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Composite Materials COMMENTARY

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Temporal separation of assembly and fixation programs Ångström-scale ion sieving

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Graphene oxide membranes have become prominent candidates for precision separation because they combine rapid water transport with adjustable subnanometre channels.[1-3] Yet the structural features that enable this performance also create a persistent materials dilemma. Oxygen containing groups facilitate nanosheet assembly and provide reactive sites for chemical modification, but they also promote hydration and swelling in aqueous environments. Conventional stabilisation methods, including covalent crosslinking, molecular intercalation and ionic coordination, can partially suppress this swelling. However, the resulting channel dimensions are usually fixed or restricted to discrete values determined by the geometry of the inserted species. The central challenge is therefore not simply to create a narrower or more stable channel. It is to regulate the interlayer spacing continuously at subångström precision while preserving aqueous stability, ion selectivity and high permeance. Lu and colleagues[4] address this longstanding problem by shifting attention from the chemical identity of a rigid spacer to the timing of molecular organisation and chemical fixation. Rather than forcing the membrane into a predetermined structure through immediate crosslinking, they exploit the distinct phase behaviour of water under nanoconfinement to control molecular mobility. Dopamine molecules are allowed to assemble while confined water remains liquid, their organisation is arrested by further cooling and the resulting structure is subsequently stabilised through slower chemical reactions. This temporal separation goes beyond simply sequencing assembly and fixation by using the distinct phase behaviour of bulk and confined water to actively control when molecular organisation is arrested and chemically fixed.

The fabrication strategy proceeds through assembly, arrest and fixation. At a selected assembly temperature, T_A, for example −10°C, the surrounding bulk water is frozen while the nanoconfined water between adjacent nanosheets remains mobile. The surrounding ice restricts macroscopic swelling, while the mobile confined water allows dopamine molecules to diffuse through the interlayer galleries and form nanoscale assemblies (Figure 1A). The system is then rapidly cooled to a lower reaction temperature, T_R, below -30°C, where the confined water converts into nano-ice and further molecular rearrangement is suppressed. The assembled structure is thereby preserved at a selected interlayer spacing. Dopamine polymerisation and covalent reactions with oxygen containing groups on graphene oxide continue more slowly and convert the temporary assemblies into stable polydopamine nanopillars. The conceptual advance lies in separating the formation of molecular organisation from its chemical immobilisation. In conventional crosslinking, these processes occur concurrently and are difficult to regulate independently. Here, structural organisation develops under conditions that preserve molecular mobility and is fixed only after the desired arrangement has formed. By varying dopamine concentration and assembly time, the interlayer spacing can be adjusted continuously from approximately 5.9 to 10.2 Å (Figure 1B). Selected target spacings show standard deviations below 0.1 Å across more than 50 independently prepared membranes, indicating strong batch reproducibility. The nanopillars also suppress aqueous swelling and provide mechanical support, allowing the composite membranes to retain structural order during prolonged immersion and rapid water flow. This control translates into sustained desalination and selective ion recovery. At an optimised thickness of about 90 nm, the membranes balance structural integrity, permeance and salt rejection. With a 2000 ppm NaCl feed, they maintain a water permeance of 67.9 L m^{-2} h^{-1} bar^{-1} and approximately 99 percent rejection over about 700 hours of continuous cross flow operation. Experiments with pretreated seawater further increase the Li^+ molar fraction from 5.3 percent to 90.8 percent. A sequential membrane configuration also achieves an Rb^+ to K^+ separation factor of 5320, despite a difference in hydrated diameter of less than 0.1 Å.

The effectiveness of this approach arises from the coupling of confinement thermodynamics with reaction kinetics. Molecular simulations suggest that nanoconfinement weakens interactions between dopamine and water while leaving interactions among water molecules largely unchanged (Figure 1C). This asymmetric change may reduce the energetic preference for dopamine hydration and thereby favour local aggregation. The assemblies form preferentially near regions containing oxygen functional groups, where the resulting polydopamine pillars can stabilise adjacent nanosheets. Regions with lower oxidation remain comparatively unobstructed and continue to provide pathways for rapid water transport. Density functional theory calculations further indicate that dopamine polymerisation and covalent bonding encounter higher energy barriers than initial physical aggregation. This difference supports the temporal sequence in which rapid assembly precedes slower fixation. The resulting composite-GOM membranes were subsequently evaluated for desalination and ion-sieving performance using the cross-flow filtration configuration shown in Figure 1D. The observed ion selectivity also extends beyond static size exclusion. Several hydrated ions are larger than the nominal channel height and must partially shed their hydration shells before entering the graphene galleries. Small variations in interlayer spacing can consequently alter both steric accessibility and the energetic cost of partial dehydration.[5] Precise channel regulation can amplify differences in dehydration energy and translate them into pronounced variations in permeation probability, providing a plausible basis for separating ions with almost indistinguishable hydrated dimensions. Nevertheless, geometric confinement and dehydration are unlikely to determine transport alone. Surface charge, specific interactions with graphene oxide or polydopamine, competition among multiple ions and concentration polarisation may also contribute. Their relative roles will require experiments that vary channel dimensions, surface chemistry and feed composition independently. A further question concerns the relationship between average structural precision and the dimensions of local transport pathways. A narrow interlayer spacing distribution measured by diffraction demonstrates reproducibility at the membrane scale, but it does not establish that every active channel has the same dimensions. Edge pathways, local defects and variations through the membrane thickness may dominate transport even when the average spacing is tightly controlled. Direct measurements of local channels in the wet state, under pressure and in concentrated mixed salt solutions, will be needed to connect statistical structural uniformity with the dimensions of individual

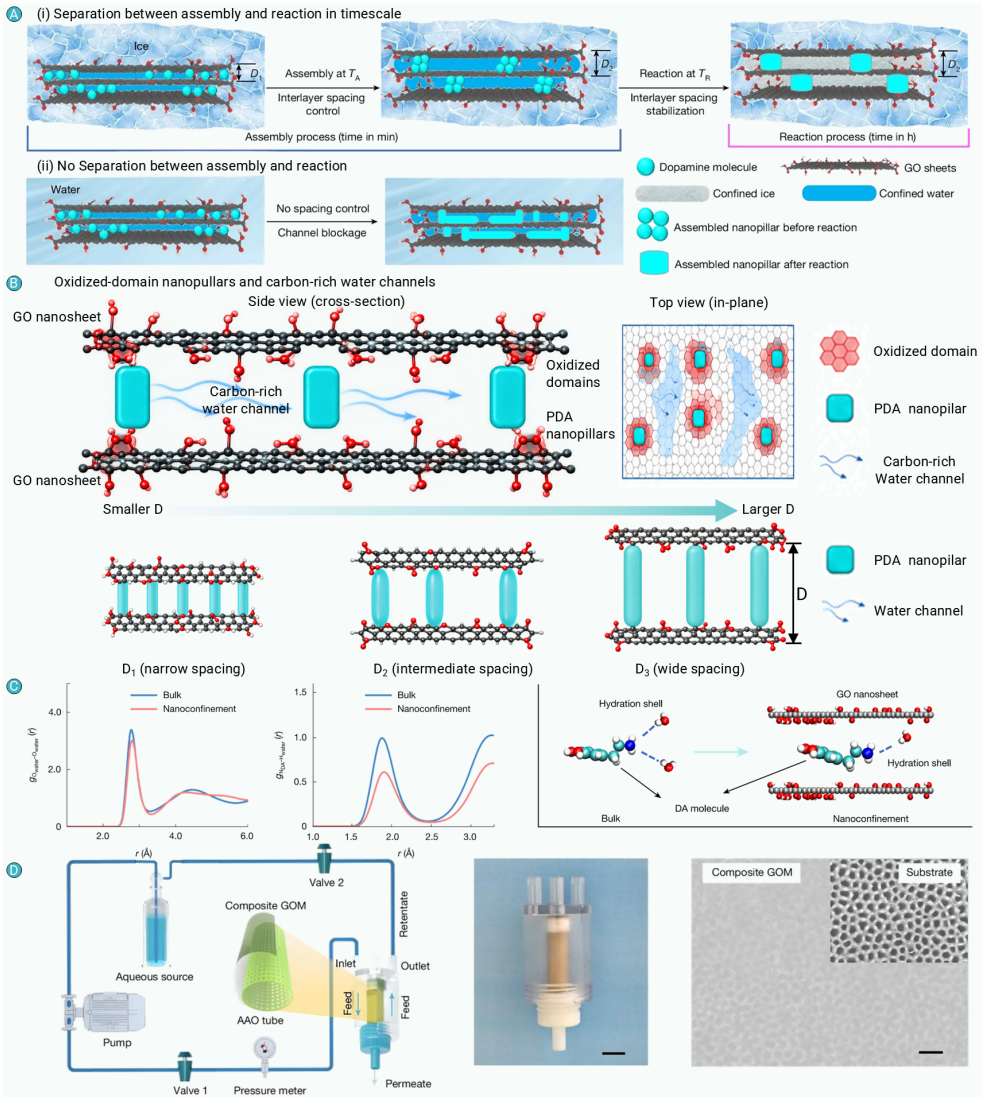


Figure 1. Schematic design and application demonstration of polydopamine-pillared graphene oxide membranes (A) Timescale-separated assembly and reaction strategy, showing bulk-water freezing, confined-water-mediated dopamine assembly, further cooling, and polydopamine fixation. (B) Spatially selective PDA nanopillars form at oxygen-containing GO regions, preserve carbon-rich transport pathways, and enable continuous regulation of the interlayer spacing. (C) Molecular simulations reveal weakened dopamine-water interactions under nanoconfinement, promoting dopamine aggregation within the GO interlayers. (D) Cross-flow filtration platform, composite-GOM device, and membrane morphology used for desalination and ion-sieving tests. Scale bars, 1 cm (device photograph) and 1 μm (SEM image).

ion sieving sites.

Several challenges remain before this concept can develop into a practical and broadly transferable membrane strategy. The current effective area is approximately 10.6 cm^2, while fabrication requires molecular infiltration, controlled freezing, subzero assembly, further cooling, prolonged reaction and freeze drying. Extending this process to square metre membranes will require uniform control over temperature, solvent distribution, nanosheet orientation, membrane thickness, substrate adhesion and nanopillar growth. Spatially programmed cooling, roll-to-roll processing with sequential thermal zones, or modular membrane fabrication may provide feasible routes to preserve the required assembly-fixation window while minimizing thermal gradients and defect accumulation during scale-up. However, repeated subzero cooling, prolonged reaction and freeze-drying may increase energy demand, reduce manufacturing throughput and complicate continuous processing. The ion recovery experiments also use pretreated seawater. Natural and industrial feeds contain organic matter, colloids, silica, microorganisms and multiple competing ions that may alter channel structure, surface chemistry and fouling behaviour. Chemical stability, cleaning durability, recovery efficiency, membrane lifetime and process economics must therefore be evaluated under untreated and dynamically changing conditions. The proposed principle may also apply to MXenes, covalent organic frameworks and other lamellar materials, but such generality cannot be assumed. Differences in surface chemistry, hydrophilicity and interfacial structure will modify the phase behaviour and mobility of confined solvents. Transferability will therefore require stable and accessible nanoconfined galleries, appropriate surface chemistry and hydrophilicity, confinement-sensitive solvent phase behaviour, and sufficient kinetic separation between molecular assembly and chemical fixation. By controlling how long molecules remain mobile and when their organisation becomes chemically immobilised, materials synthesis can move beyond compositional optimisation towards the coordinated programming of structure in space and time. The lasting influence of this concept will depend on whether such temporal control can preserve molecular precision across larger areas, chemically diverse lamellar systems and realistic operating environments.

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DECLARATION OF INTERESTS

The authors declare no competing interests.