Large-area single layer graphene membrane by crack-free transfer for gas mixture separation

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Nanoporous single-layer suspended graphene films have been predicted to be the ultimate membranes, capable of providing orders of magnitude higher permeance that that from the state-of-the-art membranes[1-3]. In this respect, the development of methods of fabricate crack- and tear-free suspended graphene films that possess size-selective pores with a narrow pore-size-distribution is highly attractive. Here we report a highly-scalable, nanoporous carbon mediated, crack- and tear-free graphene transfer technique, leading to successful fabrication of 1 mm^2-sized single-layer graphene membranes. Attractive gas sieving performance (H_2 permeance up to 4.1 x 10^{-7} mol m^{-2} s^{-1} Pa^{-1} with H_2/CH_4 selectivities up to 25) were achieved from graphene film with a minuscule porosity of 0.025%. Membranes performance of stable during multiple cycles of heating and cooling, and at least up to moderate transmembrane pressure differences (7 bar). Use of gas mixture feed did not reduce either the H_2 permeance or the H_2/CH_4 separation selectivity. Finally, we report post-synthetic performance tuning of the graphene membrane by ozone-functionalization, improving H_2 permeance (up to 300%) as well as H_2/CH_4 selectivities (up to 150%, Fig. 1). Overall, the methods developed here can be instrumental to realize large-scale deployment of the nanoporous two-dimensional membrane.

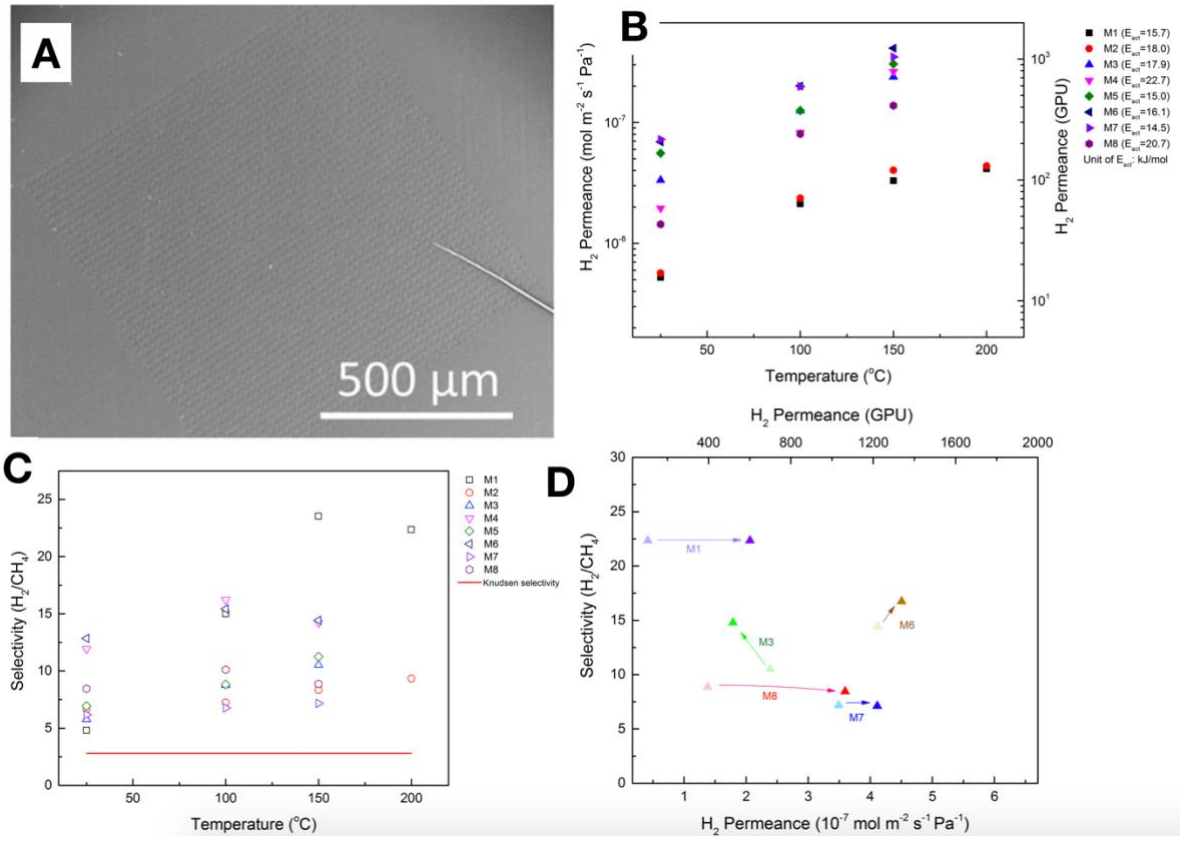


Fig. 1: Development of crack-free, gas sieving single-layer graphene membranes. A) SEM image of a single-layer chemical vapor deposition derived graphene film on a macroporous substrate with an area of 1 mm^2. Temperature-dependent H_2 permeances (B) and H_2/CH_4 separation selectivities (C) from 8 different membranes studied here. The extracted activation energies for the H_2 transport for the 8 membranes is provided in the legend of (B). D) A performance optimization trajectory for the single-layer graphene membrane obtained using in-situ ozone functionalization.

References

1. Jiang, D.-E., Cooper, V. R. & Dai, S. Porous graphene as the ultimate membrane for gas separation. *Nano Lett.* **9,** (2009).
2. Koenig, S. P., Wang, L., Pellegrino, J. & Bunch, J. S. Selective molecular sieving through porous graphene. *Nat. Nanotechnol.* **7,** 728–732 (2012).
3. Celebi, K. *et al.* Ultimate permeation across atomically thin porous graphene. *Science* **344,** 289–92 (2014).