How permeable is the impermeable graphene?

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Abstract

It is widely believed that, despite being one-atom thick, graphene and other defect-free 2D crystals are completely impermeable to all gases and liquids. This statement has extensively been justified in theory. In addition, the lowest detection limit (that is, highest sensitivity) achieved in the past experiments supporting graphene's impermeability was about 10^5–10^6 helium atoms s^{-1} for micrometer-scale membranes, or 10^{17}–10^{18} atoms m^{-2} s^{-1}.
In this talk, I will present my recent research[1-3] on the topic "How permeable is the impermeable graphene?" Using monocrystalline container made from atomically flat graphite, which is tightly sealed with graphene, our team have achieved measurements that put the permeation limit through 2D materials at 8–9 orders of magnitude lower than previously, such that we would discern (but did not observe) just a few helium atoms per hour crossing micrometer-size membranes. This detection limit is also valid for all other gases tested (neon, nitrogen, oxygen, argon, krypton and xenon), except for hydrogen. Hydrogen shows noticeable permeation, even though its molecule is larger than helium and should experience a higher energy barrier. This observation is attributed to a two-stage process that involves dissociation of molecular hydrogen at catalytically active graphene ripples, as shown by experiments[3], followed by adsorbed atoms flipping to the other side of the graphene sheet with a relatively low activation energy of about 1 electronvolt, a value close to that previously reported for proton transport[4,5].
The described device can identify only a few gas molecules per hour piercing a micrometer size membrane. This remarkable sensitivity allows detection of subtle transport phenomena that were not possible to observe previously, as exemplified by the "anomalous" hydrogen-gas permeation through defect-free graphene as discussed above. On the other hand, to move a step forward and make the generally "impermeable" graphene not only "permeable" but also highly "selective" toward gas molecules with a tiny difference in size, our team have developed a controllable perforation technique, which involves a short-time exposure of the graphene membrane to a low-energy electron beam. Using the same monocrystalline containers, we are able to study gas transport through the created individual graphene pores with an effective diameter of only 2 angstroms, or about one missing carbon ring. Helium and hydrogen permeate easily through these pores whereas larger molecules such as xenon and methane are blocked. Permeating gases experience activation barriers that increase quadratically with the kinetic diameter, and the transport process crucially involves surface adsorption.
The presented research would be important not only for fundamental understanding of the newly emerged physics and chemistry regarding molecular transport under atomic scale confinement, but also for developing new technologies for sustainable applications in energy and environment (for example, highly sensitive molecular detection and sensing techniques, inexpensive and nonmetallic graphene-based catalysts, and angstroporous 2D membranes for filtration and separation).

References

[1] Sun, P. Z., et al. Nature 579 (2020), 229–232.
[2] Sun, P. Z., et al. Nat. Commun. 12 (2021), 7170.

[3] Sun, P. Z., et al. PNAS (2023), in press.
[4] Hu, S. et al. Nature 516 (2014), 227–230.
[5] Lozada-Hidalgo, M. et al. Science 351 (2016), 68–70.