PRF# 56144-DNI10
New Dimensions in Designing Nanohybrid Membrane Materials for Energy-Efficient Gas Separations

PI: Ruilan Guo, Associate Professor
Department of Chemical and Biomolecular Engineering, University of Notre Dame

Project Progress: The project goal is to develop a new composite membrane platform that utilizes supramolecular interaction of iptycene units to address interface incompatibility issue in composite membranes for gas separations.

- *Nano-composite membranes based on ZIF-90 or modified ZIF-90 nanoparticles.*

In the past reporting period, we published a paper reporting the composite membranes prepared from pristine ZIF-90 nanoparticles and a triptycene-based polyimide (i.e., TP-6FDA). The key finding was that hierarchical triptycene units effectively assist in the nanoparticle dispersion and prevent aggregation leading to desired interfacial morphology and consequently excellent separation performance that surpassed the 2008 upper bounds. Following this work, research efforts on preparing ZIF-90 based mixed-matrix membranes were focused on surface modification of ZIF-90 nanoparticles to further modify the interfacial morphology so as to explore the tunability in microstructure and gas transport properties of composite membranes. Specifically, surface modification of ZIF-90 nanoparticles was carried out via condensation reaction between the amine functional groups of select iptycene derivatives and the aldehyde functionality of ZIF-90 particles. It was found that grafting with TPDA-d showed the balanced reactivity whereby the ZIF-90 crystallinity was well maintained after grafting without forming the "crosslinked" particles. A series of composite films were prepared from modified ZIF-90 nanoparticles (10-30 wt%) using the same TP-6FDA polyimide matrix. SEM images (**Fig. 1a**) showed defect-free interfaces in all composite membranes suggesting very tight contact between the filler particles and the polymer matrix due to the strong supramolecular interactions between triptycene units. As a result, the composite membranes were less permeable than expected due to possible pore blockage upon surface modification of ZIF-90 particles and very tight filler-polymer interaction. In general, gas permeabilities increased as the filler loading increased, with relatively stable selectivities (**Fig. 1b**). It was also demonstrated that adjusting surface grafting density (i.e., via adjusting reactants feed ratio) provided an efficient way to tailor the gas transport properties of composite membranes (**Fig. 1c**), which represents a new dimension in modifying filler-polymer interfacial morphology in composite membranes.

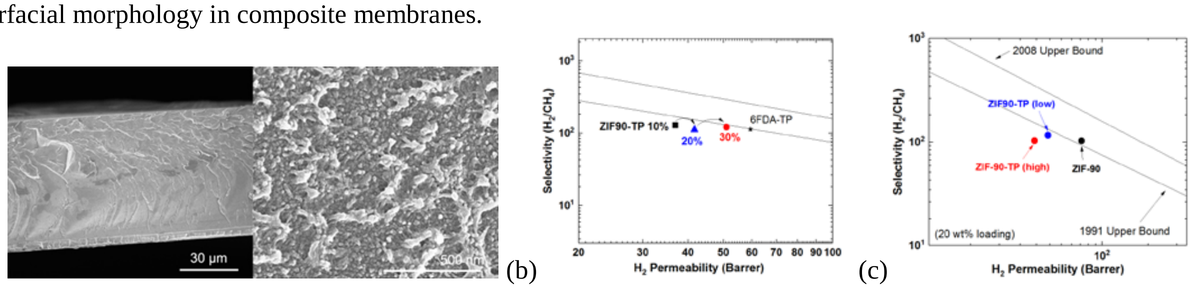
(a) (b) (c)


Fig. 1. (a) Representative SEM cross-sectional images of a composite membrane containing 30 wt% modified ZIF-90 particles (i.e., ZIF90-TP); Dependence of gas separation performance on (b) filler content and (c) surface grafting density (i.e., high *vs*. low).

- *Preparation of nano-composite membranes using single-walled carbon nanotubes (SWNTs).*

Work was done to explore the potential of using SWNTs as nanofillers. It is hypothesized that the strong π-π interaction between the graphene wall of SWNTs and the benzene rings of triptycene units will promote dispersion of SWNTs and filler-polymer interfacial compatibility to construct desired pathways for fast and selective gas transport. To investigate the effects of filler content, surface functionality and aspect ratio of SWNTs on gas transport properties, three types of SWNTs, i.e., as-purchased AP-SWNT, purified P-SWNT and acid-treated A-SWNT, were explored in the preparation of composite membranes using abovementioned TP-6FDA polyimide as polymer matrix. Specifically, purified P-SWNTs differ from AP-SWNTs in its –COOH surface functionality and higher purity; A-SWNTs were prepared from P-SWNTs via strong acid treatment, and thus had much shorter bundle length and higher –COOH surface functionality than P-SWNTs. Composite membranes were prepared from each type of SWNTs, all of which were defect-free as well as mechanically and thermally robust. As shown by SEM images (**Fig. 2**), desirable interfacial morphology was achieved, suggesting the formation of possible supramolecular complexes between

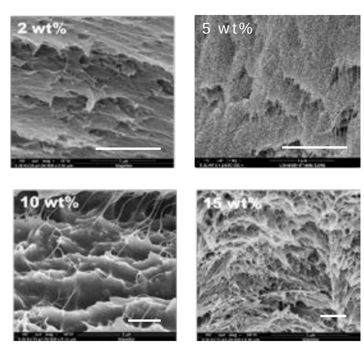


Fig. 2. SEM images of SWNTs-based composite membranes with varying SWNTs content (scale bar: 1 μm).

SWNTs and polymer matrix via π-π interaction. This supramolecular interaction was confirmed by RBM peak shift of SWNTs in composite membranes due to augmented charge transfer between filler and polymer matrix in Raman spectra as well as fluorescence quenching observed in fluorescence spectra. Additionally, no aggregation of SWNTs occurred in all cases as evidenced by the well-maintained SWNT bundle diameter in polymer matrix. Pure-gas permeation tests were performed on all composite membranes. An unexpected non-linear relationship was observed between the filler content and gas permeability in a series of composite membranes containing 2-15 wt% AP-SWNTs (**Fig. 3a**). A composite membrane with 2 wt% AP-SWNTs is almost four time more permeable and almost the same selective compared to pristine polyimide film. Increasing filler content did not lead to further improvement of permeability until a high loading of 15 wt%. This is likely due to the competition between carbon walls acting as barriers blocking gas transport and hollow tubes facilitating transport. The effects of filler purity, surface functionality and aspect ratio were explored via comparing composite membranes containing different type of SWNTs at the same 2 wt% loading (**Fig. 3b**). In general, membranes containing SWNTs with higher purity and increasing –COOH surface functionality are more selective towards CO_2, e.g., CO_2/CH_4 selectivity is in the order of A-SWNT > P-SWNT > AP-SWNT. The slightly decreased gas permeability is likely due to tighter interactions between surface-functionalized, shorter SWNTs and polymer matrix. The membrane containing 2 wt% A-SWNTs outperformed the 1991 upper bounds.

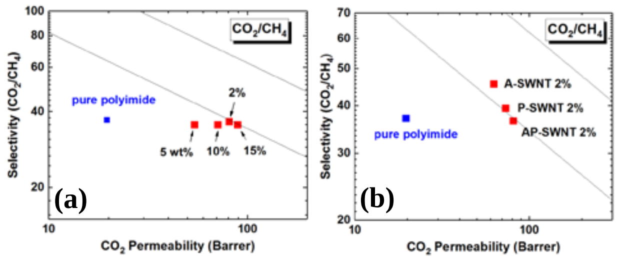


Fig. 3. Dependence of gas transport properties on (a) filler loading and (b) filler type for composite membranes containing SWNTs.

- *Preparation of super-rigid triptycene-based polyimide as new polymer matrix.*

Synthesis was initiated to explore new triptycene-based polyimides with more rigid backbone as matrix materials since high polymer backbone rigidity improves gas permeability as demonstrated in our previous studies. In this regard, a new triptycene monomer where diamine groups are placed directly on the triptycene skeleton eliminating flexible ether linkages in previous triptycene-based polyimides. This new triptycene-polyimide had about two orders of magnitude higher permeability than those with flexible ether linkages (**Fig. 4**), making it highly promising candidate as matrix materials. Composite membranes were successfully prepared from this new triptycene-polyimide and SWNTs described above with systematically varied content. All films are defect free with even dispersion of SWNTs in the polymer matrix. Pure-gas permeation tests are underway and the results will be reported in a future publication.

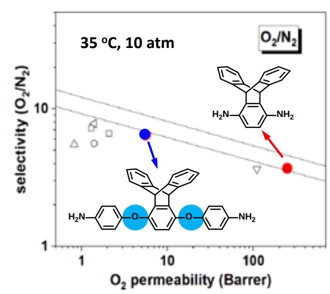


Fig. 4. Permeability enhanced by polymer backbone rigidity.

<u>Impact</u>: This ACS PRF grant supported one female graduate student (Qinnan Zhang) who has had co-authored five publications and several presentations at professional conferences (AIChE, SWE, etc.). Graduate student (Greg Kline), who was partially supported by the grant, defended his doctoral thesis in August 2018 and will start a postdoctoral position at RPI in December 2018. This grant also involved an undergraduate researcher (Tyler Bear), who is mentored by the graduate student, Qinnan Zhang, and won Slatt Fellowship by ND Energy to perform research in the PI's laboratory. He is continuing his second year of undergraduate research and will be co-authors of two papers that are to be submitted soon. In the past reporting period, PI Guo was recognized as one of "the 2017 (inaugural) Class of Influential Researchers" by *I&ECR* and gave five invited/keynote talks on polymer and polymer-based membranes for gas separations highlighting this ACS PRF project. Although this project officially ended on August 31, 2018, work is still ongoing to expand the spectrum for both nanofillers and polymer matrix materials.

<u>Publications acknowledging ACS PRF support</u>:

- Zhang, Q., et al. Preparation and Gas Separation Performance of Mixed-Matrix Membranes Based on Triptycene-containing Polyimide and Zeolite Imidazole Framework (ZIF-90), *Polymer*, **2017**, *131*, 209-216.
- Zhang, Q., et al. Tailoring Interfacial Morphology via Supramolecular Interaction in SWCNT-based Mixed-Matrix Membranes for Gas Separations, *to be submitted*, **2018**.
- Zhang, Q., et al. Surface Modification of ZIF-90 Nanoparticles for the Preparation of Mixed-Matrix Membranes for Gas Separations, *to be submitted*, **2018**.
- Zhang, Q., et al. Preparation and Gas Separation Performance of Mixed-Matrix Membranes Prepared from a Super Rigid Triptycene-containing Polyimide and SWCNTs, *in preparation*, **2018**.