m2 /g) and have gained wide popularity in the research community over the last decade. They are being investigated for a variety of applications such as CO2 capture, H2 and natural gas storage, catalysis, drugdelivery, semiconductors, bio-mimetic mineralization etc. MOFs are versatile and can be synthesized using different metal atoms as well as organic ligands of various shapes, sizes and functionalities. Thousands of frameworks with significantly different characteristics are reported every year. The focus of this presentation will be on understanding and exploiting these differences in MOFs for various adsorption applications. The role of several aspects in structure-property relationships such as the choice of metal atom and its coordination in the framework, functionalization of the organic linkers, doping of heavy metal atoms, structural flexibility, synthesis conditions, surface area and physical properties of the gases will be discussed. Examples of MOFs synthesized and characterized in our laboratory will be presented to experimentally validate these observations. Understanding such relationships will not only help in screening novel frameworks without extensive experimentation, but also help in developing frameworks for targeted gas separation and storage applications. Some MOFs exhibit structural flexibility, wherein the MOF framework undergoes a structural transformation due to change in an external environment and thereby its adsorption characteristics are significantly affected. In case of MIL-53(Al) MOF, structural changes result in shrinkage of pore volume by more than 30 % upon adsorption of CO2. We will demonstrate how these structural changes can be used to tune the MOF for yielding better adsorption characteristics and performance in a cyclic adsorption process. Similarly, it will be demonstrated that simple variation in the choice of constituent metal atoms in the MOF structure results in change of selectivity by several folds. Attempt will be made to rationalize these behaviors with the structure and properties of the adsorbent framework and physical properties of the adsorbates. It will be demonstrated that careful selection of adsorbate gases, and subtle variation in the adsorbent structure can be effectively used to experimentally understand the structure-property relationships in MOFs.

9. Adsorbed Natural Gas for Onboard Storage: Challenges in Multiscaling from Molecules to Transport

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Abstract

Development of natural gas storage solutions for the transportation sector are important in mitigating global greenhouse gas emissions. The challenge lies in the synthesis of novel nanostructures to meet target gas storage capacities. Studies have shown that selective functionalization of mesoporous materials such as activated carbons and metal organic frameworks, offers a flexible means to improve their existing gas storage potentials. In this talk I will present an overview of our research in this area, and address the challenges related to development of novel materials using a multiscale approach covering in silico methods, materials development at the laboratory scale and engineering challenges for onboard transportation. At the molecular scale, we study gas-solid interactions using ab initio quantum chemical methods and use classical Monte Carlo simulations to obtain gas adsorption isotherms. Our study indicates that specific functionalization can be used to tailor selectivity for gas adsorption and provide a guide for rational novel materials design to achieve target storage requirements. Adsorption isotherms obtained from the molecular scale are used as input into continuum transport models to understand the heat and mass transfer effects to assess the performance of an on-board adsorbent charge and discharge characteristics.

10. Hydrogen Stable Olefin/Paraffin Separation Membranes

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McKetta Department of Chemical Engineering

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Olefins are a key building block of the petrochemicals industry because they are precursor materials for numerous chemical products and plastics. The current commercial production method is steam cracking of ethane followed by cryogenic distillation of olefin/paraffin mixtures, which involves large energy consumption and greenhouse gas footprint. Membranes using facilitated transport show promising olefin/paraffin selectivity due to the presence of carriers that specifically complex with olefins. Unfortunately, facilitated transport-based membranes for olefin/paraffin separation have not been viable because the silver carriers deactivate rapidly in the presence of any H2, which chemically reduces the silver salts to inactive silver metal. While a number of groups have shown that supported ionic liquid (IL)/silver salt membranes (SILMs) and polymer/silver salt membranes show good olefin/paraffin selectivity, we have discovered that some silver salts and ILs provide protection of the silver salts from reduction by H2, leading to stable performance over long times. Our work shows that IL/silver salt mixtures in ceramic supports and polymeric/silver salt composites show excellent olefin/paraffin permeability and resistance to reduction by hydrogen. These innovations pave the way for selective olefin/paraffin separation with dramatically reduced energy consumption, that is viable from laboratory to commercial scale operation.

Abstracts by Poster presenters

Removal of Pesticidal Agents from Aqueous Environment with Hydrophobic Deep Eutectic Solvent: A Molecular Dynamic Study

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ABSTRACT

Hydrophobic Deep Eutectic Solvents has emerged as an excellent green solvent in the removal of various pharmaceutical products from waste-water systems. DL-menthol and long-chain carboxylic acid-based DESs have been used in the extraction of pesticides from water and their excellent hydrophobicity have made them suitable for water-related treatment processes. With the proper amalgamation of the experiments and MD simulation, we can understand the insights into the extraction mechanism. Our present work includes MD simulation of the extraction of thiamethoxam (pesticide) from an aqueous environment with DL-menthol: Octanoic acid (1:1) DES. We have studied non-bonded interaction energy, radial and combined distribution function, hydrogen bond analysis, HOMO-LUMO gap to grasp the molecular level insights of the system. The MD simulated results were found to be in good agreement with the experimental findings based on the literature (Florindo et al).

Water-DES-thiamethoxam ternary system was prepared for the simulation study of pesticide extraction from the corresponding mole fraction in line with the respective molecules of the experiment. We have considered the equal mass of DES and water for the simulated system with 5 molecules of thiamethoxam initially present in the aqueous phase. The simulation was carried out with a 6 ns minimization run in the NVE ensemble, followed by heating at 298.15 K for 0.5 ns. It was then equilibrated for 10 ns with an NPT ensemble. Finally, the 100 ns production run with NVT ensemble at 298.15 K and 1 atm pressure was carried out. Periodic Boundary Condition (PBC) is applied with a system box dimension of 29.02 Å × 17.41 Å × 17.41 Å.
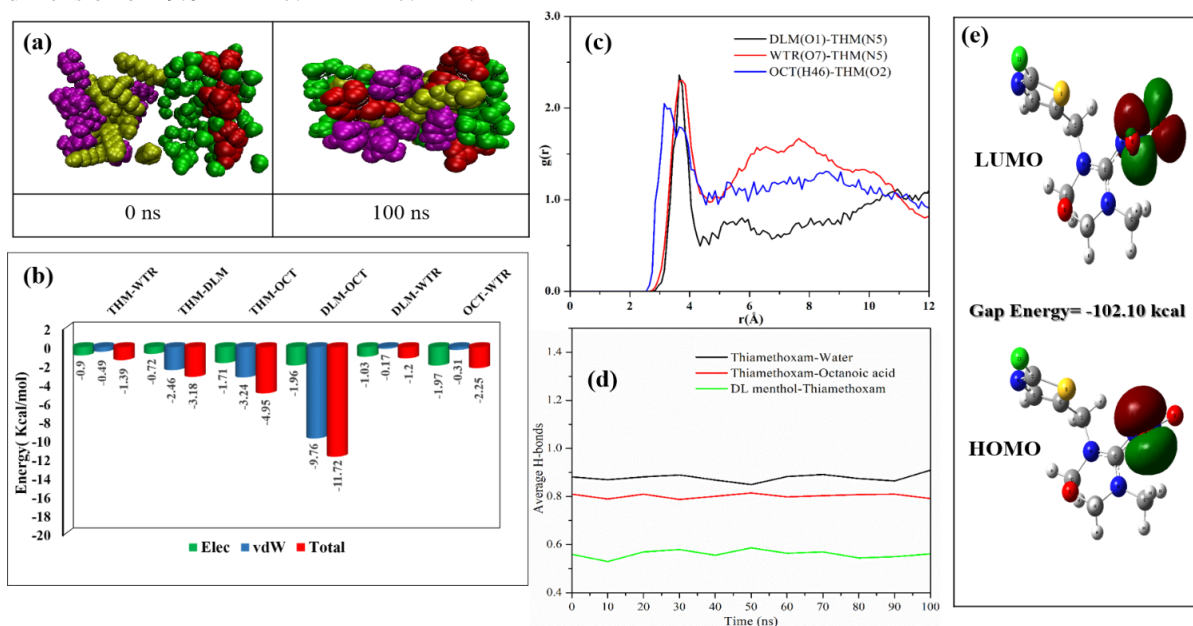
The results obtained from the MD simulation of the thiamethoxam-DES-water systems are shown in Figure 1, where Figure 1a displays the system snapshots at 0 and 100 ns of the production run, respectively. The non-bonded interaction energy among the different components is shown in Figure 1b, where it has been found that the thiamethoxam entity is having higher interactions with the DES components as compared to water molecules. Figure 1c and 1d confirms the same as they represent the RDF and hydrogen bonding, respectively. It has been noticed that water is having comparable hydrogen bonding with thiamethoxam as with octanoic acid, by which one can explain the relatively lower extraction efficiency (44%). The lower HOMO-LUMO gap inFigure 1e suggests that the drug is less stable when mixed with water and thus interacts highly with the water molecules which in turn leads to lower extraction by DES.

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Water Desalination Using Conventional Membrane Distillation and Photothermal Membrane Distillation

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ABSTRACT

Water is an essential requirement of any society, and with the increasing global population and water footprint, world water availability is facing a severe threat. Studies suggest that by 2030 half of the world population will be living in areas of high-water stress [1]. Desalination removing salt from seawater can be an alternative by which the influx of water can be increased to resolve this demand-supply imbalance. Currently, many countries in the middle east, like Saudi Arabia, etc., are dependent on desalination for their freshwater requirements. As the water requirement will increase, this desalination capacity will rise exponentially in the coming decades. Still, the issue is that majority of desalination capacity is fossil driven. As the desalination process is very energy-intensive and moving along, the energy crisis is also following us, therefore to mitigate the energy footprint in the water-energy nexus and for a long-term solution, we need desalination that is renewable driven.

In this context, membrane distillation (MD), a thermally driven separation technique in which a microporous hydrophobic membrane separates two liquids [2], has enormous potential as the operating temperature range for MD is such that it can run on alternate energy sources like solar, geothermal, etc. With the advancement in new membrane material and fabrication techniques, the membrane-based separation technique has become quite prominent and widely used in various domains, including desalination, material recovery, and other physical separation processes [3].

The membrane distillation for water desalination is among the best alternative for renewable-driven desalination techniques. A numerical simulation of direct contact membrane distillation (DCMD) coupled with a nanofluid-based direct absorption solar collector has been carried out for optimum performing membrane distillation system [4]. In the DCMD system, the latent heat recovery and enhanced heat transfer in the feed and permeate channel can be helpful and enhance the system's performance and efficiency. As the temperature gradient is the driving force for the MD system, the temperature polarization in the conventional MD system is the major hindrance for the effective temperature gradient across the membrane, which leads to a reduction of system performance.

The alternative techniques like direct heating of the membrane using photothermal membrane distillation (PMD), in which the localized heating at the surface of the feed side of the membrane by solar irradiation alone, drives the distillation can be beneficial. The photothermal coating in the conventional Polyvinylidene-fluoride (PVDF), Polytetrafluoroethylene (PTFE) membrane works as a heating source for the process. This direct heating of the membrane surface is beneficial as it reduces the earlier drawbacks that conventional membrane distillation was having like temperature polarization, feed transportation losses, pumping power requirement (as PMD operate at relatively lower flowrate). Also, the operating temperature range of PMD is not that high, which leads to a reduction in scaling and other crystal deposition over the membrane. The PMD is a new technology, and in its initial state, it can be the best alternative for off-grid, off-shore areas and remote locations for community scale desalination. The numerical investigation of the co-current flow PMD system has been carried out, and it showed that heat recovery could lead to enhancement of system performance. For the future scope, a counter-flow PMD system is being modeled for single and multistage PMD systems.

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Bio-inspired membranes engineered from Interpenetrating polymeric networks for effective antibiotic and pH-triggered dye removal

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ABSTRACT

A mussel inspired membrane was engineered from Interpenetrating polymeric network (IPN) technique and it was adopted to target stringent and quick response towards antibiotics and pH responsive dye removal. These mechanically stable and environmentally sustainable membranes were rendered selective and effective towards specific dyes and antibiotics by thorough pore engineering via a synergistic effect of bond formation and charge variation. Such molecular architecture in confined nanoscale spaces led to specific chemical interactions, and thus promoted separations. The final pore engineered membrane was characterized using various spectroscopic and microscopic techniques, Zeta potential analysis, TGA and Water contact angle measurements. It could successfully reject >97% of both Methylene blue (cationic dye) and Congo Red (anionic dye) under various pH over several cycles of operation. Additionally, it could remove more than 96 % of both Amoxicilin and Azithromycin antibiotics through synergistic charge and pore-based sieving. This pore-engineered bioinspired IPN engineered membrane is cost-effective, robust, stable, non-cytotoxic, shows effective separation of antibiotics and organic dyes, which makes it a prospective candidate in water remediation.

Enhanced water evaporation through functionalized nanoporous graphene: A molecular dynamics study

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ABSTRACT

We report enhanced water evaporation through different functionalized nanoporous graphene (FNPG), using molecular dynamics simulations. With the increase in hydrophilicity of the nanopore, evaporation flux increases. Along with rapid hydrogen bond dynamics, the functional groups terminating the nanopores of FNPGs render rapid translational and rotational dynamics to the water molecules, resulting in reduced surface tension at the water-vapor interface and hence a reduced free energy barrier for water evaporation through the nanopores.
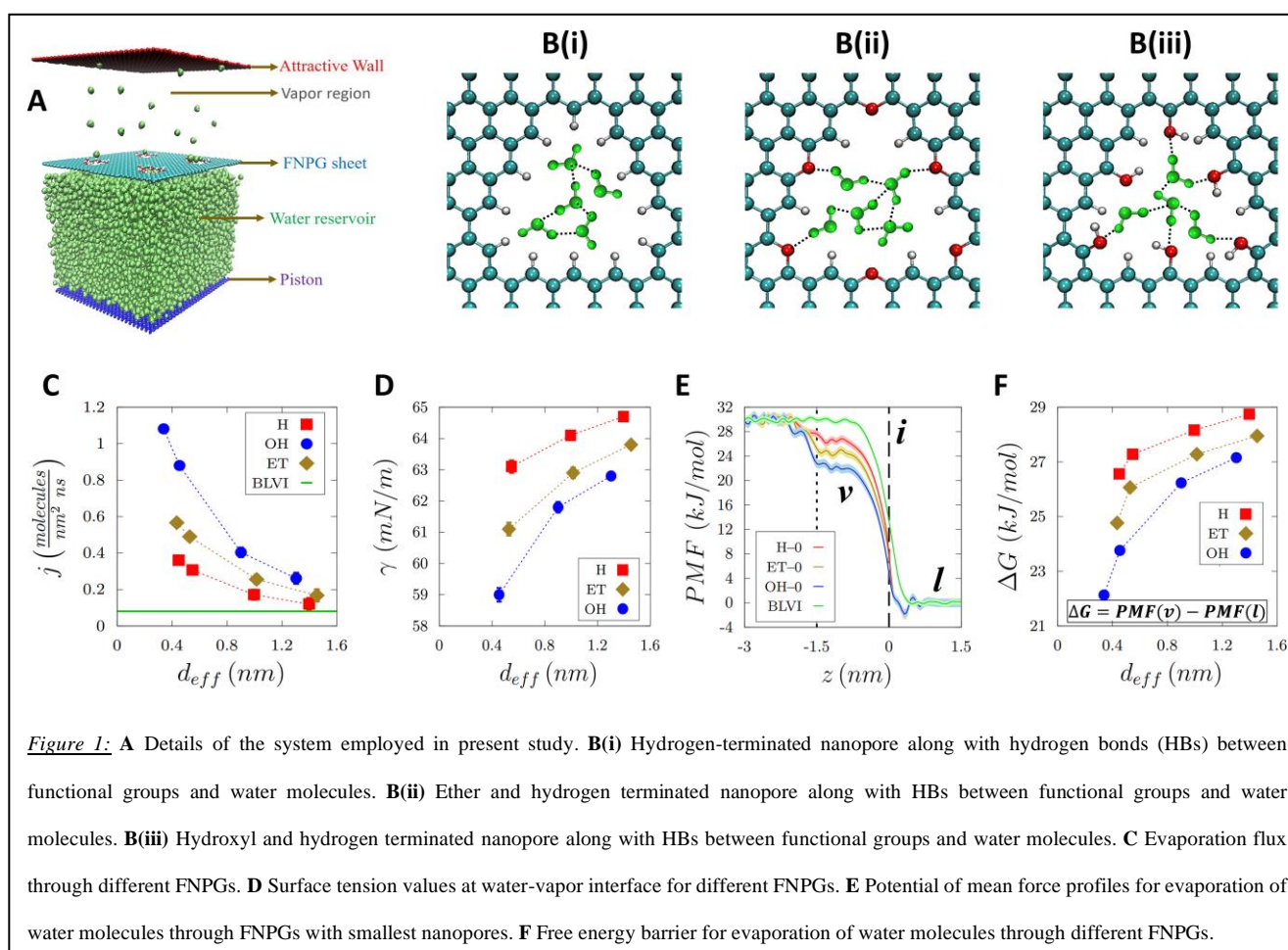
Figure 1: **A** Details of the system employed in present study. **B(i)** Hydrogen-terminated nanopore along with hydrogen bonds (HBs) between functional groups and water molecules. **B(ii)** Ether and hydrogen terminated nanopore along with HBs between functional groups and water molecules. **B(iii)** Hydroxyl and hydrogen terminated nanopore along with HBs between functional groups and water molecules. **C** Evaporation flux through different FNPGs. **D** Surface tension values at water-vapor interface for different FNPGs. **E** Potential of mean force profiles for evaporation of water molecules through FNPGs with smallest nanopores. **F** Free energy barrier for evaporation of water molecules through different FNPGs.

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Molecular sieving through 'layer-by-layer' self-assembly of polyelectrolytes and highly crosslinked graphene oxide

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ABSTRACT

A novel thin-film composite (TFC) membrane was fabricated by 'layer-by-layer' self-assembly of poly-dopamine (PDA) and polystyrene sulfonate (PSS) supported on a highly crosslinked graphene oxide (GO) membrane to selectively sieve ions and to enhance the chlorine tolerance performance. This GO membrane was sandwiched between layers of various nanoporous polyvinylidene difluoride (PVDF) membranes obtained by selectively etching out the PMMA component from the demixed blends. The blend membranes were designed following the melt-extrusion process and subsequent quenching to facilitate confined crystallization of PVDF and selective etching of PMMA. The membranes with different pore sizes were tuned by varying the blends' composition, and a gradient in microstructure was achieved by stitching the membranes. Pure water flux, salt rejection, dye removal, and antibacterial activity were performed to study the membrane's efficiency. The GO membrane was chemically crosslinked with methylenediamine to impart dimensional stability and to enhance rejection efficiency through the nanoslits that GO offers. Besides effective rejection, the sandwiched membrane was modified with layer-by-layer self-assembly of polyelectrolytes on the surface to improve the chlorine tolerance performance. This strategy resulted in an excellent salt (about 95 % and 97 % for monovalent and divalent ion, respectively) and dye rejection (99% and 98% for both cationic and anionic dye respectively), besides facilitating excellent chlorine tolerance performance. Moreover, this modified membrane showed superior antifouling properties (flux recovery ratio is more than 90%) and excellent antibacterial performance (near about 3 log reduction).

Investigating the Gas Separation Properties of Carbon Molecular Sieve Membranes using Multi-scale Molecular Simulations

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ABSTRACT

Carbon capture and storage (CCS) is a technology implemented to extract and store carbon dioxide (CO_2) generated after combusting any carbon-based fuel, like coal or natural gas. CCS is a key solution to alleviate climate change by reducing any plant or industry's net carbon footprint. In this regard, membrane-based CO_2 capture offers significant advantages, including stability, scalability and improved performance while being hazard-free. This work employs computational techniques to analyze the structural properties and adsorption performance of carbon molecular sieve (CMS) membranes derived from the pyrolysis of glassy polymer precursor (6FDA/BPDA-DAM) [1]. We perform all-atom molecular dynamics (MD) simulations to build the adsorbent frameworks, followed by grand-canonical Monte-Carlo (GCMC) simulations to study their adsorption properties. We find that these membranes show significantly higher loading and selectivity towards CO_2 from a mixture of gases compared to current industry standards. The distribution of ultra-micropores greatly determines the performance capabilities of the frameworks. Our simulations help understand how the extent of polymerization of individual monomers determines the formation of these pores and cavities. We find that the chain length of each polymer strand governs their structural morphologies, namely density, stacking, accessible volume and pore size distribution, thereby governing their adsorption performance. The nature of these pores and the flexibility of individual monomers play an important role in forming interconnected pathways inside the polymer matrix. Moreover, the swelling of these membranes can open newer pathways for gases to sieve through. Permeation of gas molecules through these membranes thus require fabricating materials having several microns thickness. Replicating such length scales in simulations is computationally expensive and inefficient. Additionally, computing the diffusion coefficients of trapped gases become a bottleneck owing to the sub-diffusive nature of their mean squared displacement (MSD). To get around these challenges, we implement a trajectory extending kinetic Monte-Carlo (TEKMC) technique. MD simulations of a few nanoseconds can be successfully used as inputs for obtaining MSD of durations extending up to microseconds that sample the Fickian regime, enabling us to obtain diffusion coefficients of CO_2 molecules inside our CMS membrane. The same technique may be extended for other systems of interest, giving reliable permeabilities in dense polymer membranes when used in conjunction with adsorption results.

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