

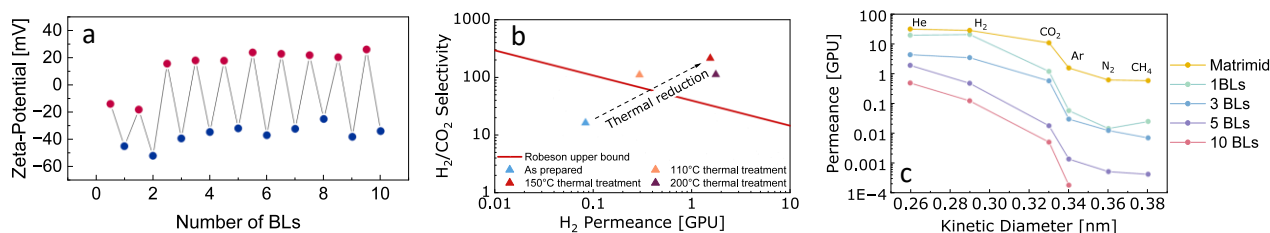
Graphene Oxide Multilayers for Next-Generation Thin Film Gas Separation Membranes

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Carbon capture and storage (CCS) is a key short-term countermeasure to reduce greenhouse gas emissions, which are among the main contributors to global warming. In this context, polymeric membranes offer an energy-efficient alternative to conventional techniques for CO₂ separation, thanks to their versatility, cost-effectiveness, and ease of processing. However, their gas separation performance is inherently limited by the trade-off between permeability and selectivity, as depicted in the Robeson upper bound. Since gas permeance is inversely proportional to the membrane thickness, reducing the thickness is an effective strategy to enhance gas transport rates and minimize material usage. This work investigates a strategy to overcome the Robeson limit by integrating thin polymeric films with graphene oxide (GO) multilayers. GO, with its monoatomic-layer structure and large lateral size, enables molecular sieving by allowing the passage of small gas molecules while acting as an efficient barrier to larger species. Its oxygen containing functional groups ensure good water dispersibility, making GO particularly suitable for Layer-by-Layer (LbL) deposition. LbL is a robust technique for the controlled fabrication of homogeneous multilayer coatings, achieved by the alternative adsorption of negatively charged GO sheets and a polycationic solution, such as poly(diallyldimethylammonium chloride). This study exploits the versatility of the LbL method by applying GO multilayers to dense polymer membranes (50 μm thickness) and extending this deposition onto thin polyimide films with thicknesses below 10 μm, fabricated via knife casting. These ultrathin films offer reduced mass transfer and are ideal candidates for high-performance membrane development, but they pose significant challenges in terms of mechanical robustness, surface defect sensitivity, and solvent interactions. The homogeneity of the coatings is assessed by zeta potential analysis and microscopy techniques (AFM and SEM). Gas permeation properties are evaluated through ASTM D1434-82 standard tests and can be tailored by adjusting the number of bilayers of the coating, GO dispersion concentration, and by applying thermal treatments. In particular, thermal reduction treatment introduces nanopores, boosting the selectivity up to 200 for H₂/CO₂ and 1000 for H₂/CH₄. The combination of reduced thickness and tunable selective coatings offers a promising pathway for designing advanced membrane, with clear potential in CCS and demanding gas separation.



Keywords: CCUS, GO-based membranes, permeability, Layer-by-Layer, ultrathin films

