Dynamic microstructure of graphene oxide membranes and the permeation flux

Jeng Yi Chong\textsuperscript{a,b}, Bo Wang\textsuperscript{a,b}, Cecilia Mattevi\textsuperscript{c}, Kang Li\textsuperscript{a,b,*}

\textsuperscript{a} Department of Chemical Engineering, Imperial College London, London SW7 2AZ, UK
\textsuperscript{b} Barrer Centre, Department of Chemical Engineering, Imperial College London, London SW7 2AZ, UK
\textsuperscript{c} Department of Materials, Imperial College London, London SW7 2AZ, UK

\textbf{ARTICLE INFO}

Keywords:
Graphene oxide membranes
Membrane microstructure
Transport mechanism
Nanofiltration

\textbf{ABSTRACT}

Graphene oxide (GO) membranes have been reported to be a promising separation barrier that can retain small molecules and multi-valent salts because of the well-defined interlayer space between GO flakes. However, while some studies suggested fast liquid transport through the extremely tortuous transport path, contradictory observations (e.g. low permeation flux) have also been obtained. This paper revealed the dynamic microstructure of GO membranes, which affected the membrane performance significantly. We showed that all GO membranes prepared by varied methods and on different substrates presented a severe reduction in water permeability during filtration, due to the compaction of their original loose microstructure. The water flux could drop continuously from tens of LMH bar\textsuperscript{−1} to < 0.1 LMH bar\textsuperscript{−1} after more than ten hours. This result demonstrated that the structure of GO membranes prepared by current approaches was far from the ideal lamellar structure. The high permeability of GO membranes observed could be contributed by the disordered membrane microstructure. Therefore, the transport mechanisms assuming perfect laminar structure in GO membranes, and the fast transport hypothesis may not fully describe the water transport in GO membranes. Interestingly, the loosely packed microstructure of GO membranes was also found reversible depending on the storage conditions.

\textbf{1. Introduction}

Graphene-based materials have been studied extensively for thin film and membrane applications because of their unique two-dimensional structure and one-atomic thickness [1–4]. With excellent chemical and mechanical properties, graphene-based thin films can be applied as separation membranes or protective barriers in environmental and chemical engineering applications [5–9]. Graphene oxide (GO) is a cost effective precursor for large scale production of graphene-based materials [10]. With a high area-to-thickness ratio and a large number of surface functional groups, GO flakes can be stacked on top of each other to form large area GO thin films/ membranes with thickness less than 100 nm, or GO papers with thickness more than 1 μm [11–14]. GO flakes are bonded with hydrogen bonding, forming a laminar structure with interlayer space of 6–13 Å, depending on the water content in the membrane [6,15,16]. With the well-defined interlayer space, GO membranes can separate molecules of different sizes through size exclusion.

GO membranes have been tested for aqueous and solvent nanofiltrations to retain small molecules with molecular weights of few hundreds Dalton [15,17–19]. It has also been reported that they have a very impressive pure water permeation flux, up to 71 LMH bar\textsuperscript{−1} (L m\textsuperscript{−2} h\textsuperscript{−1} bar\textsuperscript{−1}), which was remarkably higher than most of the current nanofiltration membranes [20–22]. However, these filtration results were inconsistent among different researchers. For example, GO hollow fibre membranes were prepared by using a sacrificial layer, and they were impermeable to gases and exhibited extremely low permeability to water and acetone under pressure-driven nanofiltration conditions, with only 0.074 LMH bar\textsuperscript{−1} of pure water flux for a 150 nm thick membrane [23].

When looking into the transport passage in GO membranes, it is difficult to justify a high water permeation flux under the pressure-driven conditions. It is believed that the effective transport passage of water in GO membranes is through the tortuous spaces between the stacked GO flakes [6,22]. Considering the high aspect ratio of GO flakes (width-to-thickness ratio up to several thousands), the tortuosity of the transport path is very high in GO membranes; the effective transport path is very long even when the apparent thickness of the membrane is as little as tens of nanometres. Taking a 100 nm thick GO membrane with an average GO flake width of 5 μm as an example, a typical structural characteristics of a GO thin film, the effective transport
GO membranes. One famous hypothesis suggested that water can pass through such a GO membrane would be extremely slow, $-8 \times 10^{-6} \text{LMH bar}^{-1}$, which is several orders of magnitude lower than the reported fluxes 
[20,21].

To explain the high permeation flux of water obtained, some hypotheses have been proposed to describe the transport mechanism in GO membranes. One famous hypothesis suggested that water can pass through GO membranes in a low-friction flow [6]. This hypothesis is based on the unique structure of GO flakes, where the oxygen-containing groups on the flakes tend to form segregated nano-sized domains. These oxidised domains would link to the same domains on the neighbouring GO flakes, acting as spacers in the interlayer space in GO membranes. The graphic domains then form interconnected pathways that are wide enough to allow water molecules to pass through. The low-friction flow hypothesis suggests that the graphic domains are hydrophobic and water can pass through at a much faster speed than what predicted by the classic H-P model, because of the low friction between the water and the pore wall. However, even with an advancement factor of 1000 times as predicted from some studies under a slip-flow condition, the calculated water flux is still far lower than what has been reported in many experimental studies. Another hypothesis suggesting that the defects on GO flakes could greatly shorten the effective passage for mass transport, thereby significantly enhancing the permeability [7]. However, this is still insufficient to justify the high fluxes observed in GO membranes. Assuming the defective pores in GO flakes can lead to a significant reduction in flux size to an equivalent flux size of 100 nm, even in a GO membrane with a thickness of 10 nm, the classic H-P model only gives a water flux of about 0.6 LMH bar$^{-1}$, which is still two orders of magnitude lower than fluxes reported by many studies.

When trying to understand the transport mechanism, the microstructure of GO membranes such as the stacking of GO flakes in the membranes is often overlooked. Though the characteristic interlayer space of GO membranes is important in determining the separation properties of the membranes [15], the microstructures of GO membranes such as the stacking or self-assembly of GO flakes and laminae, and the alignment of defects within membranes, have a significant influence on the performance of the membranes [13]. The microstructure of GO membranes was shown to be affected by the membrane preparation methods used [13,24]. However, it is still unclear to what extent the microstructure will affect the permeation flux, and this has prevented us from understanding the transport in GO laminar structures. Chong et al. showed that a pristine, well-laminated GO membrane could be turned into a more disordered structure by UV irradiation, and the water permeation was improved from 0.074 to 2.75 LMH bar$^{-1}$ [23]. The finding demonstrates a critical role of the microstructure when understanding the transport mechanism in GO membranes.

In this paper, we systematically studied the change in permeation performance and microstructure of GO membranes during the pressure-driven filtration process. We demonstrate here that of all membrane preparation methods used, GO membranes underwent serious compaction and the microstructure turned from a loose structure into a tighter structure, and consequently reduced the water permeability significantly. The loose microstructure was restored when the membrane was dried and therefore the decline in permeability could be reproduced in repeated measurements. This result suggested that the reported high fluxes through GO membranes are not an intrinsic property of GO laminae, and the disorder induced short pathway in the membranes could have contributed to most of the measured high fluxes. Therefore, the explanation of high water permeation flux using the slip-flow fast transport hypothesis may need further verification.

![Fig. 1. Schematics of GO membrane syntheses on PES flat sheet substrates: (a) high and low pressure filtration; (b) high temperature evaporation; (c) dip coating.](image-url)
molecule and is a good indicator for rejection tests as the molecular size is close to the molecular weight cut-off of GO membranes. The permeate was collected in a test tube and the dye concentrations of the feed and the permeate were determined by using a UV-spectrometer (UV-2101PC, Shimadzu, UK).

2.3. Material characterization

The morphology of the membranes was observed by a scanning electronic microscope (LEO Gemini 1525 FEGSEM and Zeiss Auriga Crossbeam). XRD (Xpert Pro PANalytical) was used to determine the average interlayer space between the GO flakes in GO membranes. Only GO flat sheet membranes were used in XRD to ensure accurate diffraction angle measurements.

3. Results and discussion

3.1. Water flux reduction in GO membranes

In this study, GO membranes were prepared by several commonly used methods. Besides the most used filtration method, GO membranes were also prepared using dip coating and evaporation/drop casting. Two different pressures, 1 and 10 bar, were applied in the filtration method as pressure could be an important variable affecting the compaction of GO membranes.

Fig. 2(a-d) show the images of GO membranes on PES substrates. All of them had a smooth surface though GO membranes prepared by evaporation and dip-coating had slightly uneven coatings which could be due to the uncontrolled evaporation or drying process. In a study reported by Tsou et al., peeling off of GO flakes was observed in GO membranes prepared by an evaporation method [24]. However, that did not happen in our study when GO membranes were prepared using the evaporation method at 80 °C. The high evaporation rate at high temperature may have enhanced the GO self-assembly process in forming continuous GO membranes. Besides flat sheet GO membranes, hollow fibre GO membranes were also successfully prepared and they showed very even coating, as illustrated in Fig. 2e.

Fig. 3(a-h) show the SEM images of the top surfaces and the cross-sections of the flat sheet GO membranes prepared by all these methods. They showed similar top surface morphology with wrinkles on the membrane surface, which were also commonly observed in GO membranes from previous studies [20,21,24]. From the cross-sections, GO membranes showed a uniform laminar structure attaching closely on the PES substrates. The thickness of the GO layers shown in Fig. 3 ranged from 400 to 500 nm.

The water permeation fluxes of all the GO membranes were measured, and the membranes prepared by different methods showed a variation in the initial fluxes: 6.06 LMH bar⁻¹ for 1-bar filtration, 1.52 LMH bar⁻¹ for 10-bar filtration, 1.71 LMH bar⁻¹ for evaporation, and 8.56 LMH bar⁻¹ for dip coating. For easy comparison, normalized water fluxes based on their initial fluxes were plotted over time and shown in Fig. 4. During the water permeation tests, all the membranes showed a decrease in water flux and the fluxes reached a steady state lower than 10% of their initial fluxes. GO membranes prepared by evaporation and 10-bar filtration showed very similar trends in the decrease in water fluxes and the fluxes reached a steady state faster than the other two methods.

The aforementioned GO flat sheet membranes were relatively thick, but our study showed that the reduction in water permeation flux happened consistently regardless of the membrane thickness. As shown in Fig. 5, thin GO membranes (thickness ≈ 90 nm) prepared by both 1-bar and 10-bar filtrations showed very high water fluxes, 32.2 and 18.5 LMH bar⁻¹, respectively, at the beginning of the permeation tests. Such high water permeation flux was previously reported in some GO membrane studies [21,26]. However, the membranes also showed a rapid decrease in water flux over time and reached a low steady state flux, lower than 10% of the initial flux. The decrease in water flux did not only happen in flat sheet GO membranes. For GO membranes coated on YSZ hollow fibre substrates, the membranes also showed similar decrease in water flux, as shown in Fig. 6.

The results showed clearly that all GO membranes prepared by varied methods and on different substrates presented a severe reduction in water permeability, and the flux dropped continuously from tens of LMH bar⁻¹ down to the range < 0.1 LMH bar⁻¹ after more than ten hours. The decrease in initial water flux was observed constantly in our lab but was seldom reported in previous studies. A decrease in the initial pure water of rGO membranes was reported by Han et al. [22] However, the water permeation of the membranes was shown reaching a steady state in less than an hour, and the extent of the flux reduction was not as severe as observed in our study on GO membranes. Besides, the cause of the flux reduction was not further examined in their studies. Similar decline in water flux in GO membranes was recently reported by Wei et al. [27] They attributed the observation to membrane compaction during filtration which resulted in narrower wrinkles and a flux decline in the membrane substrates.

3.2. Hierarchical microstructure of GO membranes

Membrane compaction or flux reduction is a well-known phenomenon in polymeric membranes due to their high elasticity and low

Fig. 2. Pictures of GO flat sheet membranes prepared by 4 different methods: (a) low pressure filtration; (b) high pressure filtration; (c) high temperature evaporation; (d) dip coating. (e) A picture of GO hollow fibre membrane on a stainless steel holder.
Fig. 3. SEM images of the surfaces (a-d) and the cross-sections (e-h) of GO membranes prepared by 4 different methods: (a, e) 1 bar filtration; (b, f) 10 bar filtration; (c, g) evaporation; (d, h) dip coating. (Scale bar: (a) 2 µm (b) 3 µm (c) 1 µm (d) 1 µm (e) 300 nm (f) 1 µm (g) 500 nm (h) 1 µm).

Fig. 4. Normalized water flux of GO membranes prepared by 4 different methods. The steady state water fluxes were lower than 10% of the initial fluxes.

Fig. 5. Water permeation flux of GO membranes as a function of time. The membranes were prepared using filtration at 1 bar and 10 bar, with thickness about 90 nm for the thin membranes and 450 nm for the thick membrane.
mechanical strength [28]. During pressure-driven applications, the pressure applied could compact the membranes and change their microstructure, thus lowering the permeation flux. However, inorganic membranes such as ceramic membranes seldom experience compaction under high pressure because of their high rigidity [29]. GO membranes showed compaction consistently on both polymeric and ceramic substrates, and the compaction should not be caused by the substrates. Ultrapure de-ionised water was used in the water permeation tests in our study and the reduction of membrane flux should not be due to fouling or concentration polarization, two common causes of drop in membrane permeability. During water permeation, it is widely assumed that water molecules transport through the interlayer space between the GO flakes when pressure is applied on one side of the GO membranes [6]. The interlayer space was created by the hydrogen bonding formed between the GO flakes, and it is easy to estimate based on the Lennard-Jones potential of hydrogen bonding that the equivalent interlayer space will not be affected by the pressure applied during the filtration tests. Therefore, the observed reduction in water flux should not be due to the change in the interlayer space either.

The assumption that water transports through the interlayer space may not reflect the actual structure of GO membranes. Under an ideal situation, GO flakes would stack flake by flake perfectly on top of each other, and this may be the case when GO membranes have only several layers of GO flakes. However, this is difficult to achieve in practice as a sufficient number of GO layers are needed to ensure a full coverage of the substrate surface. In most of the situation, thicker GO membranes are fabricated and the laminar structure of the membranes is not perfect. Hierarchical structures of GO membranes/papers have previously been observed, especially when the thickness is in a length scale of above 100 nm [30]. In these hierarchical structures, there are mainly two levels of structure formed by the stacking of GO flakes. The primary structure is from a highly ordered flake-by-flake stacking, which forms a GO lamina that may be thicker than 10 nm. The secondary structure is a looser stacking of the primary structures, but it may also mix with a certain extent of flake-by-flake structure to form a complete membrane structure.

The hierarchical structure is illustrated in Fig. 7. Recently, the formation mechanism of the hierarchical structure in GO membrane was studied by Nandy et al. using a stop-motion animation imaging technique to observe the evolution of membrane microstructures [31]. For GO membranes prepared using vacuum filtration, formation of interconnected proto-lamellar 3-D network was observed during the filtration process, which was slowly compressed into dense GO lamellae. A similar formation mechanism was also observed in the evaporation method but the growth of the dense lamellae started from the water-air interface at a lower rate. During the membrane formation process, GO flakes did not stack one by one from one end to the other, but started with forming proto-lamellar network. Therefore, the formation of imperfect stacking of GO flakes in GO membranes was inevitable.

The spaces and cavities in the loosely stacked hierarchical structure create extra paths for water molecules to transport through the membranes and subsequently increase the water permeability of the membrane. However, when pressure is applied during water permeation, membrane compaction would happen to the loose and less ordered microstructure. The compaction may not have changed the interlayer distance of the membranes created by strong hydrogen bond, but could compress the spaces and cavities between the laminae, leading to a more ordered microstructure in GO membranes. As the GO membranes are more densely packed and have minimum shortcuts in the more orderly microstructure, the effective transport path of water molecules in the membranes would become significantly longer, causing a drastic decrease in water permeability. It can also be expected that with the denser structure in GO membranes, the non-ideal flow passages that deviate from the theoretical interlayer space of the flake-by-flake stacking would be minimised or eventually eliminated, leading to a higher rejection rate to the probing molecules.

This hypothesis was verified by the dye rejection experiment using methyl red (Mw = 269.3 Da) as the probing molecule (Fig. 8). During the rejection test, the rejection rate was relatively low initially (88.7%), but improved after 4 h to above 95% accompanying the reduction of permeation flux. The improvement in rejection performance has given an additional evidence of the change in microstructure of GO membranes during pressure-driven water filtration. Such improvement in rejection performance over time could only be observed when dyes with a smaller size such as methyl red were used. When larger dye molecules such as tartrazine (Mw = 534.3 Da) and brilliant blue (Mw = 792.9 Da) were tested, GO membranes showed a high rejection rate (> 95%) even at the beginning of the test, which indicated the cavities in the hierarchical structure were very small and still within the nanofiltration range. Though GO membranes may have a less ordered microstructure in the beginning of the compaction / water permeation tests, the less ordered laminar structure could still reject most of the molecules larger than 500 Da.

The permeation flux reduction shown in Fig. 4 can be well explained based on the hierarchical structure model of GO membranes. The variation in the initial flux of the GO membranes prepared by different methods can be attributed to the initial level of disorder (e.g. the number of spaces and cavities between the GO laminae) in the membranes. GO membranes prepared by evaporation and 10-bar filtration showed lower initial fluxes, 1.71 and 1.52 LMH bar⁻¹, respectively, which could be attributed to the more ordered microstructure in the membranes. In contrast, GO membranes prepared by dip coating showed a much higher initial flux, 8.56 LMH bar⁻¹ as the GO membranes fabricated by this method could have a less ordered microstructure due to the relatively difficult control process especially for flat sheet substrates. The speed of coating, the thickness of wetted liquid film and the drying process could affect the integrity of GO coating. The disorder might happen not only at the laminar level, but the packing between the layers formed in each dip could also contribute to the less ordered microstructure. In addition, the more ordered microstructure in GO membranes prepared by evaporation and 10-bar filtration was also reflected by the shorter time taken to reach the steady state permeation flux, compared to membranes prepared by the other two methods.

Aforementioned evidence clearly shows that a more ordered microstructure can be achieved after the compaction of GO membranes. However, will the more ordered microstructure in GO membranes be retained when the pressure is released after the permeation test? To answer this question and to further understand the dynamic microstructure of GO membranes, we ran the water permeation /compaction tests in several cycles. In the cycle test, two dry fresh GO membranes...
prepared by high pressure filtration were first tested for water permeation for 2 days. After that, the membranes were stored either in air (dry cycle run), or in water (wet cycle run) for 3 days before the second cycle tests were carried out. In both of the cycle runs (Fig. 9), the fresh GO membranes experienced flux reduction, similar to other membranes tested in our study. However, different compaction behaviours were observed in the second and the following cycles. In the dry cycle run, flux reduction continued to happen in each of the following 5 cycles; the membrane showed a high initial water permeation flux in each cycle and eventually reached a very low steady water flux, below 0.1 LMH bar⁻¹. It is apparent that the disorder microstructure of the membrane could be regenerated during drying, leading to the re-occurring of flux reduction in every cycle.

On the other hand, repeated membrane compaction was not observed in the wet cycle and the water permeation flux of GO membrane remained low in the second and third cycle. The more ordered GO laminar structure may have been maintained when the membrane was stored in water continuously as there was no external force causing the disruption of microstructure like during the drying process. Correspondingly, GO membranes after the wet cycle run showed high initial dye rejection rate to methyl red (> 97%) and other larger dye molecules (Fig. 10). This was expected from the water permeation tests as the more ordered microstructure was well preserved when storing in water. The cycle tests provided an important clue for the understanding on the change in microstructure in GO membranes. The repeated membrane compaction in the dry cycle revealed that the disordered microstructure of GO membranes was restored when drying or storing in the air. The drying process could be critical for the microstructure of GO membranes and the disorder-to-order microstructure of GO membranes was reversible depending on the conditions where the membranes were stored (Fig. 7c). This result coincided with our previous study on the stability of GO membranes, where long duration of storage of GO membranes in air was shown to lead to a defective membrane due to excessive defects developed in the membranes [17]. By storing GO membranes in water, the microstructure and the performance of the membranes could be well preserved.

We further studied the effects of drying and storage conditions on the microstructure of GO membranes by monitoring the change in XRD peak intensity over a longer period of time. GO membranes were stored in the air for 4 weeks and 1 year, and the same samples were scanned with XRD over the storage duration (Fig. 11). The intensity of the peak (2θ = 9–10°) corresponding to the interlayer space of GO membranes with the same thickness decreased after 4 weeks and 1 year. The lower
peak intensity indicated a change in microstructure of GO membranes, with increasing disorder over time when the membranes were stored in air even at room temperature. The big band at $2\theta = 18^\circ$ was contributed by the PES substrate and it could be also used as a reference during the scan. It was revealed in our previous study that the shrinkage of GO membranes during drying was one of the apparent reasons to lead the generation of microstructural imperfections, but the underlying reason behind the destructive drying process was the high surface tension of water, which generated enormous capillary force in the sites of the membrane. Because of the size difference of the spaces, uneven capillary forces would be distributed in the GO membranes during drying, and thus intensifying the deviation from the ideal flake-by-flake stacking, and restoring the loose disorder membrane structure. It has also been demonstrated that by replacing water with low surface tension solvents, the disorder structure can be largely minimised, leading to a very low permeation flux [17].

### 3.3. Discussion of water transport mechanism in GO membranes

Water transport in GO membranes has been puzzling in the membrane field, and it has caused a theoretical problem for researchers working on transport mechanisms. The classic Hagen-Poiseuille equation is a starting point used to understand water transport in GO membranes and the calculation is shown in the supporting document. As mentioned in the introduction, the water permeation flux predicted using the equation was much lower than the water flux reported so far.

As shown in Fig. S1, even by reducing the membrane thickness to 20 nm, GO membranes still could not achieve a high water flux. The flux might be greatly improved if the size of GO flakes is reduced to below 100 nm. However, a full coverage of GO on the substrates will be very difficult to attain with the small flake aspect ratio. This also showed that the high aspect ratio of GO flakes have very much contributed to the long transport path in GO membranes and water would transport at a very slow rate in an ideal flake-by-flake structure. In addition, the large GO flake size also contributed to a low “effective porosity” on the membrane surface with less than 0.1% of the surface available for water molecules to enter the membrane [6].

Noticing the long transport path in GO membranes, many studies attempted to explain the reported high water permeation using the fast water transport hypothesis. Dynamic molecular simulation technique has been used to study the water transport in GO membranes and to support the fast transport hypothesis. Nair et al. showed that water molecules could have a low friction, ultrafast transport through the carbon hydrophobic network in GO membranes with a high effective capillary pressure [6]. However, their simulation study simplified the transport channels to an all-carbon network with no hydrophilic functional groups, which did not reflect the real situation in GO membranes. When including the surface effect, water molecules will interact with the hydrophilic functional groups and the side-pinning effect will slow down the transport of water in the carbon channel network in GO membranes due to the strong hydrogen bond interaction [32,33]. Continuum theory was used in a recent study to predict the fast transport of water in GO membranes with low friction flow of water in carbon channels but the prediction again did not include the hydrophilic surface effects in the membranes [34]. Besides, the simulation by Nair et al. focused on the high capillary pressure in the interlayer space and water was set to be evaporated on the permeate side of the membrane. While the capillary pressure in the membranes could be high due to the small interlayer space, the driving force in evaporation was different from the pressure-driven filtration where water did not change to the vapour phase when exiting the pore.

This paper demonstrated that the stacking of GO flakes was far from perfection and the membranes formed a hierarchical structure. The transport mechanisms proposed in previous studies that assumed perfect GO laminar structure may not fully describe the water transport in GO membranes. The exceptional performance of GO membranes in water permeation reported has been explained by using the hypothesis of fast transport in GO membranes, but may in fact caused by the loosely packed membrane microstructures, as observed at the beginning of the permeation test in this study. The experimental data in this study also suggested that the permeation tests should be conducted for at least 12 h in order to have an accurate measurement of the performance of GO membranes. Additionally, the reduction in water flux may be avoided if GO membranes with a highly ordered microstructure can be fabricated. This may be achieved if the thickness of GO membranes can be further reduced to a few nanometres.

### 4. Conclusions

GO membranes demonstrated a dynamic microstructure; they showed a serious reduction in water flux during the permeation tests, which could be due to the change in the membrane microstructure. Interestingly, their loosely packed microstructure was found reversible depending on the storage conditions. The high water flux observed in previous studies and also at the beginning of the permeation tests in this study could have been contributed by the disorder of GO flakes and the loosely packed hierarchical microstructure in GO membranes, and therefore might not be an intrinsic property of GO laminae. GO membranes showed a low steady state water permeation flux in pressure-driven filtration due to the extremely high tortuosity in the membranes.
The transport mechanisms assuming perfect laminar structure in GO membranes may not fully describe the water transport in GO membranes given the hierarchical microstructure observed, and the low friction flow proposed by previous studies may need further verification.

Acknowledgements

The authors gratefully acknowledge the research funding provided by EPSRC in the United Kingdom (Grant no. EP/M022250/1).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.memsci.2017.12.018.

References

[1] Y. Zhu, S. Murali, W. Cai, X. Li, J.W. Suk, J.R. Potts, R.S. Ruoff, graphene and graphene oxide: synthesis, properties, and applications, Adv. Mater. 22 (2010) 3986–3994.
[2] J.S. Bunch, S.S. Verbridge, J.S. Alden, A.M. van der Zande, J.M. Parpia, H.G. Craighead, P.L. McEuen, Impermeable atomic membranes from graphene sheets, Nano Lett. 8 (2008) 2458–2462.
[3] Z.P. Smith, B.D. Freeman, Graphene Oxide, A. New, Platform for high-performance gas- and liquid-separation membranes, Angew. Chem. Int. Ed. 53 (2014) 10286–10288.
[4] G. Liu, W. Jin, N. Xu, Graphene-based membranes, Chem. Soc. Rev. 44 (2015) 5016–5030.
[5] S.P. Koenig, L. Wang, J. Pellegrino, J.S. Bunch, Selective molecular sieving through porous graphene, Nat. Nanotechnol. 7 (2012) 728–732.
[6] R.R. Nair, H.A. Wu, P.N. Jayaram, I.V. Grigorieva, A.K. Geim, Unimpeled permeation of water through helium-leak-tight graphene-based membranes, Science 335 (2012) 442–444.
[7] H. Li, Z. Song, X. Zhang, Y. Huang, S. Li, Y. Mao, H.J. Ploehn, Y. Bao, M. Yu, Ultrathin, molecular-sieving graphene oxide membranes for selective hydrogen separation, Science 342 (2013) 95–98.
[8] H.M. Hegab, L. Zou, Graphene oxide-assisted membranes: fabrication and potential applications in desalination and water purification, J. Membr. Sci. 484 (2015) 95–106.
[9] J.Y. Chong, B. Wang, K. Li, Graphene oxide membranes in fluid separations, Curr. Opin. Chem. Eng. 12 (2016) 98–105.
[10] S. Park, R.S. Ruoff, Chemical methods for the production of graphenes, Nat. Nanotechnol. 4 (2009) 217–224.
[11] D.A. Dikin, S. Stankovich, E.J. Zimney, R.D. Piner, G.H.B. Dommett, G. Evmenenko, S.T. Nguyen, R.S. Ruoff, Preparation and characterization of graphene oxide paper, Nature 448 (2007) 457–460.
[12] C. Chen, Q.-H. Yang, Y. Yang, W. Lv, Y. Wen, P.-X. Hou, M. Wang, H.-M. Chong, Self-assembled free-standing graphite oxide membrane, Adv. Mater. 21 (2009) 3007–3011.
[13] H.W. Kim, H.W. Yoon, S.-M. Yoon, B.M. Yoo, B.K. Ahn, Y.H. Cho, H.J. Shin, H. Yang, U. Paik, S. Kwon, J.-Y. Choi, H.B. Park, Selective gas transport through few-layered graphene and graphene oxide membranes, Science 342 (2013) 91–95.
[14] D.R. Dreyer, S. Park, C.W. Bielawski, R.S. Ruoff, The chemistry of graphene oxide, Chem. Soc. Rev. 39 (2010) 228–240.
[15] R.K. Joshi, P. Carbono, F.C. Wang, V.G. Kravets, Y. Su, I.V. Grigorieva, H.A. Wu, A.K. Geim, R.R. Nair, Precise and ultrafast molecular sieving through graphene oxide membranes, Science 343 (2014) 752–754.
[16] N.V. Meddekar, A. Ramanubramaniam, R.S. Ruoff, V.B. Shenoy, Hydrogen bond networks in graphene oxide composite paper: structure and mechanical properties, ACS Nano 4 (2010) 2300–2306.
[17] N.F.D. Aba, J.Y. Chong, B. Wang, C. Mattevi, K. Li, Graphene oxide membranes on ceramic hollow fibers – microstructural stability and nanofiltration performance, J. Membr. Sci. 484 (2015) 87–94.
[18] P. Sun, M. Zhu, K. Wang, M. Zhong, J. Wei, D. Wu, Z. Xu, H. Zhu, Selective ion penetration of graphene oxide membranes, ACS Nano 7 (2012) 428–437.
[19] B. Mi, Graphene oxide membranes for ion and molecular sieving, Science 343 (2014) 746–747.
[20] A. Akbari, P. Sheath, S.T. Martin, D.B. Shinde, M. Shahbani, P.C. Banerjee, R. Tkacze, D. Bhattacharyya, M. Majumder, Large-area graphene-based nanofiltration membranes by shear alignment of discotic nematic liquid crystals of graphene oxide, Nat. Commun. 7 (2016).
[21] H. Huang, Y. Mao, Y. Ying, Y. Liu, L. Sun, X. Peng, Salt concentration, pH and pressure controlled separation of small molecules through lamellar graphene oxide membranes, Chem. Commun. 49 (2013) 5963–5965.
[22] Y. Han, Z. Xu, C. Gao, Ultrathin graphene nanofiltration membrane for water purification, Adv. Funct. Mater. 23 (2013) 3693–3700.
[23] J.Y. Chong, N.F.D. Aba, B. Wang, C. Mattevi, K. Li, UV-enhanced sacrificial layer stabilised graphene oxide hollow fibre membranes for nanofiltration, Sci. Rep. 5 (2015) 15799.
[24] C.-H. Tsou, Q.-F. An, S.-C. Lo, M. De Guzman, W.-S. Hung, C.-C. Hu, K.-R. Lee, J.-Y. Lai, Effect of microstructure of graphene oxide fabricated through different self-assembly techniques on 1-butanol dehydration, J. Membr. Sci. 477 (2015) 93–100.
[25] K. Li, Ceramic Membranes for Separation and Reaction, Wiley, 2007.
[26] H. Huang, Z. Song, N. Wei, L. Shi, Y. Mao, Y. Ying, L. Sun, Z. Xu, X. Peng, Ultrafast viscous water flow through nanostrand-channelled graphene oxide membranes, nature, Communications 4 (2013).
[27] Y. Wei, Y. Zhang, X. Gao, Y. Yuan, B. Su, C. Gao, Declining flux and narrowing nanochannels under wrinkles of compacted graphene oxide nanofiltration membranes, Carbon 108 (2016) 568–575.
[28] K.M. Persson, V. Gekas, G. Trägårdh, Study of membrane compaction and its influence on ultrafiltration water permeability, J. Membr. Sci. 100 (1995) 155–162.
[29] M. Lee, Z. Wu, B. Wang, K. Li, Micro-structured alumina multi-channel capillary tubes and monoliths, J. Membr. Sci. 489 (2015) 64–72.
[30] C.D. Wood, M.J. Palmeri, K.W. Putz, Z. An, S.T. Nguyen, L. Catherine Brinson, Hierarchical structure and properties of graphene oxide papers, J. Appl. Mech. 80 (2013) (040913-040913).
[31] K. Nandy, M.J. Palmeri, C.M. Burke, Z. An, S.T. Nguyen, K.W. Putz, L.C. Brinson, Stop motion animation reveals formation mechanism of hierarchical structure in graphene oxide papers, Adv. Mater. Interfaces (2016) (n/a-n/a).
[32] H. Yoshida, L. Bocquet, Labyrinthine water filtration membrane for water purification, Adv. Mater. 30 (2018) 385–392.