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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.202014893

Link to VoR: https://doi.org/10.1002/anie.202014893
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Abstract: The implementation of mixed matrix membranes (MMMs) for sub-angstrom scale gas separations remains a grand challenge. Meanwhile, the elucidation of structure and formation mechanism of elusive interface pathways is urgently needed yet largely unmet. Herein, a series of analogous mixed matrix membrane (AMMs) were constructed via molecular-level hybridization by utilizing reactive ionic liquid (RIL) as continuous phase and graphene quantum dot (GQD) as nanofiller for sub-angstrom scale ethylene/ethane (0.416 nm / 0.443 nm) separation. With a small number of GQDs (3.5 wt.%) embedded in GQD/RIL AMMs, ethylene permeability soared by 3.1 times, and ethylene/ethane selectivity simultaneously boosted by nearly 60% and reached up to 99.5, which outperformed all previously reported state-of-the-art membranes. Importantly, the interfacial pathway structure was visualized and their self-assembly mechanism was revealed, where the non-covalent interactions between RIL and GQDs induced the local arrangement of IL chains to self-assemble into plenty of compact and superfast interfacial pathways, contributing to the combination of superhigh permeability and selectivity. This study shed light on the rational design of interface pathways and sustainable prosperity of MMMs for energy-intensive gas molecule separations.

Mixed matrix membranes (MMMs) composed of dispersed discrete organic/inorganic fillers into the continuous polymeric matrix (sometimes organosilicon or others), synergistically combine the easy processability of polymers with the distinctive features of nanofillers, where the versatile interfaces are constructed to provide enormous pathways for accessing the improved separation permeance or selectivity. By subtly tailoring the dimension, shape, size, chemistry and connectivity of nanofiller or judicious combination of polymer with filler, separation performances of MMMs can be precisely manipulated for various gas separations, such as hydrogen recovery, natural-gas upgrading, carbon dioxide capture and olefin/paraffin separations, which create significant energy and environmental savings. Recently, with the flourishing of functional liquid family such as ionic liquids (ILs), deep eutectic solvents (DESs), porous liquids and metallic liquids, functional liquid derived membranes have attracted intensive interests and have been widely utilized for gas separation, particle separator, power generation, antifouling, anti-icing and even gating. Compared with macromolecular polymer, the small molecules of functional liquid possess more flexibility and structure-designability, contributing to the construction of compact and void-free interface pathways with tunable microenvironments. Moreover, the excellent attributes of self-healing nature, dynamic reconfigurability, stability, faster molecule transport in liquid than solid make functional liquids promising for more easier construction of defect-free MMMs with excellent permeances. However, MMMs with functional liquid as continuous phase have not been reported and validated. One major challenge is the difficulty of obtaining stable dispersion of nanofillers within liquids; another problem is the precipitation of nanofillers during membrane fabrication.

On the other hand, engineering interfaces by regulating polymer-nanofiller interactions is the core and research mainstream of MMMs. The interface interactions not only manipulate the distribution of nanofiller but also induce the mobility and rearrangement of polymeric chains, where ideal interface pathways should avoid aggregation of nanofillers, and selectively and fast transport the target gas molecules. Unfortunately, poor interfacial compatibility always gives rise to irregular morphology and defective interface structure, such as noneselective voids, cages and polymer rigidification, which result in inferior separation performances or limited enhancement of gas permeability or selectivity. Despite the significant advances of interfacial design to improve the compatibility, the lack of understanding of the interface pathway structure severely hampers the further development of high performance MMMs, and the formation mechanism of interface pathways has never been revealed.

Herein, for the first time, as an extension and cousin of traditional polymer based MMMs, we designed and constructed an analogous mixed matrix membrane (AMMs) by utilizing reactive ionic liquid (RIL) as continuous phase instead of traditional polymer and electing graphene quantum dots (GQDs) as nanofiller via molecular-level hybridization for sub-angstrom scale ethylene/ethane (0.416 nm / 0.443 nm) separation, where the compactly low-selective (selectivity ≈1 ) and high-selective interface pathways were constructed. Currently, the ethylene/ethane separation still remains worldwide challenging, and the ethylene/ethane selectivity of previously reported MMMs are generally lower than 10, which is far from being commercially attractive. In contrast, RILs composed of IL and ethylene-facilitated transport carriers (AgNO3) warrant potential for ethylene/ethane separation and are the leading candidate as continuous phase for developing MMMs with superior performance. GQDs, as a 0D nanofiller, have merits of abundant functional groups and molecular-level size (2-10 nm), which render them with super-stable...
dispersion within RIL and intimate molecular-level mixing with the RIL matrix.\textsuperscript{[20]} As a result, the GQD/RIL AMMMs acquired significantly soared performances for ethylene/ethane separation with a combined high ethylene permeance of 371 Barrers, ethylene/ethane selectivity of 99.5, and long-term stability, which is superior to most ethylene/ethane separation membranes. More importantly, with assistance of various spectroscopic characterizations and molecular dynamics simulation, the visualization of interfacial pathway structure was conducted and its self-assembly mechanism was elucidated. To the best of our knowledge, this is the first report on the AMMMs for sub-angstrom scale precise separations as well as the in-depth elucidation of self-assembly mechanism of interfacial pathways, relieving the longstanding interface issues associated with MMMs and also paving an avenue to the novel molecule separation membranes.

Figure 1. Fabrication and characterization of GQDs. (a) Fabrication of GQD by two steps: pyrolysis of citric acid and dialysis. (b) TEM image of GQDs. (c) HRTEM images of GQDs with lattice fringes. (d) AFM image of GQDs and height profiles along the white line. (e) Size distribution of GQDs. (f) Chemical groups of GQDs characterized by ATR-FTIR spectra.

The GQDs were fabricated with a facile bottom-up method by directly pyrolyzing abundant nature-based citric acid,\textsuperscript{[21]} and then a transparent flavescent GQD suspension was obtained by the dialysis of resulting pyrolysis product, remaining super-stable even after storage for months (Figure 1a). The TEM image of GQDs revealed their dot-like morphology and displayed uniform GQD size distribution with average diameter of 5 nm, where most GQDs located in the range of 2-8 nm (Figure 1b and 1c). The HRTEM image clearly showed two different parallel lattice fringes with lattice spacings of 0.20 nm and 0.33 nm (Figure 1c), corresponding to the (100) and (002) crystal planes of sp\textsuperscript{2} graphene.\textsuperscript{[22]} The AFM image further confirmed the uniform GQDs and its corresponding height profile suggested that the thickness of GQDs was 1.5-2 nm, comprising 2-3 graphene monolayers (Figure 1d). The ATR-FTIR spectrum of GQDs was somewhat similar to precursor of citric acid, where the broad peak around 3028 cm\textsuperscript{-1} was ascribed to the stretching vibration OH, while the peaks at 1702 cm\textsuperscript{-1} and 1174 cm\textsuperscript{-1} were attributed to asymmetrical and symmetrical stretching vibrations of COOH, respectively (Figure 1f). The ATR-FTIR of GQDs indicated their abundant functional groups, which were attractive for the generation of non-covalent interactions with continuous RIL.\textsuperscript{[20]}

A novel POAN RIL containing ethylene transport carriers was voted as continuous matrix to construct AMMMs according to our previous research,\textsuperscript{[16a, 23]} which exhibited advantages of easy synthesis via proton-transfer reaction, facile tunability of carrier activity, typical protic acidic property to ensure the carrier stability and economic feasibility.\textsuperscript{[16b, 24]} Another two reported ILs of PAN and BAN were also included to elucidate the effect of matrix structure on performances of AMMMs (Figure 2a). Benefiting from abundant functional groups and weeny size, the GQDs afforded the molecular-level mixing with the RIL matrix. Therefore, the GQD/RIL membrane liquid achieved by the exchange of water with RIL remained highly stable and underwent no precipitation within one week (Figure 2b). In contrast, the mixture of RIL and graphene oxide nanosheets suffered from the nanosheet precipitation during 24 hours (Figure S1). The GQD/RIL AMMMs were easily constructed by the accommodation of GQD/RIL, membrane liquid within the porous nylon support via a pressure-based technique according to the same procedure in our previous reports (Figure 2c).\textsuperscript{[25]} Figure 2d showed the photo of GQD/RIL AMMMs, where the lucid observation of Waterloo logo further manifested the successful fabrication of GQD/RIL AMMMs. After the embedment of GQDs within RIL, the GQD/RIL AMMMs were endowed with compactly low-selective and high-selective interfacial pathways due to the self-assembly between GQDs and RIL, which was greatly manipulated by their non-covalent interactions. The low-selective interfacial pathways favored the simultaneous transport of ethylene and ethane molecules (Figure 2e), which increased the ethylene permeability. In addition, the high-selective interfacial pathways purposively facilitated the fast transport of ethylene molecules, which improved ethylene permeability and ethylene/ethane selectivity synchronously (Figure 2f). By virtue of these two different types of interfacial pathways, the GQD/RIL AMMMs achieved one-bullet-two-objects goal that the ethylene permeability was significantly increased accompanying with the enhancement of ethylene/ethane selectivity.

The microstructures of GQD/RIL AMMMs were investigated by FE-SEM and AFM. Top-view FE-SEM image of support showed its hierarchical and irregular pore structure with interconnected macropores in the range of 200 nm - 1 \(\mu\)m (Figure 2g). After membrane construction, all the support macropores were saturated by the homogeneously distributed GQD/RIL due to the positive capillary forces, where a dense and defect-free GQD/RIL layer was accumulated on the top surface of the support (Figure 2h). No visible GQDs were separated out during membrane fabrication due to molecular-level hybridization, and the addition of GQDs made it easier to obtain dense GQD/RIL layer in relative to the pure RIL based membrane (Figure S2). In comparison with GQD/RIL AMMMs, the GO nanosheets were easily separated out from the GO/RIL liquid and a clear GO layer deposited on support surface, which further verified the importance of molecular-level hybridization (Figure S3).\textsuperscript{[26]} The cross-section image of GQD/RIL AMMMs showed a sandwich structure with a fiber-penetrating interlayer, which conferred sufficient mechanical robustness. Meanwhile, the inserted image confirmed the main-body of support remained partially filled, which contributed to fast gas transport through AMMMs (Figure 2i). Furthermore, the 3D surface AFM analysis further observed the surface topography and confirmed the roughness of the
membranes (Figure 2k and Figure S2). The roughness of GQD/RIL AMMs was sharply decreased compared with the pristine support and pure RIL base membranes, which was in good coordination with the result of FE-SEM observations. Finally, the TG curves of GQD/RIL AMMs confirmed their satisfactory thermal stability (Figure S4).

The non-covalent interactions such as cation-anion electrostatic interactions and hydrogen bonding interactions between GQDs and RIL were probed by DSC, ATR-FTIR and 1H NMR characterizations, while their inductively self-assembled interfacial pathways were manifested and elucidated by molecular dynamics simulation and Multiwfn-visualization. The DSC curves suggested that glass transition temperature (Tg) obviously increased upon adding carrier into IL due to the introduction stronger cation-anion electrostatic interactions (Figure 3a). In contrast, the incorporation of GQDs into RIL contributed to the slight increase of Tg, which indicated the good compatibility between GQDs and RIL and presence of weak interactions within AMMs. The ATR-FTIR spectra of AMMs witnessed different degrees of red shifts for stretching vibrations of N-H and O-H groups with varying GQD contents, which indicated the newly formed hydrogen bonding interactions between GQD and RIL. The COOH stretching vibration of GQDs exhibited blue shifts, revealing the possible electrostatic interactions between GQDs and RIL, which were further confirmed by the blue shifts of NO3 anion within AMMs (Figure 3b and Figure S5). The 1H NMR spectra of GQD/RIL AMMs shifted to down-field, for example, the chemical shifts of N-H and O-H varied from 7.73 to 7.84 ppm and from 4.41 to 4.59 ppm, respectively, which were indicative of the hydrogen bonding interactions between RIL and GQD (Figure 3c and Figure S7). These obvious interactions rendered GQDs with molecular-level hybridization with RILs, and also induced the local arrangement of IL chains to self-assemble into the compactly low-selective and high-selective interfacial pathways, which were certified by molecular dynamics simulation.

The snapshot of the GQD/RIL AMMM bulk structure (Figure 3d) and the correspondingly splitting snapshots of IL cation and NO3 during molecular dynamics simulation (Figure S7), as well as the radial distribution functions of IL cation-NO3 anion, IL cation-cation and NO3 anion-NO3 anion (Figure S8) revealed the RIL exhibited the heterogeneous nanostructure after incorporation of GQDs, which were composed of the bi-continuous polar and apolar domains, where the NO3 anions were associated exclusively with the NH3+ to construct polar domains, whilst the adjacent alkyl groups of cations were aggregated together to construct apolar domains. The radial distribution functions verified that most of IL cation chains are staggered stacking in RIL. It was also observed that the silver ions mainly resided in polar domains or around the GQDs (Figure S9). The well-defined nanostructure of AMMs further confirmed the good compatibility and molecular-level hybridization between GQDs and RIL, which
Figure 3. Visualization of nanostructure of GQD/RIL AMMMs and correspondingly self-assembled interfacial pathways. (a) DSC curves of GQD/RIL AMMMs. (b, c) Demonstration of weak non-covalent interactions between GQD and RIL by ATR-FTIR (b) and HNMR (c) spectra. (d) Nanostructure of GQD/RIL AMMMs, where the OH group of IL cation, alkyl group of IL cation, NH$_2$ of IL cation and NO$_3$ anion, silver cation and GQD are highlighted by red, green, blue, yellow and Tiffany blue, respectively. (e) Snapshots of molecular dynamics simulations of GQD/RIL AMMMs and highlights of GQD precise distribution within RIL: C gray, H white, O red, N blue and Ag cyan, GQD yellow. (f, g) Visualization of compactly high-selective interfacial pathways and analysis of the weak non-covalent interactions. (h, i) Visualization of compactly low-selective interfacial pathways and analysis of the weak non-covalent interactions.
selectivity of POAN based AMMMs increased sharply with varying GQD concentration from 0 to 3.5wt.%. In contrast, as the GQD concentration further increased from 3.5wt.% to 7 wt.%, the ethylene permeability increased slightly but the ethylene/ethane selectivity decreased sharply, which could be probably explained by the aggregation of GQDs at its high concentration to cause undesirable interfacial defects. Specifically, the ethylene permeability and ethylene/ethane selectivity of GQD/RIL AMMMs reached up to 371 Barriers and 99.5, respectively, which was attributed to the elaborate design of interfacial pathways. The excellent performances of GQD/RIL AMMMs were further confirmed by comparing with other ethylene/ethane separation membranes (Figure 4c). The performances reported in this study well exceeded the upper bound of 2013,[16, 27] and were also superior to the previous polymer based MMMs, the traditional polymer membranes and state-of-the-art carbon molecular sieves membranes (CMS).[28] The GQD/RIL AMMMs were also far better than or comparable with the advanced IL and DES based membranes.

Fortunately, the GQD/RIL AMMMs exhibited good stability during 160 h operation under ideal ethylene/ethane mixture, which made them attractive for ethylene/ethane separation (Figure 4d). Meanwhile, the appearance of membranes and the ethylene/ethane separation performances remained unchanged after the membranes were stored in pure H2 or C2H6 atmospheres for two weeks (Figure S13), which further confirmed the great potential of GQD/RIL AMMMs for ethylene/ethane separation even suffering from H2 and C2H6 harsh atmospheres. However, it should be noted that the long-term membrane performances under real feeds of ethylene, ethane, H2, C2H6 and H2S are still needed.[29] Besides, pretreatment of mixed gas to eliminate to C2H6 and H2S contaminants before membrane separation is also a reliable method for the sake of long-term membrane stability. Finally, the effects operating conditions were also evaluated and optimized (Figure S15 and S16), where the lower operating transmembrane pressure led to higher permeability and selectivity, while the lower operating temperature resulted in higher selectivity but lower ethylene permeability.

**Figure 4.** Separation performances of GQD/RIL AMMMs for precise ethylene/ethane separation. (a) Enhancement of separation performances with GQDs in AMMMs and the effect of different ILs. (b) Evaluation of performances of AMMMs with different GQDs concentrations. (c) Comparison of GQD/RIL AMMMs with other previously reported membranes. (d) Long-term stability of GQD/RIL AMMMs for continuously operating 160 hours.

In conclusion, for the first time, advanced GQD/RIL AMMMs were fabricated by the impregnation of GQDs within RIL, where the important roles of IL structure and the concentration of GQDs were systematically evaluated. The compactly low-selective and high-selective interfacial pathways were constructed within the resulting AMMMs due to the non-covalent interactions between GQDs and RILs, which was certified by various spectral characterizations and molecular dynamics simulation. By the synergistic effects of these two different types of interfacial pathways, the GQD/RIL AMMMs exhibited an unprecedented separation performance with remarkably improved ethylene permeance of 371 Barriers and ethylene/ethane selectivity of 99.5 as well as good long-term stability for 160 h. Therefore, our pioneering attempt for in-depth elucidation of formation mechanism of interfacial pathways may relieve the longstanding interface issues associated with MMMs, the proposed prototype of low-selective and high-selective interfacial pathways can account for separation performance of most MMMs, our innovation of utilizing functional liquid as matrix for AMMMs not only extends and broadens the definition and scope of MMMs but also will offer unique prospects or encourage further exploitation on novel matrix for MMMs to accomplish precise molecular separation.

**Acknowledgements**

We acknowledge the financial support by Natural Sciences and Engineering Research Council of Canada (NSERC), University of Waterloo, Waterloo Institute for Nanotechnology, National Natural Science Foundation of China (21838008). Thank National Supercomputing Center in Shenzhen for computational facilities.

**Keywords:** Mixed matrix membranes • Ionic liquid • Graphene quantum dot • Molecular-level hybridization • Interfacial pathways


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