Sub-Angstrom Molecular Differentiation of Organic Liquids using Carbon Molecular Sieve Membranes

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High-performance membranes derived from carbon materials have shown excellent chemical resistance, high molecular selectivity and fast mass transport across the membrane. It is well-known that carbon molecular sieve (CMS) membranes are able to surpass the "polymer upper bound trade-off line" for many molecular pairs. CMS membranes with tailored ultramicropore and micropore dimensions show both high processability of polymeric membrane and the high selectivity of inorganic membranes. Moreover, slit-like transport pathways through the CMS materials translate into higher productivity (i.e., higher mass transport across a diffusion barrier) than that of cage-like zeolite structures due to the longer jump lengths between pore windows (**Fig. 1**). CMS membranes have been proven to be effective in a variety of gas separation processes such as olefin/paraffin separation, natural gas separation and air separations. However, the low fluxes observed in CMS hollow fibers (due to porous substructure collapse during pyrolysis) hinder scale-up of CMS membranes for industrial separation applications. The performance of carbon molecular sieve separation membranes, which exploit the effect of mass transport across a selective diffusion barrier in order to separate molecules, can be improved by reducing the thickness of the membrane. In this study, a novel post-spinning cross-linking treatment is introduced to maintain the asymmetric porous morphology in CMS hollow fiber membranes even after high temperature pyrolysis processes (**Fig. 2**). A dual-layer dry-wet spinning process was used to prepare asymmetric poly(vinylidene fluoride) (PVDF) hollow fibers with thin selective skin layers. Cross-linking of as-spun hollow fibers "locked-in" the porous substructure and the fiber morphology remained unchanged after the cross-linking process (**Fig. 2**). Moreover, this technique effectively prevented substructure collapse in asymmetric CMS hollow fiber membranes. These asymmetric CMS hollow fiber membranes have significant potential for utilization in organic solvent separations, as they exhibit essentially zero solvent-induced swelling and possess high selectivity for similarly sized molecules (**Fig. 3, 4**).

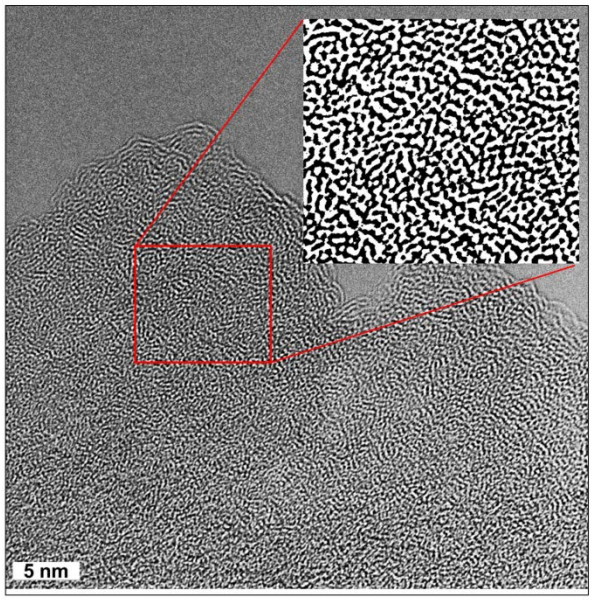


Figure 1: Nanostructure of carbon molecular sieve membranes from this work

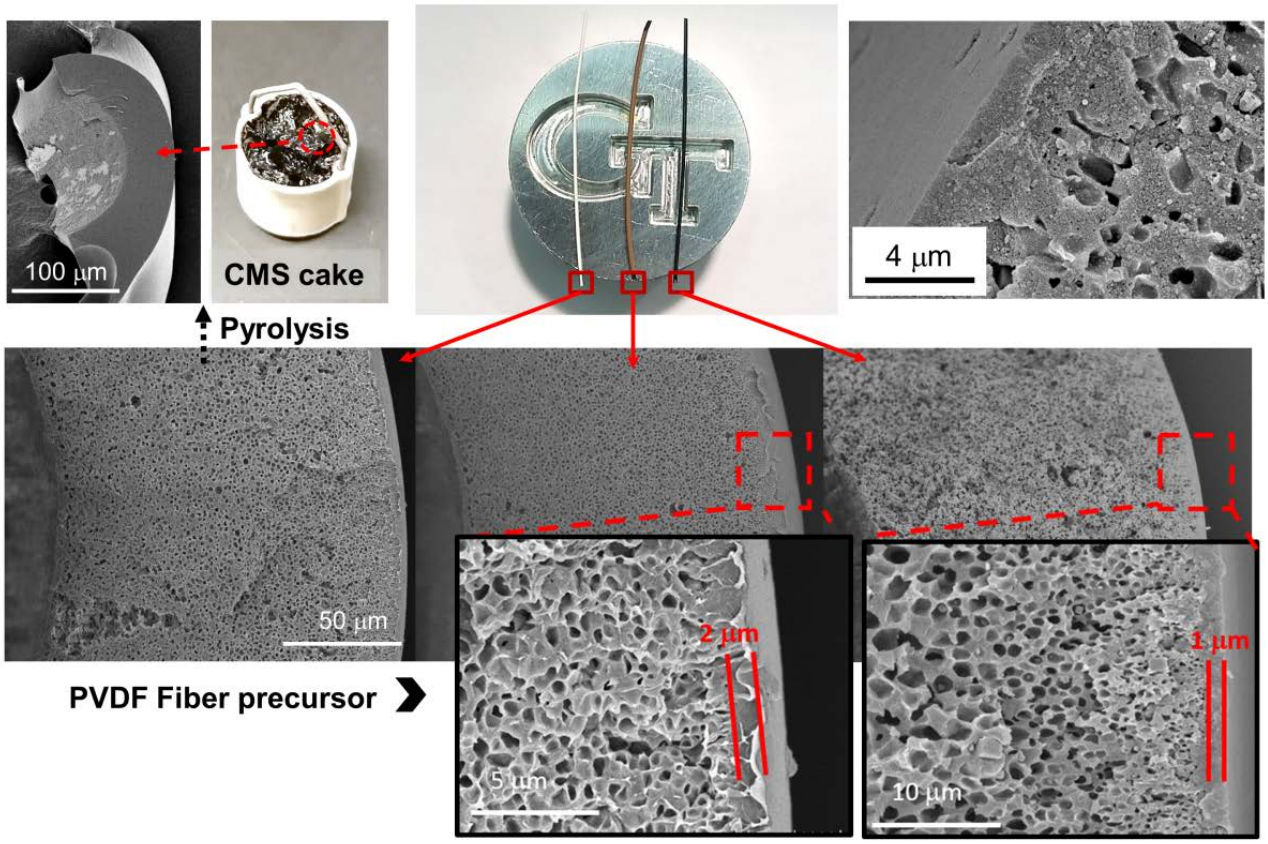


Figure 2: Neat PVDF hollow fibers (*left*) are crosslinked (*middle*), which preserves the porous asymmetry of the fibers when converted to carbon molecular sieve membranes (*right*)

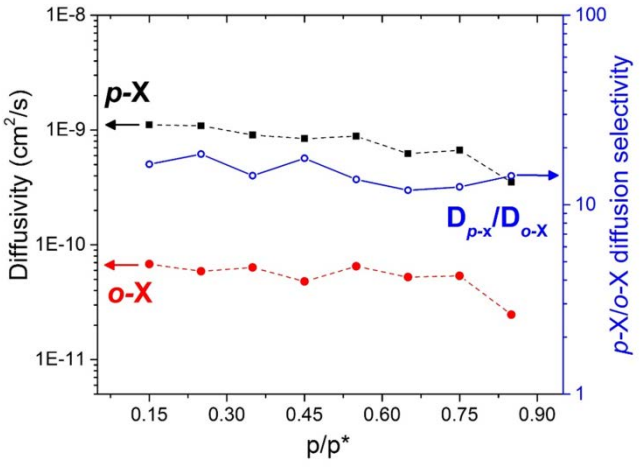


Figure 3: Diffusion selectivity of carbon molecular sieve membranes for p-xylene (p-X)/o-xylene (o-X)

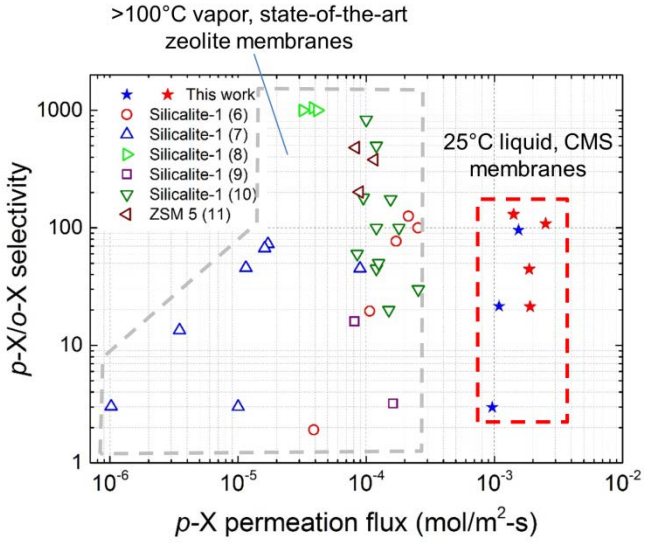


Figure 4: Mixture permeation performance of CMS membranes when challenged with p-xylene (p-X) and o-xylene (o-X)