

## **Membrane distillation for treating hydraulic fracturing produced water using zwitterionic bilayer electrospun membranes**

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Treating hydraulic fracturing flowback waters can be very challenging as they often contain TDS more than 200,000 ppm as well as dissolved surfactants and small organic compounds. Membrane distillation has been proposed as a unit operation for treatment of very high TDS wastewaters. However, while the membrane must be hydrophobic to ensure only water vapor passes through the membrane pores, the presence of organic compounds and surfactants in the produced water leads to membrane fouling and pore wetting. To solve serve fouling and pore wetting a bilayer electrospun membrane was fabricated consisting of a hydrophilic and an omniphobic layer. The base membrane polymer was PVDF. The omniphobic layer facing the permeate side was decorated by growing nanoparticles followed by silanization to lower surface energy. The hydrophilic layer facing the feed stream contained grafted epoxyed-zwitterionic polymers to form a tight antifouling hydration layer. These membranes were tested with actual hydraulic fracturing produced water and their performance compared to base PVDF membranes.

## **Cu(I/II) MOF Incorporated Nanofiltration Membranes for Toluene and Heptane Separation**

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Copper-based metal-organic frameworks (MOFs) with different oxidation states and near-uniform particle sizes have been successfully synthesized. Mixed-matrix polyimide membranes incorporating 0.1-7 wt% of these Cu MOFs were fabricated via non-solvent induced phase inversion process. These membranes are found to be solvent resistant and mechanically stable. Liquid phase nanofiltration experiments were performed to separate toluene from n-heptane at room temperature. These membranes demonstrate preferential adsorption and permeation of the aromatic toluene over aliphatic n-heptane. The amount of MOF particles incorporated, the oxidation state of the Cu ion and the particle size have a significant impact on the separation factor. However, solvent filtration flux is largely dependent on the amount of MOF particles incorporated, independent on the oxidation state of the Cu ion.

## **Membrane technology for biorefinery process to produce high-value product such as biofuels and functional food**

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We constructed an effective process by using membrane separation technology to improve enzymatic reaction with higher productivity, increase the purity & value of the end product. By the application of membrane process, we could enhance the biomass sugar concentration using membrane support to enhance the first generation biofuel. Secondly, we improved in the activity of the enzyme to speed up the reaction, where the membrane support is used for enhancing the concentration of liquid lipase product from *Aspergillus oryzae* expressing FHL on-site lipase for biodiesel production. Lastly, we improved an xylo-oligo saccharide for functional food by increasing the activity of xylanase.

## **Mechanism of Self-Assembling of Smart Electrical Responsive Graphene-PVDF membrane**

Wei-Song HUNG

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Though the membrane separation has been an efficient and energy-saving technique for dealing with the wasted mixed chemical matters, the concomitant environmental pollution has become a big issue in the development of membrane field. Consequently, the active-responsive smart membrane appears to be the new trend for membrane development in coming future, which shows great potential to deal with the obstacles. Here, we demonstrate the preparation of a smart electric-responsive membrane, PVDF/graphene composite membrane, in which the graphene induces self-assembly of PVDF chains, showing a highly  $\beta$  phase and thus a unique piezoelectric property. The resultant nanochannels in the membrane could be reversibly adjusted by electric-driving, resulting in tailored alcohol selectivity on the single membrane. The membrane was utilized to challenge the dehydration of MeOH/water mixture, which offered a  $> 99.5$  rejection to MeOH molecules with high water flux, achieving precise molecule separation performance. Overall, the novel active membrane separation process proposed in this work opens the gates towards the development of novel generation of active smart membrane, which is imperative for the future sustainable society.

# **Design of PVDF Membranes: Structure Formation, Surface Modification, and Potential Applications**

Yung CHANG

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In the past 15 years, R&D center for Membrane Technology (RDCMT) has conducted systematic research on poly (vinylidene fluoride) membranes and published nearly 100 articles in Journal of Membrane Science, covering PVDF membrane filtration, selectivity, formation, structure, scaling, processing and application. Research. In this presentation, I will introduce the new research works with highlight RDCMT in PVDF Membrane study for the past two years in 2019-2020, covering important research results in three aspects: Structure Formation, Surface Modification, and Potential Applications using PVDF system.

## **Potential application of inkjet printing technology on depositing nanomaterials for thin-film composite membrane fabrication and its modification**

Ho Kyong SHON

University of Technology Sydney

Thin film composite (TFC) membranes have been widely applied for water purification and water desalination for over few decades, as well as in application of many chemical industries for efficient solute/solvent separations. Although currently commercially available TFC membranes such as reverse osmosis (RO) and nanofiltration (NF) represent high enough performance in large-scale applications, yet, a lot of efforts have been made to improve the membrane performance to overcome trade-off between permeability and selectivity. One of most promising approaches is adaption of nanomaterials such as graphene oxide (GO) or carbon nanotubes (CNTs) in interfacial polymerization (IP) process, either it incorporates in polyamide (PA) selective layer or it utilizes as interlayer to control PA layer thickness. Such approaches are known to provide low resistant path for solvent or water permeation as well as desirable anti-fouling properties which effectively enhance the membrane performances. However, such chemical processing approaches of the membrane production are not effective and environmentally friendly in industrial scale as it produces numerous hazardous chemical wastes. Here, we introduce efficient TFC membrane manufacturing process using inkjet printing that offers simple, rapid and scalable process with high precision control of the nanomaterial or organic material deposition with minimal materials use compared to other approaches such as dip-coating, layer-by-layer deposition and vacuum filtration. One example of our study of fabricating TFC membrane for NF application was demonstrated using inkjet printing of CNTs utilizing as an interlayer. Multiple number of printings on the polyethersulfone (PES) support were conducted, to simply control the CNTs deposition and, to investigate how the CNTs interlayers thickness influences the formation of PA layer. From the results, we found out that both water permeability and salt selectivity were improved with increase in the number of CNTs deposition which is significant advancement.

## **Design of PVA nanocomposite membrane for high flux and separation pervaporation**

Stephen GRAY

Victoria University

This presentation covers the development of PVA based mixed matrix membrane for high-performance pervaporation separation applications and in-depth understanding of how the nanofillers and polymer matrix affect the separation performances of PVA based mixed matrix membranes. Facilitated transport agents and inorganic nanofillers, such as CNTs, judiciously combined in the membrane for the first time, and exhibit separation performance far exceeding state-of-the-art pervaporation membranes. In addition, the facile fabrication of the membrane will also benefit its future industrialization.

## **Defect Engineering in Metal-Organic Frameworks Towards Advanced Mixed Matrix Membranes for Efficient C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> Separation**

Mr. Tae Hoon LEE and Prof. Ho Bum PARK

Hanyang University

Highly permselective and durable membranes have been sought for C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> separation in petrochemical industries. Mixed-matrix membranes (MMMs) comprising a mechanically strong polymer matrix and embedded metal-organic frameworks (MOFs) are promising candidates for this application; however, the rational matching between matrix and filler is challenging and their separation performances need to be further improved. Here, we propose a novel strategy of “defect engineering” in MOFs as an additional degree of freedom to design advanced MOF/polymer MMMs. MMMs incorporated with defect-engineered MOFs exhibit exceptionally high C<sub>3</sub>H<sub>6</sub> permeability (more than 10-fold higher than the pure polymer) and maintain C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> selectivity with enhanced stability under industrial operation conditions. The gas transport, sorption, and material characterizations reveal that the defect sites in MOFs provide the resulting MMMs with not only ultrafast diffusion pathways but also favorable C<sub>3</sub>H<sub>6</sub> sorption by forming  $\pi$ -complexation with unsaturated open metal sites, confirmed by in-situ FT-IR spectroscopy. Most importantly, the concept is also valid for different systems, demonstrating its versatile potential.



## **Membrane process for treatment of recalcitrant pollutants in water**

Wei HAN

The Hong Kong University of Science and Technology

Chemicals in household and personal products are increasingly found to pollute water. Many are refractory and difficult to treat, and thus persists in water for a long-time. Some of these chemicals are endocrine disruptor that interferes with the normal biological functions of organisms, others are toxic and mutagenic. This report explores the use of membrane process to treat and remove these compounds from the water.

# **Seawater Membrane Distillation (SWMD) Towards Stand-alone Zero Liquid Discharge Desalination**

Helen JULIAN

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Seawater Membrane Distillation (SWMD) is a promising separation technology due to its ability to operate as a stand-alone desalination unit operation. The unique features of SWMD, namely the ability to operate with extremely high salt rejection and at extreme feed concentration, highlight the SWMD potential to be operated under Zero Liquid Discharge (ZLD) conditions, which results in the production of high-purity water and simultaneous salt recovery, as well as the elimination of the brine disposal cost. A detailed comparison of SWMD and Sea Water Reverse Osmosis (SWRO) is presented to further analyze the critical shortcomings of SWMD. Possibility of applying selected strategies to push forward ZLD SWMD commercialization are highlighted. In particular, the application of dense membrane to overcome wetting in SWMD application is explored.

## **Potential application of inkjet printing technology on depositing nanomaterials for thin-film composite membrane fabrication and its modification**

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Ion-exchange membrane (IEM) is a charged membrane that has a strategic role, especially in the field of water and energy. Electrodialysis (ED) is an IEM-based process that has long been commercialized for brackish water desalination. Meanwhile, electrodeionization (EDI), which is the latest evolution of ED, has been commercialized for the production of ultrapure water. In the future, one of the main prospects of IEM is for energy storage devices such as redox flow batteries (RFB). RFB has many advantages, such as high energy efficiency, low investment costs, and long-life cycles. Properties of IEM determine to a very large extent the efficiency of IEM-based processes, including the RFB. To produce high energy density with low operational cost, the IEM should be highly conductive, highly permselective, and chemically stable. However, electrolyte crossover usually occurs through the IEM which leads to the low energy efficiency. Therefore, various strategies are reported to address this issue. Here, preparations of selective, conductive, and durable IEM for vanadium redox flow battery (VRFB) are presented.

## **Precisely Tuning the Interlayer Channels of GO Membranes for Molecule or Ion Transport**

Wanqin JIN

Nanjing Tech University

Dr. Wanqin Jin is a professor of Chemical Engineering at Nanjing Tech University, Fellow of Royal Society of Chemistry, the Deputy-director of the State Key laboratory of Materials-oriented Chemical Engineering and the Chief-scientist of the National Basic Research Program of China (973 Program) and Major Program of National Natural Science Foundation of China (NSFC). He received his Ph.D. from Nanjing University of Technology in 1999. He was a research associate at Institute of Materials Research & Engineering of Singapore (2001), an Alexander von Humboldt Research Fellow (2001-2013), visiting professors at Arizona State University (2007) and Hiroshima University (2011, JSPS invitation fellowship). His currently research focuses on the development of membrane materials and processes. He has published nearly 300 refereed journal publications including Nature, Nat. Comm., Adv. Mater., Angew. Chem., J. Am. Chem. Soc., AIChE J., J. Membr. Sci., Chem. Eng. Sci. with 14000+ citations; written 2 monographs, contributed 6 book chapters and hold 40 authorized patents. He was co-chair of the 10th International Congress on Membrane and membrane Processes (ICOM2014), and he is now an editor of Journal of Membrane Science and a council member of Aseanian Membrane Society (AMS). In 2019, his research has been recognized by the IChemE (UK) Underwood Medal for his leading research in the area of separation.

## **Metal-Organic Framework Mixed-Matrix Membranes for Gas Separation**

Gongping LIU

Nanjing Tech University

Dr. Gongping Liu is a professor in Chemical Engineering at Nanjing Tech University, China. He received his PhD degree in chemical engineering in 2013 at Nanjing Tech University under the supervision of Prof. Wanqin Jin. Following completion of his PhD, Dr Liu joined Nanjing Tech University as a lecturer, and undertook a post-doctoral position in Bill Koros Group at Georgia Tech during 2015-2017. He was promoted to a full professor in 2019. His current research focuses on rational designing and engineering of advanced membranes mainly derived from MOF mixed-matrix, two-dimensional materials such as graphene oxide and asymmetric hollow fibers, which are applied for energy and environment based on molecular separations including CO<sub>2</sub> removal/capture, volatile organic compounds recovery and purification, and water desalination. Dr. Liu had about 90 journal papers in Nature Materials, Nature Communications, Angewandte Chemie, Chemical Society Reviews, Journal of Membrane Science, AIChE Journal et al., with over 4100 citations and H-index 32 (Google Scholar); 1 monograph and 5 book chapters; gave over 20 presentations at international conferences. He has received the North American Membrane Society (NAMS) Young Membrane Scientist Award in 2018.

## **Dual-layer Hollow Fiber Photocatalytic Membranes for Wastewater Treatment**

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Universiti Teknologi Malaysia

Photocatalyst has been used as a versatile tool for environmental remediation owing to their capability to degrade a wide range of organic compounds. Recently, the feasibility of photocatalytic membranes has been explored, where the photocatalyst is embedded within a polymer host to address some issues related to photocatalyst recovery and secondary pollutions. Simultaneously, the photodegradation also helps to mitigate the fouling issue related to typical membrane separation process. This presentation focuses on the development of photocatalytic membranes for a wide range of wastewater treatment application, including oily wastewater treatment, micropollutant removal and colour pigment removals. The development of visible light-driven photocatalysts as well as the fabrication of dual layer hollow fiber membranes with these photocatalysts are highlighted in this presentation.

## **D Microporous Organic Polymers-based Membranes for Molecular and Ionic Separation**

Liping ZHU

Zhejiang University

Membranes with high permeability and high selectivity are desirable in membrane separation technology. However, all synthetic membranes are subjected to an intrinsic trade-off between permeability and selectivity. Microporous Organic Polymers (MOPs) with pore size less than 2 nm have attracted much attention and show great potential in membrane separation in recent years due to their unique porous characteristic. Currently the major challenge for the application of MOPs in separation membranes is their poor processibility due to their crosslinked and rigid chemical structure and difficult to be processed into thin films. In the on-going work, we incorporated microporous polymers into polymeric composite membranes by various strategies such as dip-coating, blending and interfacial copolymerization. It is expected to develop high performance composite membranes used in molecular and ionic separation. It was found that the incorporation of microporous polymers in the composite membranes could bring a good compromise between membrane permeability and selectivity.

## High-flux and robust PSf-b-PEG nanofiltration membrane

Yunxia HU

Tiangong University

Novel high-flux nanofiltration (NF) membranes were fabricated using polysulfone-block-polyethylene glycol (PSf-b-PEG) block copolymer through the non-solvent induced phase separation (NIPS) method. The PSf-b-PEG NF membranes present a very dense sponge-like porous structure with rich interconnected pores, contributing to its superior mechanical strength of  $22.4 \pm 0.9$  MPa. The membrane molecular weight cut off (MWCO) towards dyes is about 655 Da. The membrane water permeance reaches to  $49.3 \pm 0.9$  LMH·bar<sup>-1</sup> and exhibit a precise separation of salts and dyes with high above 98% Congo Red dye rejection and nearly 100% Na<sub>2</sub>SO<sub>4</sub> passage. Furthermore, the pore size of the PSf-b-PEG NF membranes were tailored through the addition of volatile solvents in the casting solutions and also the PEG length in the PSf-b-PEG block copolymer.



## **Boron nitride nanosheets-based nanostructured interfaces for membrane application**

Philippe MIELE

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The most fundamental aspects for nanostructured membrane are the control of interfaces. The performances can be controlled by the enhanced geometric area of the nanostructured interfaces. Thus, an accurate control of the geometry (size, porosity etc.) and interfaces is primordial to achieve the balance between large/control interface areas and efficient transport conditions.

On the other hand, 2D materials are very attractive for many applications particularly as sensors, electronics, adsorbents and catalysis devices. In the case of boron nitride, novel properties can arise from BN nanosheets (BNNS) due to the high surface area and the edge structures. Here, we used the exfoliation as the main tool for the creation of controlled two-dimensional nanostructured interfaces in order to investigate their performances. We will show examples of how these methods can be used to create membranes for water treatment and bio-nanocomposites materials for packaging. Recent works using the Pickering emulsions technique for the preparation of membranes will be described.

## **Preparation of FO membranes using exfoliated 2D nanosheets with controlled interlayer spacing**

Damien VOIRY

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Membrane separation plays an important role in various fields including water treatment, molecular purification and food processing. Thanks to their atomic thickness and the confined interlayer spacing, nanolaminated membranes could theoretically lead to enhanced separation performance.

Exfoliated nanosheets of transition metal dichalcogenides (TMDs) constitute attracting platforms for the fabrication of nanolaminates. Indeed, the lamellar structure similar to that of graphene shows rather improved stability. In addition, chemical modifications of the surface of the nanosheets have opened avenues in both fields of gas and molecular separation.

In this presentation, I will introduce our recent presence on controlling the interlayer spacing of MoS<sub>2</sub> nanolaminates. I will notably present how using covalent functionalization allows to precisely control the membrane behavior in reverse (RO) and forward osmosis(FO).

## Recent research activities at Membrane Center of Kobe University

Hideto MATSUYAMA

Research Center for Membrane and Film Technology,  
Kobe University

As the first and only-one university-driven membrane research center in Japan, the Center for Membrane and Film Technology (MaFTech Center) of Kobe University was established in 2007. In 2015, the integrated membrane research building (6000m<sup>2</sup>) finished its construction and started its operation. Currently we are collaborating with more than 80 industrial companies, as well as partnering 14 academic membrane research centers overseas.

In this presentation, MaFTech center's recent research related to organic solvent reverse osmosis (OSRO) membrane. Organic liquid mixtures are frequently produced in numerous industries for example petroleum refining process, and therefore the separation processes used for organic liquid separation play an essential role for product purification. The market currently relies heavily on energy-intensive thermal separation approaches such as evaporation and distillation. However, the continuously increasing industrialization requires more sustainable, efficient, and economical processes. In contrast, membrane process differentiates between molecules based on their different molecular properties such as chemical affinity or molecular size without liquid vaporization, which can be an order of magnitude more energy-efficient than thermal-based separations which use basic evaporation and/or distillation.

The past few decades have witnessed the burgeoning development of organic solvent nanofiltration (OSN), which can distinguish between molecules with at least one order of magnitude size difference. OSN provides high throughput in separating valuable components larger than 200 Da (such as peptides, antibodies, dyes, catalysts, oils, and pharmaceutical intermediates) from organic liquids; however, OSN cannot efficiently separate organic liquids (such as alkanes, alcohols, aromatics, and cyclic alkanes) due to the small molecular sizes (<1 nm) of common organic liquids and subtle size differences (less than 0.1–0.3 nm) among them. In general, a 0.5–0.6 nm pore size of membranes is necessary to enable feasible separation of organic liquids, such as n-heptane/isooctane, isobutane/isooctane, p-xylene (p-X)/o-xylene (o-X), and benzene/ethylbenzene mixtures. Compared with OSN, OSRO provides a smaller pore size (below 1 nm), which marks the next step toward molecular specificity greater than that of OSN. Although OSRO membrane is more difficult to fabricate and much less developed than OSN, OSRO has its more excellent molecular differentiation against the challenging organic liquids.

In addition to OSRO research, the researches on membrane fouling, oil/water separation, nano-sheet membrane and CO<sub>2</sub> separation membrane will be covered as well.