

## CHALLENGES IN GRAPHENE NANOPORE- (NANOWINDOW)-BASED MOLECULAR SEPARATIONS: A CRITICAL REVIEW

Fernando Vallejos-Burgos\*, Carlos A. León y León

*Morgan Advanced Materials  
Carbon Science Centre of Excellence, State College, PA 16803, USA*

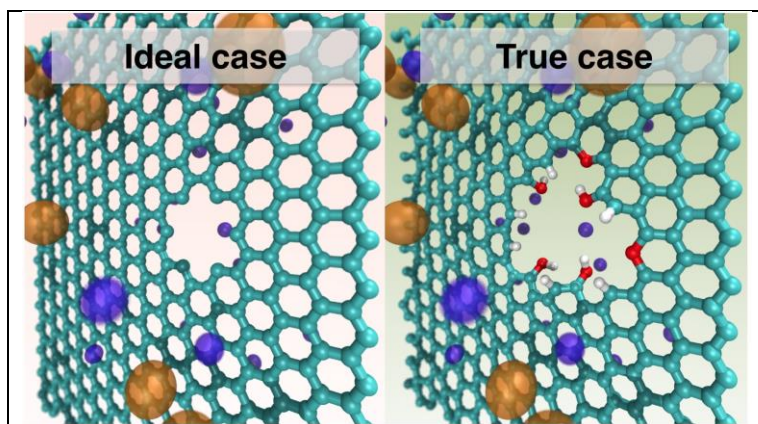
\*Presenting author's e-mail: fvb@vallejos.cl, Fernando.VallejosBurgos@morganplc.com

### Introduction

Opening holes in a graphene layer (nanowindows) can arguably create the thinnest possible separation membrane. This has been amply explored and exploited almost since the isolation of graphene in 2004, as clearly shown in the exponential growth in the number of publications claiming to use graphene as a single-layer separation membrane.<sup>1</sup> However, the knowledge and synthesis techniques have, to this date, not been sufficiently developed to produce an efficient separation system. In this literature review we analyze and discuss the main reasons for this outcome and will provide some guidelines to address areas where possible advances can be achieved to take us closer to producing an ideal membrane-based molecular separation system.

### Discussion

It is known that the experimentally synthesized membranes in most cases do not provide anywhere near the separation selectivities or permeation rates predicted by computer simulations. An important cause of this is that most of the computer simulation models currently available are too simplistic to account for what happens in a realistic situation.



**Figure 1.** The simplest model of a graphene nanowindow (left) is not enough, anymore, to model all the relevant phenomena occurring at the nanoscale. More advanced models are required (right) that take into consideration the heteroatoms, partial charges, nanowindow asymmetry and flexibility of the framework.

Most molecular dynamics (MD) models ignored<sup>2-10</sup> many relevant phenomena occurring at the nanoscale level (see **Figure 1**), such as the presence of heteroatoms, a lack of nanowindow symmetry<sup>11</sup>, partial electric charges<sup>12</sup> and flexibility of the graphene network. Despite this, there are examples in the literature where some authors acknowledged the real behaviour of practical nanowindows and recognized properties which would not have been identified if only an ideal model was considered.<sup>13-16</sup>

A powerful workaround to these limitations is to directly employ *ab-initio* quantum chemistry methods

such as density functional theory (DFT) to estimate the permeation energies of molecules through nanowindows.<sup>17,18</sup> Once the surface chemistry of the nanowindow rim is defined, well-posed DFT

simulations do not need to make strong assumptions on the system, and inherently must consider all types of interactions. Their obvious drawback is that they are many orders of magnitude more computationally expensive than MD; this has restricted the use of DFT to modelling single molecule permeation behaviour instead of encompassing up to thousands of molecules as in MD.

## Conclusions

We show how the literature on molecular permeation through graphene nanowindows has matured from very simple molecular dynamics simulations, which neglected relevant molecular phenomena, to richer and more rigorous simulations which have identified and account for new molecular permeation mechanisms.

## References

1. Malekian, F., Ghafourian, H., Zare, K., Sharif, A. A. & Zamani, Y. Recent progress in gas separation using functionalized graphene nanopores and nanoporous graphene oxide membranes. *Eur. Phys. J. Plus* **134**, 212 (2019).
2. Suk, M. E. & Aluru, N. R. Water Transport through Ultrathin Graphene. *J. Phys. Chem. Lett.* **1**, 1590–1594 (2010).
3. Wells, D. B., Belkin, M., Comer, J. & Aksimentiev, A. Assessing Graphene Nanopores for Sequencing DNA. *Nano Lett.* **12**, 4117–4123 (2012).
4. Hu, G., Mao, M. & Ghosal, S. Ion transport through a graphene nanopore. *Nanotechnology* **23**, 395501 (2012).
5. Chen, H. & Ruckenstein, E. Nanomembrane Containing a Nanopore in an Electrolyte Solution: A Molecular Dynamics Approach. *J. Phys. Chem. Lett.* **5**, 2979–2982 (2014).
6. Li, D. *et al.* Separation of Hydrogen Gas from Coal Gas by Graphene Nanopores. *J. Phys. Chem. C* **119**, 25559–25565 (2015).
7. Darvishi, M. & Foroutan, M. Mechanism of water separation from a gaseous mixture via nanoporous graphene using molecular dynamics simulation. *RSC Adv.* **5**, 81282–81294 (2015).
8. Ohba, T. Consecutive Water Transport through Zero-Dimensional Graphene Gates of Single-Walled Carbon Nanohorns. *J. Phys. Chem. C* **120**, 8855–8862 (2016).
9. Strong, S. E. & Eaves, J. D. Atomistic Hydrodynamics and the Dynamical Hydrophobic Effect in Porous Graphene. *J. Phys. Chem. Lett.* **7**, 1907–1912 (2016).
10. Strong, S. E. & Eaves, J. D. The Dynamics of Water in Porous Two-Dimensional Crystals. *J. Phys. Chem. B* **121**, 189–207 (2017).
11. Sint, K., Wang, B. & Král, P. Selective Ion Passage through Functionalized Graphene Nanopores. *J. Am. Chem. Soc.* **130**, 16448–16449 (2008).
12. Cohen-Tanugi, D. & Grossman, J. C. Water Desalination across Nanoporous Graphene. *Nano Lett.* **12**, 3602–3608 (2012).
13. Vallejos-Burgos, F., Coudert, F.-X. & Kaneko, K. Air separation with graphene mediated by nanowindow-rim concerted motion. *Nature Communications* **9**, 1812 (2018).
14. He, Z., Zhou, J., Lu, X. & Corry, B. Bioinspired Graphene Nanopores with Voltage-Tunable Ion Selectivity for Na<sup>+</sup> and K<sup>+</sup>. *ACS Nano* **7**, 10148–10157 (2013).
15. Nieszporek, K. & Drach, M. Alkane separation using nanoporous graphene membranes. *Phys. Chem. Chem. Phys.* **17**, 1018–1024 (2014).
16. Qu, Y., Li, F., Zhou, H. & Zhao, M. Highly Efficient Quantum Sieving in Porous Graphene-like Carbon Nitride for Light Isotopes Separation. *Scientific Reports* **6**, srep19952 (2016).
17. Jiang, D., Cooper, V. R. & Dai, S. Porous Graphene as the Ultimate Membrane for Gas Separation. *Nano Lett.* **9**, 4019–4024 (2009).
18. Ambrosetti, A. & Silvestrelli, P. L. Gas Separation in Nanoporous Graphene from First Principle Calculations. *J. Phys. Chem. C* **118**, 19172–19179 (2014).