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## Functionalized two-dimensional membranes and materials for solar-to-fuel devices: a multiscale computational approach

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## ***CHAPTER 1***

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# Introduction

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# 1.1 The 2D materials quest in the energy transition

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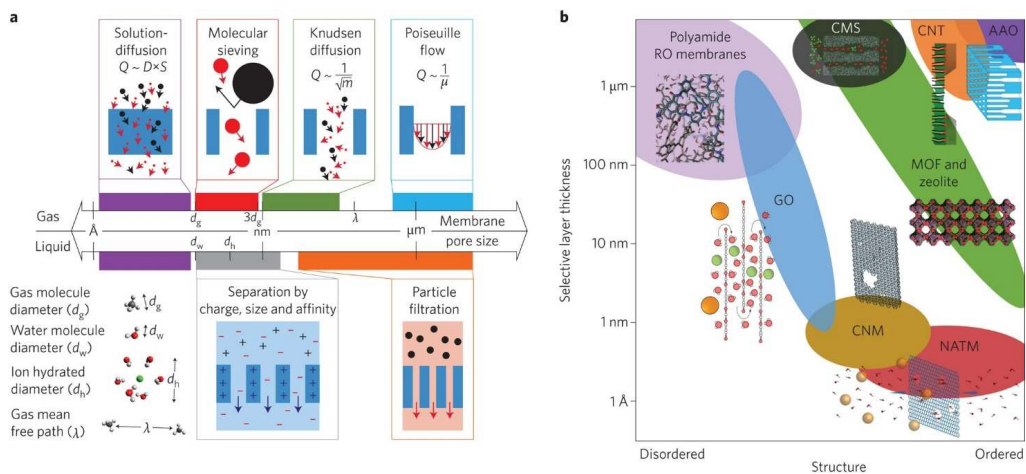
Nowadays, there is an urgent need to find practical solutions for sustainable global energy supplies to preserve our world and its ecosystem. The genetic evolution of living beings and climate change are undeniably majorly influenced by the choices made by human society. It is essential to have foresight in future decisions, as responsible participants in nature, by fostering genuine collaboration among various sectors of society. Reaching an agreement between disciplines such as science, politics, economics, philosophy, history, psychology, and so on, with a guiding principle of fair, ethical, and unified progress, lays the foundation for understanding the needs of our world, ensuring a better future for all beings. Science plays a pivotal role in the advancements and discoveries, particularly in the field of energy conversion of recent decades, demonstrating the potential of research. In material science, the research and device production at the atomic scale represents a cornerstone for yet another potential scientific revolution, and protection and respect of our and only Planet.

## *1.1.1 The advent of the 2D material in membrane and transport technology*

Just 20 years ago, the isolation of graphene was reported by Novoselov and Geim,<sup>1,2</sup> which sparked the beginning of the atomic two-dimensional (2D) material revolution in Science.<sup>3,4</sup> Following this discovery, numerous other non-carbon-based 2D materials with remarkable chemical-physical properties were developed, such as hexagonal boron nitride (hBN),<sup>5</sup> different transition metal chalcogenides (TMCs),<sup>6,7</sup> and others like germanene, silicene, phosphorene and oxides. Recently, new classes of 2D materials have emerged with intriguing properties, notably covalent organic frameworks (COFs),<sup>8</sup> metal-organic frameworks (MOFs),<sup>9</sup> MXenes,<sup>10</sup> heterostructures<sup>11</sup> and novel carbon-based 2D materials.<sup>12,13</sup> This increased focus on 2D materials can largely be attributed to their potential for various technological applications, such as electronic devices, barriers, sensors, catalysis, energy conversion and storage devices, where their exceptional electrical, optical, chemical, and thermal properties can be fully utilized.<sup>14–16</sup> 2D materials offer an attractive societal prospect in advancing the design of novel energy devices and accelerating an efficient energy transition.<sup>17</sup>

This Ph.D. dissertation primarily focuses on computationally investigating new 2D-structures for use in membrane fields. The discovery of graphene<sup>18</sup> opened up new

possibilities in atomistic technologies<sup>19</sup> due to its exceptional atomic-scale properties,<sup>20,21,22</sup> offering the potential for atomistic tunable nanopores and thickness,<sup>23</sup> to be used as efficient membranes.<sup>16</sup> Studying the transport mechanism at the molecular level helps optimize membrane characteristics to achieve an optimal balance between selectivity and permeability. Membranes accomplish selective transport through various mechanisms effective across different length scales (Figure 1.1). Selectivity arises from differences in the solubility and diffusivity of various species within the membrane material. To address potential trade-offs, additional mechanisms need to be explored.<sup>24,25</sup> In solution, transport through 2D- or 3D- materials is influenced by specific molecular properties (Figure 1.1a).<sup>26</sup> This dissertation focuses mainly on electrostatic interactions and steric effects. Transport processes in membranes are complex, but the use of Nanostructured Architectures for Transport Membranes (NATMs) provides an ideal solution for achieving a good balance between permeability and selectivity of ions and small molecules in water solutions (Figure 1.1b).<sup>16</sup>



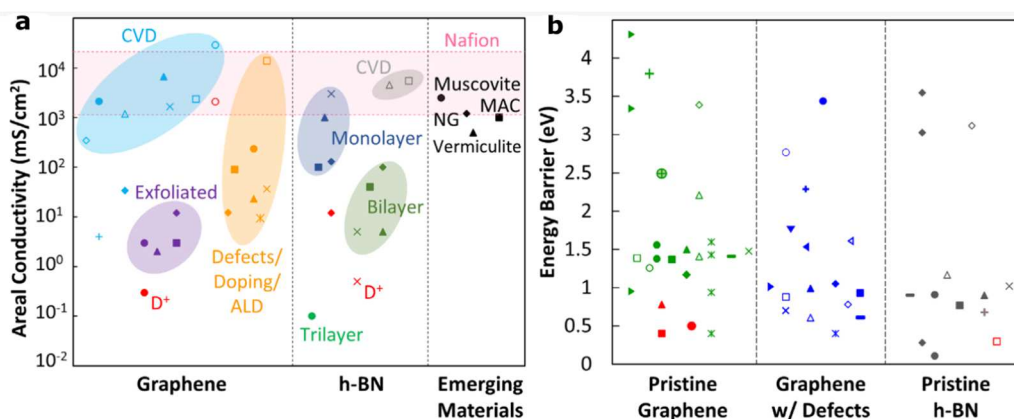
**Figure 1.1.** **a**, The membrane transport mechanisms depend on the length scale. The graph illustrates potential separation mechanisms for gas and liquid based on increasing pore size in the membrane. The sizes of gas molecules, water and solvated ions are schematically shown in the bottom left. **b**, The thickness of the selectivity layer varies in different materials based on the structure order/disorder. This Ph.D. dissertation focuses on Nanostructured Architectures for Transport Membranes (NATMs).<sup>16</sup> This figure is adapted from a study by Wang, L. *et al.*, Fundamental transport mechanisms, fabrication, and potential applications of nanoporous atomically thin membranes. *Nature Nanotech* 12, 509–522 (2017). Reprinted with permission from Springer Nature.

### *1.1.2 Proton Exchange Membranes: state-of-the-art, challenges, design requirements*

In general, an important requirement in designing an efficient proton exchange membrane (PEM) based on graphene is to achieve a balance between proton permeability and selectivity. Currently, Nafion-based membranes are considered the best for transporting protons in PEMs.<sup>27</sup> However, Nafion faces challenges such as reactant crossover, which leads to the unwanted leakage of reactants reducing selectivity, swelling, and the need for highly hydrated environments to facilitate proton conduction.<sup>27,28</sup> Additionally, the need for hydration limits the maximum operational temperature, hindering efforts to improve efficiency.<sup>27–29</sup> Using 2D-materials along with Nafion appears a promising route to address selectivity issues, but it also decreases proton conductance.<sup>30–33</sup> Furthermore, the introduction of 2D materials can potentially raise the expenses of PEMs fabrication.<sup>34</sup> Further investigation is required to evaluate the long-term durability and chemical stability of 2D materials under actual operating conditions in fuel cells.<sup>35</sup> Currently, the most promising approach to enhance PEM features is a hybrid graphene-Nafion “sandwich” approach.<sup>36</sup>

The presence of defects, nanopores, and vacancies in a 2D-material can enhance the balance between permeability and selectivity in membranes, and overcome the limits of Nafion. Graphene is considered an excellent candidate for an optimal use as a 2D-PEM. A few years ago, Geim and coworkers reported proton permeation through pristine graphene, as shown in Figure 1.2a.<sup>37</sup> This behavior was attributed to quantum tunneling effects, which meticulously were theoretically investigated by Tkatchenko and coworkers.<sup>38</sup> Theoretical investigations have suggested various mechanisms, such as hydrogenation or protonation, and diverse transport routes, including physisorption or chemisorption, to explain the observed proton conductivity in graphene.<sup>38–43</sup> The hydrogenation of the graphene and the resulting distortion of the graphene plane can reduce the energy barrier for the proton penetration (see also Figure 1.2b).<sup>40,44</sup> However, the prevailing view in the scientific community suggests that only the presence of defects, vacancies, and nanopores can enable an efficient proton permeation,<sup>45–47</sup> as extensively demonstrated in the case for chemical vapor deposition (CVD) graphene.<sup>44,48</sup> A recent significant study by Unwin and coworkers clarified on this dilemma, confirming that the presence of defects allows proton transport through CVD graphene in a Nafion sandwich.<sup>49</sup> This interpretation on CVD graphene with defects aligns with the measured proton conductivity in exfoliated graphene by Geim and coworkers.<sup>37</sup> In practical applications, large-area 2D materials synthesized through scalable methods like CVD will be necessary, however, these methods inevitably

introduce the overmentioned intrinsic defects such as vacancies, and nanopores, which may impact the ratio of permeability- to- selectivity ratio in proton transport.<sup>44,45,47,48,50-52</sup> Therefore, a list of various experimental strategies can be employed to carefully generate specific defect types and sizes, *i.e.* such as ion beam bombardment,<sup>47,53</sup> and plasma treatment.<sup>54</sup> The size and shape of the experimentally detected nanopores<sup>55,56</sup> are consistent with a range of vacancies that can allow the flow of protons while excluding by steric hindrance larger ions with bigger solvation shells ( $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Cl}^-$ ) and small molecules like water.<sup>57,58</sup> Moreover, the inclusion of functionality at the edge of a nanopore, defects and vacancies appears as an appealing strategy<sup>59-63</sup> to adjust the selectivity and transport properties through a 2D-material like graphene. An alternative self-assembly approach using specific building blocks can be utilized for the rational design of 2D-materials with tunable nanopores, defects and vacancies.<sup>8-13</sup> Finally, the exponential growth of Machine Learning (ML) techniques in designing new efficient 2D-materials will significantly aid in the development of the membranes field.<sup>64</sup>



**Figure 1.2.** **a**, Experimental measurements of areal proton conductivity have been reported in the literature for various materials. **b**, Energy barriers for proton transport have been calculated and experimentally determined for pristine graphene, graphene with defects, and pristine h-BN. These calculations and measurements offer insights into the energy needed for proton transport through these materials.<sup>15</sup> This information is adapted from Kidambi, P. R., Chaturvedi, P. & Moehring, N. K. Subatomic species transport through atomically thin membranes: Present and future applications. *Science* 374, eabd7687 (2021).<sup>15</sup> Reprinted with permission from AAAS.

### *1.1.3 The example of photoelectrochemical cells and the alternative role of 2D materials*

Artificial photosynthesis is a promising solution for replacing fossil fuels with clean and sustainable solar fuels.<sup>65,66</sup> In this field 2D-materials are of interest not only as PEMs, but also when combined with water oxidation catalysts (WOCs) for effective and stable use in heterogenous catalysis. Recently, there have been a few examples of Ruthenium-based catalysts anchored to 2D-graphitic surfaces that have shown promising results for hydrogen production.<sup>67-69</sup> These hybrid molecular systems, based on 2D-materials and WOCs, can contribute to the advancement of photoelectrochemical cells and the utilization of 2D materials not only for separation purposes but also as anodic surfaces that can be functionalized to achieve overall efficient and sustainable solar fuel production.

### *1.1.4 Aim of the Thesis and Outline*

Proton permeation through atomically thin graphene and 2D materials has the potential to lead to groundbreaking advancements in various fields. Our understanding of transport mechanisms is continually evolving, driven by advancements in measurement techniques and resolution.<sup>33</sup> The integration of 2D materials into proton exchange membranes (PEMs) for use in flow batteries, fuel cells, and proton pumps is expected to become feasible within the next 5 to 10 years.<sup>26,33</sup> As the production of these membranes increases, economies of scale can be achieved, resulting in cost savings and improved energy efficiency over their operational lifespan. Further research is necessary to advance these applications successfully. The primary objective of this dissertation is to develop and implement a multiscale computational approach for the systematic design of new functionalized 2D materials and stable 2D molecular aggregates, which can be utilized in ion transport, optoelectronics, and surface chemistry.

An overview of the computational methods used in this dissertation is presented in **Chapter 2**.

**Chapter 3** describes a computational study that examines the self-assembly of two different molecular polycyclic aromatic hydrocarbons (PAH) systems: a rigid core-rim hexa(2,2'-dipyridylamino) hexabenzocoronene (HPAHBC) and a flexible core-rim 2,2':6',2''-terpyridine (TPY). The study uses a classical Molecular Dynamics (MD) method to explore how these molecular building blocks self-assemble at the water-to-air interface. By combining MD with Density Functional Theory (DFT) and Density

Functional-based Tight Binding (DFTB) methods, the study accurately explains the main molecular interactions that occur during the aggregation process, emphasizing the significant impact that even small differences in molecular structures can have on the aggregation.<sup>12</sup>

In **Chapter 4**, an investigation was conducted on the molecular aggregation of two molecular systems under Langmuir-Blodgett-like compression conditions. This analysis helped in understanding the packing and determining the mean molecular area (MMA) of the resulting molecular aggregates along the surface-pressure isotherm. The molecular systems, decacyclene, and the B, B', B''-trianthryl-N, N', N''-tri(i-propyl) arylborazine, tend to form ordered aggregates on the water surface based on their intermolecular properties. Upon compression, the molecules undergo a reorganization process, leading to the formation of molecular assemblies with different orientations. The isotherms obtained from the computational analysis are compared with experimental data. In addition, the photochemical properties such as absorption and fluorescence spectra of the B, B', B''-trianthryl-N, N', N''-tri(i-propyl) arylborazine system are estimated computationally and compared with experimental data. The successful integration of Density Functional Theory (DFT) and Molecular Dynamics (MD) techniques demonstrates their efficiency in *de novo* design of 2D materials, as seen in the accurate prediction of the self-assembly behavior of molecular building blocks at the water surface under Langmuir-Blodgett-like compression conditions.<sup>13</sup>

In **Chapter 5** a Reactive Force Field (ReaxFF) method was used to study the Grothuss-like proton hopping mechanism in water solvated graphene nanopore systems. The metadynamics enhancing sampling approach was employed to investigate the energy barriers associated with proton transport through the graphene nanopore systems. By combining the reactive force field and enhancing sampling methods, I was able to analyze the free energy landscape of proton movement through graphene nanopores along specific reaction coordinates. The study also showed how benzenesulfonic functionalization can enhance both proton permeability and selectivity through graphene nanopores, achieving a theoretical proton diffusion coefficient comparable to or even higher than that of the state-of-the-art proton exchange membrane (PEM), Nafion.

In **Chapter 6**, a Ruthenium-based water oxidation catalyst (RuWOC) has been attached to a graphitic surface (GS) using CH- $\pi$  stacking to mimic a catalytic oligomeric structure that has been recently studied and found to be stable and efficient in the water splitting



reaction.<sup>108,109</sup> Through the use of DFT-based MD plus metadynamics sampling methods, the Proton Coupled Electron Transfer (PCET) process from the Ru<sup>IV</sup>WOC to Ru<sup>V</sup>WOC systems has been described. The CH- $\pi$  stacking not only acts as a connection between the RuWOC and the GS to stabilize the catalytic dyad system but also helps facilitate the PCET process through potential vibronic couplings. Further research in this field shows potential for developing highly efficient catalytic systems for converting solar energy into clean and storable fuels.

Finally, **Chapter 7** of my Ph.D. dissertation presents the conclusions and two types of ongoing research on force field parametrization. One aspect involves the development of an electron reactive force field (eReaxFF) for a dye-RuWOC molecular system. This aims to enable the study of the PCET event at a pseudoclassical computational level beyond DFT-based MD, allowing for longer time scales.<sup>111</sup> Additionally, a Coarse-Grained (CG) parametrization of a PAH, hexabenzocoronene (HBC) using Martini 3.0 has been explored to investigate molecular aggregation in an HBC-based nanowire at the water-to-air interface, which is computationally challenging at the atomistic level.<sup>112</sup>

## 1.2 References

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1. Novoselov, K. S. *et al.* Electric Field Effect in Atomically Thin Carbon Films. *Science* **306**, 666–669 (2004).
2. Geim, A., Novoselov, K. The rise of graphene. *Nature Mater* **6**, 183–191 (2007).
3. *Advanced Applications of 2D Nanostructures: Emerging Research and Opportunities*. (Springer Singapore, Singapore, 2021). doi:10.1007/978-981-16-3322-5.
4. Wu, Z., Qi, J., Wang, W., Zeng, Z. & He, Q. Emerging elemental two-dimensional materials for energy applications. *J. Mater. Chem. A* **9**, 18793–18817 (2021).
5. Zhang, K., Feng, Y., Wang, F., Yang, Z. & Wang, J. Two dimensional hexagonal boron nitride (2D-hBN): synthesis, properties and applications. *J. Mater. Chem. C* **5**, 11992–12022 (2017).
6. He, Y. *et al.* Self-gating in semiconductor electrocatalysis. *Nat. Mater.* **18**, 1098–1104 (2019).
7. Liu, Y. *et al.* Self-optimizing, highly surface-active layered metal dichalcogenide catalysts for hydrogen evolution. *Nat Energy* **2**, 17127 (2017).

8. Geng, K. *et al.* Covalent Organic Frameworks: Design, Synthesis, and Functions. *Chem. Rev.* **120**, 8814–8933 (2020).
9. Wang, Q. & Astruc, D. State of the Art and Prospects in Metal–Organic Framework (MOF)-Based and MOF-Derived Nanocatalysis. *Chem. Rev.* **120**, 1438–1511 (2020).
10. Malaki, M. *et al.* MXenes: from past to future perspectives. *Chemical Engineering Journal* **463**, 142351 (2023).
11. Geim, A. K. & Grigorieva, I. V. Van der Waals heterostructures. *Nature* **499**, 419–425 (2013).
12. Liu, X. *et al.* Power generation by reverse electrodialysis in a single-layer nanoporous membrane made from core–rim polycyclic aromatic hydrocarbons. *Nature Nanotechnology* **15**, 307–312 (2020).
13. van der Ham, A. *et al.* Freestanding non-covalent thin films of the propeller-shaped polycyclic aromatic hydrocarbon decacyclene. *Nature Communications* **13**, 4–11 (2022).
14. Zhang, X., Hou, L., Ciesielski, A. & Samori, P. 2D Materials Beyond Graphene for High-Performance Energy Storage Applications. *Adv. Energy Mater.* **6**, 1600671 (2016).
15. Kidambi, P. R., Chaturvedi, P. & Moehring, N. K. Subatomic species transport through atomically thin membranes: Present and future applications. *Science* **374**, eabd7687 (2021).
16. Wang, L. *et al.* Fundamental transport mechanisms, fabrication and potential applications of nanoporous atomically thin membranes. *Nature Nanotech* **12**, 509–522 (2017).
17. Wang, Y., Chen, K. S., Mishler, J., Cho, S. C. & Adroher, X. C. A review of polymer electrolyte membrane fuel cells: Technology, applications, and needs on fundamental research. *Applied Energy* **88**, 981–1007 (2011).
18. Dubertret, B., Heine, T. & Terrones, M. The Rise of Two-Dimensional Materials. *Acc. Chem. Res.* **48**, 1–2 (2015).
19. Ferrari, A. C. *et al.* Science and technology roadmap for graphene, related two-dimensional crystals, and hybrid systems. *Nanoscale* **7**, 4598–4810 (2015).
20. Bunch, J. S. *et al.* Impermeable Atomic Membranes from Graphene Sheets. *Nano Lett.* **8**, 2458–2462 (2008).
21. Lee, C., Wei, X., Kysar, J. W. & Hone, J. Measurement of the elastic properties and intrinsic strength of monolayer graphene. *Science* **321**, 385–388 (2008).
22. Chen, Y., Zou, J., Campbell, S. J. & Le Caer, G. Boron nitride nanotubes: Pronounced resistance to oxidation. *Appl. Phys. Lett.* **84**, 2430–2432 (2004).

23. Koenig, S. P., Wang, L., Pellegrino, J. & Bunch, J. S. Selective molecular sieving through porous graphene. *Nature Nanotech* **7**, 728–732 (2012).
24. Kim, S. & Lee, Y. M. Rigid and microporous polymers for gas separation membranes. *Progress in Polymer Science* **43**, 1–32 (2015).
25. Robeson, L. M. The upper bound revisited. *Journal of Membrane Science* **320**, 390–400 (2008).
26. Szymczyk, A. & Fievet, P. Investigating transport properties of nanofiltration membranes by means of a steric, electric and dielectric exclusion model. *Journal of Membrane Science* **252**, 77–88 (2005).
27. Mauritz, K. A. & Moore, R. B. State of Understanding of Nafion. *Chem. Rev.* **104**, 4535–4586 (2004).
28. Alberti, G., Casciola, M., Massinelli, L. & Bauer, B. Polymeric proton conducting membranes for medium temperature fuel cells (110–160°C). *Journal of Membrane Science* **185**, 73–81 (2001).
29. Wang, Y., Ruiz Diaz, D. F., Chen, K. S., Wang, Z. & Adroher, X. C. Materials, technological status, and fundamentals of PEM fuel cells – A review. *Materials Today* **32**, 178–203 (2020).
30. Karimi, M. B., Mohammadi, F. & Hooshyari, K. Recent approaches to improve Nafion performance for fuel cell applications: A review. *International Journal of Hydrogen Energy* **44**, 28919–28938 (2019).
31. Holmes, S. M. *et al.* 2D Crystals Significantly Enhance the Performance of a Working Fuel Cell. *Adv. Energy Mater.* **7**, 1601216 (2017).
32. Yan, X. H., Wu, R., Xu, J. B., Luo, Z. & Zhao, T. S. A monolayer graphene – Nafion sandwich membrane for direct methanol fuel cells. *Journal of Power Sources* **311**, 188–194 (2016).
33. Yoon, S. I. *et al.* AA'-Stacked Trilayer Hexagonal Boron Nitride Membrane for Proton Exchange Membrane Fuel Cells. *ACS Nano* **12**, 10764–10771 (2018).
34. B. D. James, J. A. Kalinoski, K. N. Baum,. Mass Production Cost Estimation of Direct H<sub>2</sub> PEM Fuel Cell Systems for Transportation Applications: 2016 Update.
35. Fuel Cells (Hydrogen and Fuel Cell Technologies Office, US Department of Energy); [www.energy.gov/eere/fuelcells](http://www.energy.gov/eere/fuelcells).
36. Bukola, S. *et al.* Single-layer graphene as a highly selective barrier for vanadium crossover with high proton selectivity. *Journal of Energy Chemistry* **59**, 419–430 (2021).
37. Hu, S. *et al.* Proton transport through one-atom-thick crystals. *Nature* **516**, 227–230 (2014).

38. Poltavsky, I., Zheng, L., Mortazavi, M. & Tkatchenko, A. Quantum tunneling of thermal protons through pristine graphene. *The Journal of Chemical Physics* **148**, 204707 (2018).
39. Miao, M., Nardelli, M. B., Wang, Q. & Liu, Y. First principles study of the permeability of graphene to hydrogen atoms. *Phys. Chem. Chem. Phys.* **15**, 16132 (2013).
40. Feng, Y. *et al.* Hydrogenation Facilitates Proton Transfer through Two-Dimensional Honeycomb Crystals. *J. Phys. Chem. Lett.* **8**, 6009–6014 (2017).
41. Bartolomei, M., Hernández, M. I., Campos-Martínez, J. & Hernández-Lamonedá, R. Graphene multi-protonation: A cooperative mechanism for proton permeation. *Carbon* **144**, 724–730 (2019).
42. Kroes, J. M. H., Fasolino, A. & Katsnelson, M. I. Density functional based simulations of proton permeation of graphene and hexagonal boron nitride. *Phys. Chem. Chem. Phys.* **19**, 5813–5817 (2017).
43. Zhang, Q., Ju, M., Chen, L. & Zeng, X. C. Differential Permeability of Proton Isotopes through Graphene and Graphene Analogue Monolayer. *J. Phys. Chem. Lett.* **7**, 3395–3400 (2016).
44. Achtyl, J. L. *et al.* Aqueous proton transfer across single-layer graphene. *Nature Communications* **6**, 1–7 (2015).
45. Bukola, S., Liang, Y., Korzeniewski, C., Harris, J. & Creager, S. Selective Proton/Deuteron Transport through Nafion|Graphene|Nafion Sandwich Structures at High Current Density. *J. Am. Chem. Soc.* **140**, 1743–1752 (2018).
46. Bukola, S., Beard, K., Korzeniewski, C., Harris, J. M. & Creager, S. E. Single-Layer Graphene Sandwiched between Proton-Exchange Membranes for Selective Proton Transmission. *ACS Appl. Nano Mater.* **2**, 964–974 (2019).
47. Chaturvedi, P. *et al.* Ionic Conductance through Graphene: Assessing Its Applicability as a Proton Selective Membrane. *ACS Nano* **13**, 12109–12119 (2019).
48. Walker, M. I., Braeuninger-Weimer, P., Weatherup, R. S., Hofmann, S. & Keyser, U. F. Measuring the proton selectivity of graphene membranes. *Appl. Phys. Lett.* **107**, 213104 (2015).
49. Bentley, C. L., Kang, M., Bukola, S., Creager, S. E. & Unwin, P. R. High-Resolution Ion-Flux Imaging of Proton Transport through Graphene|Nafion Membranes. *ACS Nano* **16**, 5233–5245 (2022).
50. Lozada-Hidalgo, M. *et al.* Scalable and efficient separation of hydrogen isotopes using graphene-based electrochemical pumping. *Nat Commun* **8**, 15215 (2017).

51. Walker, M. I., Weatherup, R. S., Bell, N. A. W., Hofmann, S. & Keyser, U. F. Free-standing graphene membranes on glass nanopores for ionic current measurements. *Appl. Phys. Lett.* **106**, 023119 (2015).
52. Bukola, S. & Creager, S. E. A charge-transfer resistance model and Arrhenius activation analysis for hydrogen ion transmission across single-layer graphene. *Electrochimica Acta* **296**, 1–7 (2019).
53. Song, B. *et al.* Atomic-Scale Electron-Beam Sculpting of Near-Defect-Free Graphene Nanostructures. *Nano Lett.* **11**, 2247–2250 (2011).
54. Zeng, Z. *et al.* Biomimetic N-Doped Graphene Membrane for Proton Exchange Membranes. *Nano Lett.* **21**, 4314–4319 (2021).
55. Robertson, A. W. *et al.* Atomic Structure of Graphene Subnanometer Pores. *ACS Nano* **9**, 11599–11607 (2015).
56. Chaturvedi, P. *et al.* Ionic Conductance through Graphene: Assessing Its Applicability as a Proton Selective Membrane. *ACS Nano* **13**, 12109–12119 (2019).
57. Cohen-Tanugi, D. & Grossman, J. C. Water desalination across nanoporous graphene. *Nano Letters* **12**, 3602–3608 (2012).
58. Konatham, D., Yu, J., Ho, T. A. & Striolo, A. Simulation Insights for Graphene-Based Water Desalination Membranes. *Langmuir* **29**, 11884–11897 (2013).
59. Paulus, G. L. C., Wang, Q. H. & Strano, M. S. Covalent Electron Transfer Chemistry of Graphene with Diazonium Salts. *Acc. Chem. Res.* **46**, 160–170 (2013).
60. Wang, Q. H. *et al.* Understanding and controlling the substrate effect on graphene electron-transfer chemistry via reactivity imprint lithography. *Nature Chem* **4**, 724–732 (2012).
61. Liu, J., Tang, J. & Gooding, J. J. Strategies for chemical modification of graphene and applications of chemically modified graphene. *J. Mater. Chem.* **22**, 12435 (2012).
62. Clancy, A. J., Au, H., Rubio, N., Coulter, G. O. & Shaffer, M. S. P. Understanding and controlling the covalent functionalisation of graphene. *Dalton Trans.* **49**, 10308–10318 (2020).
63. Sharma, R., Baik, J. H., Perera, C. J. & Strano, M. S. Anomalous Large Reactivity of Single Graphene Layers and Edges toward Electron Transfer Chemistries. *Nano Lett.* **10**, 398–405 (2010).
64. Sanchez-Lengeling, B. & Aspuru-Guzik, A. Inverse molecular design using machine learning: Generative models for matter engineering. *Science* **361**, 360–365 (2018).

65. Duan, L. *et al.* A molecular ruthenium catalyst with water-oxidation activity comparable to that of photosystem II. *Nature Chemistry* **4**, 418–423 (2012).
66. Zhang, B. & Sun, L. Ru-bda: Unique Molecular Water-Oxidation Catalysts with Distortion Induced Open Site and Negatively Charged Ligands. *Journal of the American Chemical Society* **141**, 5565–5580 (2019).
67. Hoque, M. A. *et al.* Water oxidation electrocatalysis using ruthenium coordination oligomers adsorbed on multiwalled carbon nanotubes. *Nature Chemistry* **12**, 1060–1066 (2020).
68. Gil-Sepulcre, M. *et al.* Surface-Promoted Evolution of Ru-bda Coordination Oligomers Boosts the Efficiency of Water Oxidation Molecular Anodes. *Journal of the American Chemical Society* **143**, 11651–11661 (2021).
69. Dürr, R. N. *et al.* Robust and Efficient Screen-Printed Molecular Anodes with Anchored Water Oxidation Catalysts. *ACS Applied Energy Materials* **4**, 10534–10541 (2021).
70. Chen, D., Zhang, H., Liu, Y. & Li, J. Graphene and its derivatives for the development of solar cells, photoelectrochemical, and photocatalytic applications. *Energy and Environmental Science* **6**, 1362–1387 (2013).
71. Penrod, K. A. *et al.* Using C-DFT to develop an e-ReaxFF force field for acetophenone radical anion. *Journal of Chemical Physics* **155**, (2021).
72. Alessandri, R. *et al.* Martini 3 Coarse-Grained Force Field: Small Molecules. *Advcd Theory and Sims* **5**, 2100391 (2022).

