

Gas Separation

Using Nanoporous Single-Layer Graphene Membranes

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Nanoporous single-layer graphene is regarded as a highly promising membrane material for gas separation due to its atomic thickness. When single-layer graphene contains a high density of gas sieving nanoscale pores, it can exhibit both a high gas permeance and a high selectivity, which is beneficial for reducing the cost of gas separation processes. However, significant challenges remain for matching theoretical predictions with experimental measurements and for the real application of graphene membranes for gas separations. To tackle these challenges, in this thesis, I carry out both theoretical and experimental investigations to understand and to improve the gas separation properties of nanoporous single-layer graphene membranes.

On the theoretical side, first, using molecular dynamics simulations, I investigate the mechanism of activated gas permeation through sub-nanometer graphene pores when energy barriers exist for pore crossing. An analytical framework is developed based on transition state theory to predict the gas permeance through a given graphene nanopore. Second, I extend the analytical framework mentioned above from sub-nanometer pores to larger pores. I formulate the transport kinetics associated with the direct impingement from the bulk and with the surface diffusion from the adsorption layer on graphene, and then combine them to predict the overall gas permeation rate using a reaction network model. Last, the theory developed above is applied to predict the total gas permeance through a pore ensemble with a realistic pore size distribution, which is generated by Kinetic Monte Carlo simulations. It is shown that the total gas permeance through a pore ensemble is dominated by a small fraction of large nanopores having low energy barriers of pore crossing.

On the experimental side, I demonstrate temperature-dependent gas mixture separation using single-layer graphene membranes. The membranes contain intrinsic nanopores formed during the chemical vapor deposition synthesis of graphene. I investigate the formation mechanism of the intrinsic graphene nanopores, and systematically control the density of the intrinsic graphene nanopores while maintaining appropriate pore sizes for gas sieving. It is found that nanoscale molecular fouling of the graphene surface where graphene pores are partially blocked by hydrocarbon contaminants under experimental conditions, affects both gas permeance and selectivity.