Three-dimensional architecture constructed by graphene oxide nanosheets - polymer composite for high-flux forward osmosis membranes

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Catalogue of ESI

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1. Supplementary Introduction

1.1. Internal concentration polarization (ICP) and structural parameter (S)

Figure S1. ICP profile across a composite membrane at FO mode

Internal concentration polarization (ICP) is a very unique phenomenon that takes place in osmotically-driven membrane processes. The cause of ICP is that the support layer of FO membrane functions as an unstirrable boundary layer to the diffusion of draw solute (inside membrane support layer). As a result, the osmotic difference across selective layer (effective osmotic driving force, $\Delta \pi_{\text{eff}}$, as shown in Figure S1) is reduced to be much lower than the osmotic difference between feed solution bulk and draw solution bulk (apparent osmotic driving force, $\Delta \pi_{\text{bulk}}$, as shown in Figure S1), regardless of whichever membrane orientation (i.e. FO mode or PRO mode) is. Taking FO mode (support layer facing draw solution, which is employed in this study) as an example, as water molecules permeate through selective layer and enter into support layer under osmotic driving force, the draw solution inside support...
layer is being diluted. This causes the osmotic pressure at the top surface of support layer ($\pi_{D,\text{eff}}$, as shown in Figure S1) to become lower than that at the bottom surface of support layer ($\pi_{D,m}$, as shown in Figure S1). The diffusion of draw solute from bottom surface to top surface inside support layer serves as the compensation to restore $\pi_{D,\text{eff}}$. Unfortunately, conventional support layers are made of tortuous 1D architecture, which severely hinders this compensated diffusion of draw solute and thus generates a remarkable osmotic gradient ($\pi_{D,m} - \pi_{D,\text{eff}}$) between bottom surface and top surface of support layer. As a result, $\Delta \pi_{\text{eff}}$ is significantly reduced from $\Delta \pi_{m}$ (the osmotic difference between membrane surfaces, as shown in Figure S1). This means $\Delta \pi_{\text{eff}}$ is much lower than $\Delta \pi_{\text{bulk}}$ because $\Delta \pi_{m}$ is equaling to or smaller than $\Delta \pi_{\text{bulk}}$ depending on the extent of external concentration polarization (ECP).

Many previous studies on FO technology have observed the phenomenon that the water flux of FO process is much smaller than theoretical prediction based upon RO performances of membrane, and they figured out ICP is the main reason for this phenomenon.\textsuperscript{1-3} The governing equation for water flux at FO mode has been developed by previous studies,\textsuperscript{4,5} as adapted into equation S1 for the quantitative analysis of ICP.

$$J_w = A \Delta \pi_{\text{eff}} = A(\pi_{D,\text{eff}} - \pi_{F,m}) = A(\pi_{D,m} \exp(-J_w K) - \pi_{F,m})$$ \hspace{1cm} (S1)

where $A$ is water permeability of FO membrane selective layer, $\Delta \pi_{\text{eff}}$ is effective osmotic driving force, $\pi_{D,\text{eff}}$ is the osmotic pressure of draw solution at the support layer top surface, $\pi_{F,m}$ is the osmotic pressure of feed solution at selective layer top surface (\textit{i.e.} FO membrane top surface), $\pi_{D,m}$ is the osmotic pressure of draw solution at support layer bottom surface (\textit{i.e.} FO membrane bottom surface), $J_w$ is the water flux of membrane at FO mode, and $K$ is solute resistivity. Specifically, $K$ is defined as equation S2.

$$K = \frac{S}{D}$$ \hspace{1cm} (S2)
where $D$ is the diffusion coefficient of draw solute inside support layer, and $S$ is structural parameter of support layer. Specifically, $S$ is defined as equation S3.

\[ S = \frac{\tau t}{\varepsilon} \quad (S3) \]

where $\tau$, $t$, and $\varepsilon$ are the tortuosity (dimensionless, $\geq 1$), thickness, and porosity (dimensionless, $0 \sim 1$) of support layer.

Based upon equation S1~S3, $\exp(-JwK)$ is termed as the ICP modulus, which is used to quantitatively analyze the adverse effect of ICP at FO mode. Equation S2 indicates $K$ is positively correlated with $S$. This means the extent of ICP is exacerbated exponentially along with the value of structural parameter: the higher $S$ value, the higher $K$ value, the smaller ICP modulus, the lower $\Delta\pi_{\text{eff}}$, the severer ICP effect, and the smaller $Jw$ will be.

Moreover, unlike ECP, ICP cannot be mitigated through increasing the flow velocity or turbulence on membrane surface. Therefore, ICP is a more stubborn problem to FO processes. The address of this issue mainly relies on the innovation of membrane structure especially the structure of support layer, in other words, the minimization of $S$ value. Based upon equation S3, the decrease of support layer thickness ($t$) or the increase of support layer porosity ($\varepsilon$) can reduce $S$ value. However, the mechanical integrity of FO membrane will be inevitably compromised. Hence, a very smart way to minimize $S$ value is through reducing the tortuosity ($\tau$) of support layer.
1.2. The physical meaning of tortuosity ($\tau$)

![Figure S2. Concept illustration on the tortuosity of support layer. (a) Support layer with segregated pores. (b) Support layer with interconnected pores, wherein the light green pores indicate the new pores formed to connect those originally segregated pores.]

The physical meaning of structural parameter ($S$) is the average distance for draw solute molecule to take when traveling through support layer from its top surface to bottom surface. In other words, $S$ represents the thickness of boundary layer that is caused by support layer for hindering the diffusion of draw solute. As mentioned in equation S3, $S$ is directly proportional to the tortuosity ($\tau$) and thickness ($t$) of support layer while inversely proportional to the porosity ($\varepsilon$) of support layer.

Briefly, the tortuosity ($\tau$) of support layer equals to the ratio of $l$ over $t$, where $l$ is the actual pathway length for water molecules to permeate through the support layer, while $t$ is the thickness of support layer, as indicated by equation S4. Noteworthily, $\tau$ is a dimensionless parameter in the range of $\geq 1$: $\tau$ value is 1 for ideal membrane while $>1$ for real membranes.

$$\tau = \frac{l}{t} \quad (S4)$$
The tortuosity is negatively correlated with pore interconnectivity (the higher pore interconnectivity, the lower tortuosity). Figure S2 compares the tortuosity of support layer between two architectures (support layer thickness is the same): architecture of segregated pores and architecture of interconnected pores. Figure S2a illustrates that the pores in conventional support layer is isolated (low interconnectivity). Water molecules have to follow the tortuous path inside each segregated channel and thus take a long pathway when permeating through the support layer from its top surface to bottom surface. As a result, $l$ value is big and hence $\tau$ value is high for architecture of segregated pores. In contrast, Figure S2b illustrates that new channels (as marked by light green color) are formed to connect those previously segregated pores to form an interconnected architecture. Water molecules can find a short pathway when permeating through this interconnected architecture. As a result, $l$ value is small and hence $\tau$ value is low for architecture of interconnected pores.

The above analysis indicates the increase of support layer pore interconnectivity can be effective to reduce support layer tortuosity, which leads to the decrease of support layer structural parameter (the decrease of ICP extent) and thus the increase of FO water flux.

Noteworthily, these newly formed pores can be created in the dimensions perpendicular to membrane thickness dimension in terms of spatial position, which further constitutes a 3D interconnected porous network. One major objective of this study is to explore a facile and economic method to construct a novel 3D architecture with interconnected channels in support layer, which is expected to minimize ICP for as-synthesized FO membrane by reducing the structural parameter of support layer.
1.3. Systematic comparison between this study and previous reports on GO-polymer support layer for FO membrane

Table S1. A systematic comparison between this study and previous reports on GO-polymer support layer for FO membrane.

<table>
<thead>
<tr>
<th>Articles</th>
<th>Overall assessment</th>
<th>Rationale</th>
<th>Scope and contents</th>
<th>Significant novelties</th>
</tr>
</thead>
<tbody>
<tr>
<td>This study</td>
<td>This is a very novel, in-depth, comprehensive, and systematic study to:</td>
<td>This study is based on the deep understanding of 3D membrane architecture and its effect to break ICP bottleneck on FO, as well as the structure, property, and potentiality of 2D nanomaterials.</td>
<td><strong>Scope</strong>&lt;br&gt;This is a very comprehensive study to systematically investigate:</td>
<td>This study achieves fundamental contributions of milestone significance to synthetic membrane and 2D nanomaterials, which include:</td>
</tr>
<tr>
<td>1.</td>
<td>explore new 3D architecture with 2D nanomaterials via a facile and economic approach for breaking the intrinsic ICP bottleneck on FO processes.</td>
<td>1. the transformation of polymer matrix architecture from 1D to 3D under different conditions.</td>
<td>[1]. For the first time, an entirely 3D architecture i.e. GO-polymer 3D architecture is created via a facile and economic phase-inversion approach.</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>discover the mechanism for the formation of 3D architecture.</td>
<td>2. the formation mechanism of 3D architecture.</td>
<td>[2]. For the first time, a new theory i.e. GO-induced microregional phase inversion is developed to reveal the mechanism for forming this 3D architecture.</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>uncover the role of 2D nanosheets in forming 3D architecture.</td>
<td>3. the role of GO nanosheets in architecture transformation</td>
<td>[3]. For the first time, the unique role of GO nanosheets in forming this 3D architecture is unveiled: GO is</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>investigate structure-function relationships for the transformation of membrane architecture under different conditions.</td>
<td>4. the effect of GO lateral size (basal</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Main content**

[1]. the effect of GO/polymer ratio (ranging from 0% to 6.67%, high incorporating ratio is investigated, and optimized 3D architecture is found at 3.33%).

[2]. the effect of polymer concentration.

[3]. the effect of different solvents.

[4]. the effect of GO lateral size (basal

A systematic study to:

1. "demonstrate that CN/rGO is an effective additive for modifying the porous substrate for the development of FO membranes" (quoted directly from abstract section).

Remarks

- No mention of the concept 3D

GO's 2D structure characteristics from a new perspective, achieve a new 3D architecture via facile and economic process, and further understand 3D architecture formation mechanism.

plane area).

5. the comparison with using PVP or PEG as hydrophilic additive.


7. Membrane separation properties.

(additional note: FO membrane selective layer is hydrogel).

not only an additive, but the essential building-block, whose 2D structure characteristics induces new phase inversion dynamics in the dimensions perpendicular to membrane thickness dimension, and thus forming 3D interconnecte d porous architecture.

4. This study sheds new light on 2D nanomaterials for developing high performance filtration membranes.

Scope

1. "Recently, the modification of hydrophobic polymer has attracted considerable attention" (quoted directly from introduction section).

2. "carbon nitride materials have the potential to enhance the composite substrate"

Main content

1. the effect of rGO/polymer ratio (only ranging from 0% to 1%).
<table>
<thead>
<tr>
<th>Remarks</th>
<th>Scope</th>
<th>Main content</th>
<th>Remarks</th>
</tr>
</thead>
</table>
| Architecture:  
- No exploration on 3D architecture formation mechanism.  
- No exploration on the role of 2D nanosheets in forming 3D architecture. | **GO nanosheets were used as fillers to modify the polysulfone (PSf) support of TFC-FO membranes** (quoted directly from introduction section). | 1. the effect of rGO/polymer ratio (only ranging from 0% to 1%).  
2. Material characterizations.  
3. Membrane separation properties. | No exploration of high incorporating ratio (no data for incorporating ratio >1%). |
| A systematic study to:  
1. “demonstrate that GO modification of membrane supports could be a promising technique to improve the performances of TFC-FO membranes” (quoted directly from abstract section). | **GO is an attractive material choice to modify the support layer of TFC-FO membranes as it abundantly contains oxygenous functional groups** (quoted directly from introduction section). | Remarks |  
- No mention of the concept 3D architecture.  
- No exploration on 3D architecture formation mechanism.  
- No exploration on the role of 2D nanosheets |  
- No exploration of high incorporating ratio (no data for incorporating ratio >1%). |

**wettability**” (quoted directly from introduction section). | **“These unique dimensional and surface properties of GO nanosheets offer great potential for making composite materials”** (quoted directly from introduction section). | (additional note: FO membrane selective layer is polyamide). | **“the overall results in this study demonstrate that, the GO-modified PSf support layer could be a promising technique to produce TFC-FO membranes with enhanced water flux and flux selectivity”** (quoted directly from conclusion section). |
Notes on Table S1.

(1) This article is the first study that creates an entirely new membrane architecture \textit{i.e.} “GO-polymer 3D interconnected porous architecture”, develops a new theory \textit{i.e.} “GO-induced (microregional) phase inversion” for exploring 3D architecture formation mechanism, and discovers the unique role of GO’s 2D structure characteristics in forming this 3D architecture.

(2) Categorical differences also exist in the objectives and scope of research: previous reports used GO or its derivative as an “additive” at relatively low incorporating ratio (GO/polymer ratio: \(\leq 1\%\)) for the basic purpose of modifying polymer matrix; \textsuperscript{6,7} while this study utilizes GO as an essential membrane building-block in high incorporating ratio (GO/polymer ratio: up to 6.67\%) to qualitatively change phase inversion process and thus discovered the new architecture \textit{i.e.} 3D interconnected porous architecture at the incorporating ratio beyond previous reports scope (GO/polymer ratio: 3.33\%).

(3) Moreover, this study provides a much more comprehensive investigation on GO-polymer composite architecture, which includes many important contents not studied by previous reports, such as the effect of polymer concentration, the effect of different solvents, the effect of GO lateral size (basal plane area), and the comparison with using PVP or PEG as hydrophilic additive.
Additionally, the material for selective layer is different: polyamide in previous reports, while hydrogel macromolecule in this study. In view of membrane selective layer, this study and previous reports synthesize different kinds of membrane.

In order to avoid any misinterpretation of previous reports, the statements and viewpoints describing previous reports are quoted directly from the Abstract, Introduction, and Conclusion sections (as shown in “italic” style) of their articles.
2. Supplementary Experimental Details

2.1. Materials

Unless stated otherwise, all chemicals were in analytical grade and used as received. GO nanosheets were synthesized via a modified Hummers’ method, with the detailed synthetic protocol recorded in our previous study. Polyethersulfone (PES, weight averaged molecular weight $M_w \approx 63$ kDa, Solvay) was employed as the polymer to prepare dope solutions. Pure $N,N$-dimethylformamide (DMF, $\geq 99.8\%$, Sigma-Aldrich), $N,N$-dimethylacetamide (DMAc, $\geq 99.8\%$, Sigma-Aldrich), or 1-methyl-2-pyrrolidone (NMP, $\geq 99.9\%$, Sigma-Aldrich) was used separately as the solvent of dope solution. Polyvinyl alcohol (PVA, $M_w \approx 93$ kDa, 99+%, hydrolyzed, Sigma-Aldrich) was used as the hydrogel macromolecule to synthesize the selective layer, with glutaraldehyde ($>99.8\%$, 25 wt% aqueous solution, Sigma-Aldrich) employed as the crosslinking agent. Sodium sulfate ($\text{Na}_2\text{SO}_4$, decahydrate, $\geq 99.0\%$, Sigma-Aldrich) was employed as the draw solute (draw solute and salt are interchangeable in this manuscript). Deionized water (DI water, 18 MΩ cm) was obtained from a Millipore Q ultrapure water system.
### 2.2. The detailed composition of various dope solutions prepared for the synthesis of support layer

#### Table S2. The detailed composition of various dope solutions investigated in this paper.

<table>
<thead>
<tr>
<th>Dope solution&lt;sup&gt;a)&lt;/sup&gt;</th>
<th>GO/polymer [%]</th>
<th>GO conc. [wt%]</th>
<th>Polymer conc. [wt%]</th>
<th>Solvent&lt;sup&gt;c)&lt;/sup&gt; [wt%]</th>
<th>Research aims</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional</td>
<td>0.00</td>
<td>0.00</td>
<td>15</td>
<td>85</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.33</td>
<td>0.05</td>
<td>15</td>
<td>84.95</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.67</td>
<td>0.10</td>
<td>15</td>
<td>84.90</td>
<td></td>
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<tr>
<td></td>
<td>1.00</td>
<td>0.15</td>
<td>15</td>
<td>84.85</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.33</td>
<td>0.20</td>
<td>15</td>
<td>84.80</td>
<td>To investigate the effect of GO/polymer ratio</td>
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<tr>
<td></td>
<td>2.00</td>
<td>0.30</td>
<td>15</td>
<td>84.70</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.33</td>
<td>0.50</td>
<td>15</td>
<td>85.50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.00</td>
<td>0.75</td>
<td>15</td>
<td>84.25</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.67</td>
<td>1.00</td>
<td>15</td>
<td>84.00</td>
<td></td>
</tr>
<tr>
<td>GO-polymer composite</td>
<td>0.00</td>
<td>0.00</td>
<td>17.5</td>
<td>82.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.33</td>
<td>0.58</td>
<td>17.5</td>
<td>82.0</td>
<td>To investigate the effect of polymer concentration</td>
</tr>
<tr>
<td>Conventional</td>
<td>0.00</td>
<td>0.00</td>
<td>20</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>GO-polymer composite</td>
<td>0.00</td>
<td>0.00</td>
<td>20</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.33</td>
<td>0.67</td>
<td>20</td>
<td>79.5</td>
<td></td>
</tr>
<tr>
<td>Conventional</td>
<td>0.00</td>
<td>0.00</td>
<td>17.5</td>
<td>82.5 (DMAc)&lt;sup&gt;d)&lt;/sup&gt;</td>
<td>To investigate the effect of different solvents</td>
</tr>
<tr>
<td>GO-polymer composite</td>
<td>3.33</td>
<td>0.58</td>
<td>17.5</td>
<td>82.0 (DMAc)</td>
<td></td>
</tr>
<tr>
<td>Conventional</td>
<td>0.00</td>
<td>0.00</td>
<td>17.5</td>
<td>82.5 (NMP)&lt;sup&gt;e)&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>GO-polymer composite</td>
<td>3.33</td>
<td>0.58</td>
<td>17.5</td>
<td>82.0 (NMP)</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a)</sup> Weight fraction (wt%) refers to the proportion of entire dope solution throughout this study.  
<sup>b)</sup> Polymer refers to polyethersulfone (PES).  
<sup>c)</sup> Solvent refers to N,N-dimethylformamide (DMF) unless stated otherwise.  
<sup>d)</sup> DMAc refers to N,N-Dimethylacetamide.  
<sup>e)</sup> NMP refers to 1-methyl-2-pyrrolidone.
The photos were taken 12 hours later after the dope solution was degassed in a vacuum desiccator and cooled down to room temperature, and the dope solution was stable at that time. These results indicate the dope solution with GO nanosheets is stable under anhydrous environment for at least 12 hours, which is sufficiently long for the synthesis of support layer (each fresh dope solution was completed in usage within the first 3 hours for support layer synthesis). The GO/polymer ratio in the above photos is 6.67%. 

**Figure S3. Optical photos of as-prepared GO-polymer composite dope solution.**
2.3. Characterizations

Transmission electron microscope (TEM, JEOL JSM 2010-H) was used to characterize the morphology of as-synthesized GO nanosheets. For TEM sample preparation, sonicated GO solution was dripped onto 400-mesh carbon coated copper grids and then dried in room temperature. Atomic force microscope (AFM, Park XE-100) was used to characterize the topography of as-synthesized GO nanosheets and membranes in non-contact mode, with silicon wafer as the substrate to immobilize the sample. Dynamic light scattering (DLS, Mastersizer 2000) was employed to characterize the lateral sizes of GO nanosheets. Field emission scanning electron microscope (FESEM, JEOL JSM 7600F) was used to characterize membrane architectures under accelerating voltage of 5 kV. Membrane samples were immediately fractured after flash-frozen in liquid nitrogen to obtain cross-sections. All FESEM samples were coated by gold for 20 s using a Cressington 108auto sputter coater. Attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR, Perkin Elmer 2000, ZnSe crystal method) was used to analyze the functional groups of membrane surface with the samples freeze-dried overnight before scanning. X-ray diffraction (XRD) patterns were investigated by a Bruker AXS D8 Advance diffractometer with a Cu Kα radiation source. Contact angle was determined on an optical goniometric equipment (AST VCA Optima) using sessile drop technique. The contact angle data was recorded at the initial moment when DI water (3 μl) fully wet membrane surface, and reported as the average of 9 random measurements. The samples for thermogravimetric analysis (TGA, Perkin Elmer TGA 7) were heated from 30 °C to 900 °C at the temperature ramp of 10 °C/min. TGA experiments were conducted under the purging gas of air or pure nitrogen gas separately.
2.4. Determination of pore size distribution on support layer top surface

Solute transport method is utilized to determine pore size distribution of support layer top surface, with different molecular-weighted polyethylene glycol (PEG, Sigma-Aldrich) and polyethylene oxide (PEO, Sigma-Aldrich) employed as the neutrally charged solid solute. Generally, the method follows the protocol published by Singh S. et al. The detailed procedure includes three steps in sequence: (1) to measure the rejection of neutrally charged solid solute by support layer, (2) to determine the Stokes diameter of solid solute, and (3) to analyze the pore size distribution of support layer top surface.

(1) To measure the rejection of neutrally charged solid solute by support layer

The rejection of neutral solid solute by support layer is determined through measuring the solute concentration in permeate and retentate at the same filtration time. In detail, 200 ppm aqueous solution of PEG or PEO was utilized as the feed solution at time 0. A custom-built cross-flow filtration module was employed to circulate the feed solution on the top surface of support layer under 1 bar transmembrane hydraulic pressure difference ($\Delta P$) at 23 ± 2 °C. The crossflow rate was kept as 1.0 L/min. And a plastic spacer (SEPA CF spacer, 17 mil) was placed on top of support layer to generate flow turbulence. Total organic carbon (TOC, Shimadzu TOC-VCSH) was used to measure solute concentration in both permeate and retentate at 90th min of filtration. And the rejection of neutrally charged solid solute by as-synthesized support layer was determined according to equation S5.

\[
Rejection = \left(1 - \frac{C_P}{C_R}\right) \times 100\% \quad (S5)
\]

where $C_P$ is the concentration of solid solute in permeate while $C_R$ is the concentration of solid solute in retentate.
(2) To determine the Stokes diameter of solid solute

The Stokes diameter of neutrally charged solid solute can be calculated by the Stokes-Einstein equation, with the specific calculation method demonstrated in equation S6 and S7.

For PEG,

\[ d_{s,\text{peg}} = 3.346 \times 10^{-2} \times M_{\text{peg}}^{0.557} \]  

(S6)

where \( d_{s,\text{peg}} \) is the Stokes diameter of PEG in the unit of nm; \( M_{\text{peg}} \) is the molecular weight of PEG in the unit of Dalton.

For PEO,

\[ r_{s,\text{peo}} = 2.088 \times 10^{-2} \times M_{\text{peo}}^{0.587} \]  

(S7)

where \( d_{s,\text{peo}} \) is the Stokes diameter of PEO in the unit of nm; \( M_{\text{peo}} \) is the molecular weight of PEO in the unit of Dalton.

(3) To analyze the pore size distribution of support layer top surface

In order to obtain pore size distribution of support layer top surface, the rejections of different molecular-weighted PEG or PEO (ranging from 10 k to 1,000 k Dalton) by as-synthesized support layers were systematically tested. Notably, the rejection of neutral solid solute by pore-flow membrane (as-synthesized support layer) has been revealed to be correlated with solute diameter according to the log-normal probability function as expressed in equation S8 and S9.  

\[ \text{Rejection} = \text{erf}(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{x} e^{-\frac{u^2}{2}} du \]  

(S8)

\[ x = \frac{\ln d_s - \ln \mu_s}{\ln \sigma_s} \]  

(S9)
where $d_S$ is the Stokes diameter of neutral solute, $\mu_S$ is the geometric mean diameter of solute at rejection = 50%, $\sigma_S$ is the geometric standard deviation about the mean diameter.

Based upon equation S8 and S9, a linear correlation can be established between rejection and $\ln(d_S)$ in the form of equation S10.

\[ \text{Rejection} = E \times (\ln d_s) + F \quad (S10) \]

where $E$ is the slope and $F$ is the intercept, respectively.

From this linear fitting on log-normal probability paper, mean solute diameter ($\mu_S$) can be calculated as $d_S$ corresponding to rejection = 50%, while $\sigma_S$ can be determined from the ratio of $d_S$ at rejection = 84.13% to $d_S$ at rejection = 50%. Furthermore, by ignoring the dependence of solute rejection on the hydrodynamic interaction between solutes and pores, the mean pore diameter ($\mu_P$) can be regarded the same as solute mean pore diameter ($\mu_S$), and geometric standard deviation ($\sigma_P$) of membrane (as-synthesized support layer) can be regarded the same as solute geometric standard deviation ($\sigma_S$). Based upon the obtained $\mu_P$ and $\sigma_P$, the pore size distribution of a pore-flow membrane (as-synthesized support layer) can be expressed as the following probability density function.

\[
\frac{df(d_p)}{dd_p} = \frac{1}{d_p \ln \sigma_P \sqrt{2\pi}} \exp \left[ -\frac{(\ln d_p - \ln \mu_P)^2}{2(\ln \sigma_P)^2} \right] \quad (S11)
\]

where $d_p$ is the pore size of membrane (as-synthesized support layer).
3. Supplementary Results and Discussion

3.1. Demonstration of the three dimensional coordinate system

Figure S4. Demonstration of the three dimensional Cartesian coordinate system for the setting of as-synthesized membranes. The top-to-bottom direction is set along z axis and the cross-section plane facing towards readers is set in xz plane.
Additional Discussion on Figure S4.

According to the 3D coordinate system as set in Figure S3, when discussing the interior pore structure of as-synthesized support layers based upon the obtained FESEM images, the term “z-axis channel” represents the fingerlike pore growing in the direction from top surface to bottom surface of support layer (in xz plane). The term “y-axis” channel represents GO-induced pore growing in the direction “from front to back” (perpendicular to z-axis and xz plane). The term “x-axis” channel represents GO-induced pore growing in the direction “from right to left” (perpendicular to z-axis but in xz plane). The terminology is further clarified in the following table.

<table>
<thead>
<tr>
<th>Term</th>
<th>Dimension</th>
<th>GO-induced</th>
<th>Perpendicular to z axis</th>
<th>Perpendicular to xz plane</th>
<th>In xz plane</th>
</tr>
</thead>
<tbody>
<tr>
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3.2. The existence of GO nanosheets in as-synthesized FO membrane of GO-polymer 3D architecture

Figure S5. FESEM and XRD characterizations of GO-polymer composite support layer. (a) High-magnification FESEM image on the bottom surface of GO-polymer composite support layer. The blue line highlights the embedded GO nanosheets, showing that GO sheets can be embedded at in-plane orientation (parallel to membrane surface) in GO-polymer composite support layer. (b) Additional high-magnification FESEM image on the bottom surface of GO-polymer composite support layer. The blue line highlights the embedded GO nanosheets, showing that GO sheets can be embedded at non-in-plane orientation (inclined to membrane surface) in GO-polymer composite support layer. The preferential orientation of embedded GO nanosheets in GO-polymer composite support layer is recommended in future study. The above two FESEM images provide eye-visible evidences for the existence of GO nanosheets in as-synthesized GO-polymer composite support layers. Besides, image (b) demonstrates that some embedded GO nanosheets experience certain curling with wrinkles formed at the surfaces and edges. (c) XRD patterns of GO, GO-polymer composite support layer, and conventional polymer support layer (GO/polymer ratio: 0.00%). As marked by the grey line, the XRD pattern of GO has a characteristic peak at 2θ = 11.6° (corresponding to interlayer spacing of ~0.74 nm). This characteristic peak is observed in the XRD pattern of GO-polymer composite support layer but absent in the XRD pattern of conventional polymer support layer, which corroborates the existence of GO nanosheets in GO-polymer composite support layer. It's worthwhile to note that GO-polymer composite support layer in this figure are synthesized at GO/polymer ratio of 6.67% with 15 wt% polymer and 84 wt% DMF.
Additional Discussion on Figure S6

Figure S6a shows that as-synthesized GO nanosheets have lower thermal stability compared to its parent material i.e. graphite (SP1, Bay Carbon, USA). Under nitrogen gas, graphite maintains 100% mass without any loss despite the increase of temperature from 30 °C to 900 °C. In contrast, as-synthesized GO nanosheets undergo weight loss along with the elevation of temperature, with only 40% weight left at 900 °C. Particularly, the slow loss of weight from 255 °C to 900 °C for GO is considered as the carbonization process, wherein molecules other than carbon are removed. Under dry air, graphite does not lose any mass until temperature elevated to 730 °C. And at 900 °C the weight left for graphite is 51%. In contrast, GO undergoes 10% weight loss from 30 °C to 100 °C, which is due to the evaporation of absorbed water or any other volatile molecules. The weight loss from 250 °C to 600 °C is 32% and attributed to thermal decomposition of oxygenic groups as well as carbon lattice. At 680 °C, nearly 0% mass is left for as-synthesized GO nanosheets.
As shown in Figure S6b, the TGA analysis results substantiate the presence of GO nanosheets in the support layer of GO-polymer 3D architecture. Generally, support layer of GO-polymer 3D architecture possesses slightly higher thermal stability compared with conventional support layer of 1D architecture. Under nitrogen gas, the decomposition is started at ~460 °C for both support layers, and the weight loss rate of conventional support layer is constantly higher than support layer of GO-polymer 3D architecture. At 900 °C, the weight left is 33% for conventional support layer of 1D architecture and 36% for support layer of GO-polymer 3D architecture. The 3% higher weight left is attributed to the incorporated GO nanosheets. Interestingly, the GO/polymer ratio to fabricate the support layer of GO-polymer 3D architecture is 3.33% (the GO nanosheets concentration and polymer concentration in dope solution are 0.5 wt% and 15 wt%, respectively). Under dry air, the weight loss curve turns to be steep as temperature exceeds 580 °C for both support layers due to the oxidation and lysis of polymer chain. At 900 °C, 0.0 wt% mass is left for conventional support layer of 1D architecture while 0.7 wt% mass is left for support layer of 3D architecture. The higher weight fraction left for support layer of 3D architecture is ascribed to the embedment of GO nanosheets in polymer matrix.
Figure S7. ATR-FTIR spectrum of as-synthesized support layer under different GO/polymer ratios. As-synthesized conventional support layer (1D architecture) has several characteristic infrared (IR) bands: 1578 cm\(^{-1}\) (C-C bond in benzene ring of polymer i.e. PES), 1487 cm\(^{-1}\) (C=C bond in benzene ring of PES), 1325 cm\(^{-1}\) (asymmetric stretching of CSO2C group), 1300 cm\(^{-1}\) (asymmetric stretching of O=S=O groups), 1244 cm\(^{-1}\) (C-O vibrations of the aromatic ether bond), 1153 cm\(^{-1}\) (symmetric stretching of O=S=O groups), and 1107 cm\(^{-1}\) (C-O vibrations of the aromatic ether bond). In addition to these IR bands, another three new IR bands are observed on as-synthesized GO-polymer composite support layers: 3400 cm\(^{-1}\) (O-H stretching of hydroxyl groups on GO nanosheets), 1733 cm\(^{-1}\) (C=O stretching of carboxyl groups on GO nanosheets), 1627 cm\(^{-1}\) (C=C stretching of unoxidized graphitic carbon), which proves that the incorporation of GO nanosheets equips as-synthesized support layer with various oxygen-containing functional groups. Therefore, FTIR results also substantiate the embedment of GO nanosheets in as-synthesized GO-polymer composite support layer.
3.3. Supplementary information on the effect of GO/polymer ratio upon the formation of GO-polymer 3D architecture

Figure S8. Optical photograph of as-synthesized support layer under different GO/polymer ratios. From left to right for the 9 support layer pieces in the above photo, GO/polymer ratio is 0.00%, 0.33%, 0.67%, 1.00%, 1.33%, 2.00%, 3.33%, 5.00%, and 6.67%, respectively; while polymer concentration and solvent in dope solution are kept as 15 wt% and DMF, respectively. The increase of GO/polymer ratio leads to the transition of support layer color from pure white to dark brown. This optical photo supplies an eye-visible evidence for the embedment of GO nanosheets in GO-polymer support layers.
Figure S9. Supplementary FESEM images on the architecture of as-synthesized support layers under GO/polymer ratio below 1.33% (inclusive). The GO/polymer ratio is (a) 0.00 wt%, (b) 0.67%, and (c) 1.33%, while polymer concentration and solvent in dope solution are kept as 15 wt% and DMF, respectively. The red circles on Figure S9b, S9c mark some typical new channels emerged in the dimensions (y-axis and x-axis) perpendicular to z-axis dimension.
Figure S10. Enlarged FESEM image on the support layer of GO-polymer 3D architecture. The red circles highlight some typical y-axis channels (perforating xz cross-section plane) with pore size at micrometer scale. Such y-axis (or x-axis) channel can be produced at the depth position as near as 6.0 μm from the top surface of GO-polymer 3D architecture. The entire thickness of as-fabricated support layer (3D architecture) is 91.2 μm, so 3D interconnected porous network spans (91.2 − 6.0)/91.2 = 93.4% thickness cross section of support layer in terms of spatial distribution. The dope solution to fabricate the GO-polymer composite support layer contains 15 wt% polymer, and 84.5 wt% DMF with GO/polymer ratio of 3.33%. 
3.4. The effect of polymer concentration upon the formation of GO-polymer 3D architecture

Figure S11. The effect of polymer concentration upon the formation of GO-polymer 3D architecture. (a) 0.00% GO/polymer ratio, 15 wt% polymer, and 85 wt% DMF. (b) 3.33% GO/polymer ratio, 15 wt% polymer, and 84.5 wt% DMF. (c) 0.00% GO/polymer ratio, 17.5 wt% polymer, and 82.5 wt% DMF. (d) 3.33% GO/polymer ratio, 17.5 wt% polymer, and 82 wt% DMF. (e) 0.00% GO/polymer ratio, 20 wt% polymer, and 80 wt% DMF. (f) 3.33% GO/polymer ratio, 20 wt% polymer, and 79.5 wt% DMF. The red circles on Figure S11b, S11d, and S11f highlight some typical new channels emerged in the dimensions (y and x axes) perpendicular to z axis.

Additional discussion on Figure S11.

To verify the universality of GO-induced transformation from 1D architecture to 3D architecture, the effects of polymer concentration and solvent are also investigated, with the corresponding results displayed in Figure S11 and Figure S12, respectively.
Figure S11 demonstrates the effect of polymer concentration upon the formation of GO-polymer 3D architecture. Figure S11a, S11c and S11e serve as the control group (GO/polymer ratio is 0.00%) for polymer concentration of 15 wt%, 17.5 wt% and 20 wt%, respectively, whose z-axis channel wall is all found to be nonporous at micrometer-scale. As highlighted by the red circles on Figure S11d and S11f, GO-induced new channels along y axis (and x-axis) that perforate z-axis channel at micrometer scale are also formed under polymer concentration of 17.5 wt% and 20 wt%. However, it’s worthy to note that the pore area perforated by y-axis (and x-axis) channel with respect to a unit area ofxz cross-section plane gets decreased along with the increase of polymer concentration from 15 wt% to 20 wt%, as compared among Figure S11b, S11d and S11f. The explanation to this phenomenon is elaborated as follows. The increase of polymer concentration results in the increase in absolute viscosity of dope solution, which makes z-axis channel wall to be thicker as evidenced by the comparison among Figure S11a, S11c, and S11e. However, thicker wall provides bigger resistance to the perforation by new channels grown along y and x axes, and consequently, the pore interconnections in y-axis and x-axis dimensions get decreased.

In short, GO nanosheets can stimulate the transformation of polymer matrix from 1D tortuous architecture to 3D interconnected architecture under a wide range of polymer concentration (at least from 15 wt% to 20 wt%, which is the typical polymer concentrations adopted for membrane manufacturing), and 15 wt% is the most beneficial polymer concentration among all examined values to synthesize 3D interconnected porous architecture.
3.5. The effect of solvent upon the formation of GO-polymer 3D architecture

Figure S12. The effect of solvent upon the formation of GO-polymer 3D architecture. (a) 0.00% GO/polymer ratio, 17.5 wt% polymer, and 82.5 wt% 1-methyl-2-pyrrolidone (NMP). (b) 0.33% GO/polymer ratio, 17.5 wt% polymer, and 82 wt% NMP. (c) 0.00% GO/polymer ratio, 17.5 wt% polymer, and 82 wt% N,N-Dimethylacetamide (DMAc). (d) 3.33% GO/polymer ratio, 17.5 wt% polymer, and 82 wt% DMAc. The red circles on Figure S12b, S12d highlight some typical new channels emerged in the dimensions (y and x axes) perpendicular to z axis.

Additional discussion on Figure S12

The solvent of dope solution has been revealed to influence phase inversion process to a significant extent. This is because (1) the stability of GO nanosheets is different in different solvents, (2) the stability of polymer is different in different solvents, and (3) the compatibility between solvent and certain nonsolvent is different among different solvents.

Figure S12 demonstrates the effect of solvent upon the formation of GO-polymer 3D architecture. Figure S12a and S12c serve as the control group (GO/polymer ratio is 0.00%) for the solvent of NMP and DMAc, respectively, whose z-axis channel wall is all found to be
nonporous at micrometer-scale. As highlighted by the red circles on Figure S12b and S12d, GO-induced new channels along y-axis that perforate z-axis channel at micrometer scale are also formed under solvent of NMP or DMAc. Particularly, Figure S12b also serves as the evident example for the formation of x-axis channel (perpendicular to z axis but in xz cross-section plane, i.e. along the direction “from right to left”). Comparing Figure S12b, S12d with S11d, the pore area perforated by y-axis (and x-axis) channel with respect to a unit area of xz cross-section plane is highest in DMF. Besides, our experiments also observed that the stability of as-synthesized GO nanosheets in DMF is higher in comparison to the stability of GO nanosheets in NMP or DMAc. Taking these results together, DMF is considered as the best solvent to the formation of GO-polymer 3D architecture. In short, GO nanosheets can stimulate the transformation of polymer matrix from 1D tortuous architecture to 3D interconnected architecture under different solvents.
Dynamic process of GO-induced phase inversion for the formation of GO-polymer 3D architecture.

Figure S1

(a) Dynamic process of conventional phase inversion, wherein (a-1) the film is cast from conventional dope solution and immediately immersed in the nonsolvent (DI water); (a-2) viscous fingering displacement proceeds merely along z axis; (a-3) consequently, the formed finger-like channels are only grown in 1 dimension (along z axis) and segregated in the other 2 dimensions (x and y axes).

(b) Dynamic process of GO-induced phase inversion, wherein (b-1) the film is cast from GO-polymer composite dope solution and immediately immersed in the nonsolvent (DI water); (b-2) as fingering displacement proceeds to the depth near GO-containing microregion, the existed GO nanosheets generate viscosity differences in x and y axes between GO-containing microregions and GO-absent microregions, which stimulates the spread of fingering displacement from original 1 dimension (along z axis) to 3 dimensions (x, y, and z axes); (b-3) as a result, the formed finger-like channels become highly interconnected in 3 dimensions at micrometer-scale, forming 3D interconnected porous architecture.
3.7 The relationship between GO’s lateral size (basal plane area) and the properties of GO-induced new channels in the dimensions perpendicular to membrane thickness dimension

Figure S14. The relationship between GO lateral size and the properties of GO-induced new channels in the dimensions perpendicular to thickness dimension. (a-1) AFM image of relatively large GO nanosheets, which are prepared by routine bath-sonication (Branson, 70 Watts, 1.5 hours at 20 °C), (a-2) DLS characterization result for the size distribution of GO nanosheets, (a-3) GO-polymer architecture synthesized with relatively large GO nanosheets (the optimized 3D architecture in this study). (b-1) AFM image of relatively small GO nanosheets, which are prepared by routine bath-sonication plus probe-sonication (VibraCellTM, 750 Watts, 1.5 hours at 20 °C). (b-2) DLS characterization result for the size distribution of GO nanosheets, (b-3) GO-polymer architecture synthesized with relatively small GO nanosheets. In the dope solution to fabricate support layers, GO/polymer ratio is 3.33%, polymer concentration is 15 wt%, and solvent is DMF.

Additional discussion on Figure S14.

It has been reported that the lateral size (basal plane area) of GO nanosheets exfoliated from graphite oxide is related to the intensity and time of ultra-sonication (Perreault et al., ACS Nano, 2015, 9, 7226). A bath-sonication (Branson, 70 Watts, 1.5 hours at 20 °C) was employed as the routine protocol to prepare the GO solutions for various dope solutions as aforementioned. Here, in order to investigate the effect of GO’s lateral size (basal plane area) on the formation of GO-polymer 3D architecture, bath-sonicated GO solution was further
probe-sonicated at high intensity (Vibra Cell™, 750 Watts, 1.5 hours at 20 °C) to produce GO nanosheets in relatively small sizes. AFM imaging displays that probe-sonication at high intensity is effective to produce GO nanosheets with smaller lateral sizes (Figure S14a-1, S14b-1). DLS characterization results reveal that the average size (mass median diameter, $d_{50}$) of GO nanosheets is reduced from 2.8 μm to 0.8 μm after probe-sonication (Figure S14a-2, S14b-2). This means the average basal plane area of routinely-prepared GO nanosheets is estimated to be ~11 times larger than that of probe-sonicated GO nanosheets (2.82/0.82=12.3). Figure S14a-3 and S14b-3 display GO-polymer architecture synthesized with GO nanosheets of different average sizes, which indicate there is a positive correlation between GO’s lateral size and GO-induced new channels in x-axis and y-axis dimensions (perpendicular to thickness dimension). In particular, at ~30% relative depth, large y-axis (x-axis) channel with pore size exceeding 15 μm can be produced by incorporating relatively large GO nanosheets (as marked by red circle in Figure S14a-3). In contrast, y-axis (x-axis) channel with pore size exceeding 15 μm is not formed by incorporating relatively small GO nanosheets, and the y-axis (x-axis) channels at ~30% relative depth are typically < 5 μm in size (as marked by the red circle in Figure S14b-3). Moreover, FO water flux of the membrane with GO-polymer support layer synthesized by relatively large GO nanosheets (the optimized 3D architecture in this study) is 18.3 ± 1.5 L m$^{-2}$ h$^{-1}$, which is evidently higher than FO water flux of the membrane with GO-polymer support layer synthesized by relatively small GO nanosheets (14.1 ± 1.2 L m$^{-2}$ h$^{-1}$). In addition, structural parameter of GO-polymer support layer synthesized by relatively large GO nanosheets is 166 ± 13 μm, which is considerably lower than the structural parameter of GO-polymer support layer synthesized by relatively small GO nanosheets (221 ± 19 μm).
The above results indicate that GO’s lateral size (basal plane area) is also important for the formation of 3D interconnected porous architecture: GO nanosheets with large lateral sizes are more effective to improve 3D interconnectivity of interior pores, and thus more effective to reduce support layer structural parameter (reduce ICP extent) for improving FO water flux.

Moreover, this result is consistent with our developed new theory i.e. “GO-induced (microregional) phase inversion”. The driving force to produce new channels in the dimensions perpendicular to membrane thickness dimension is the viscosity difference between “GO-containing microregions” and “GO-absent microregions”. GO nanosheets with large basal plane generate higher viscosity difference between microregions, and thus produce the new channels (x-axis channels and y-axis channels) in large size. On the contrary, GO nanosheets with small basal plane generate lower viscosity difference between microregions, and thus produce the new channels in small size. And if the viscosity difference between microregions becomes smaller than a certain threshold value, the microregional viscosity difference may not be sufficient to perforate the wall of z-axis channels, leading the channel formation in new dimensions (and also the formation of curvaceous channel wall structure) to become less evident.

In addition, since GO’s lateral size is related to sonication conditions (time, intensity, temperature, and instrument type), the details on sonication conditions, and more importantly, the characterization on the lateral size of GO nanosheets (as presented in Figure 2a, 2b, Figure S14) are useful data for providing the basis to compare different papers on GO-polymer nanocomposite membrane (support layer).
In the future, a systematic study on the relationship between GO lateral size and the properties of GO-induced new channels (formed in the dimensions perpendicular to thickness dimension) is recommended.
3.8. The investigation on using PVP or PEG as hydrophilic "additive" in dope solution

Figure S15. The effect of different additives in dope solution on FO membrane architecture and performances. (a) Illustration on GO-polymer composite dope solution and GO-induced phase inversion. GO-containing microregions and GO-absent microregions are formed in GO-polymer composite dope solution. The red arrows indicate GO-induced phase inversion proceeds in 3 dimensions. (b) Illustration on dope solution with PVP or PEG as additive and its phase inversion process. There is no microregional difference formed at micrometer scale for the dope solution with PVP or PEG. The red arrow indicates conventional phase inversion proceeds merely in one dimension. (c) Membrane with GO-polymer composite has 3D interconnected porous architecture, wherein plenty of new pores are formed perforating the wall of z-axis channels. (d, e) Membranes synthesized by the dope solution with PVP (d) or PEG (e) have conventional 1D tortuous architecture. (f) Water flux at FO mode (draw solution is 0.5 M Na_2SO_4 and feed solution is DI water). (g) Structural parameter of support layers. For c ~ g, the incorporating ratio is the same for GO, PVP, and PEG: GO/PES = PVP/PES = PEG/PES = 3.33%; PES concentration is 15 wt%; and solvent is DMF. M_W of PVP and PEG is 55 kDa and 40 kDa, respectively. Error bar is presented based upon the statistics of 5 independent membrane samples for each condition.
Additional discussion on Figure S15.

In order to further explore the mechanism for forming “3D interconnected porous architecture”, our established new theory i.e. “GO-induced (microregional) phase inversion” is verified by using different hydrophilic additives in dope solution. Widely-used hydrophilic additives polyvinyl pyrrolidone (PVP) and polyethylene glycol (PEG) are employed for preparing the dope solution at the same incorporating ratio (PVP/PES = PEG/PES = GO/PES = 3.33%, each dope solution contains only one additive). Membrane synthesis follows the same procedure as detailed in “Experimental” section. The results are presented in Figure S15. Figure S15d and S15e display that the FO membrane with PVP or PEG in dope solution has conventional 1D tortuous architecture: segregated pores (channels) are merely grown in z-axis dimension (membrane thickness dimension). In contrast, FO membrane with GO-polymer composite has 3D interconnected porous architecture: plenty of new channels in micrometer size are formed in the dimensions perpendicular to membrane thickness dimension, which perforate the wall of z-axis channels (Figure S15c). Moreover, Figure S15f shows that FO water flux is merely increased by 7~14 % through using PVP or PEG as additive, compared to pristine membrane (control group, dope solution without any additive). In contrast, the FO water flux of membrane with GO-polymer 3D architecture is 73% higher than that of pristine membrane. In addition, the structural parameter (S) of support layer is only reduced by 3~7% through using PVP or PEG as additive, compared to pristine membrane. In contrast, the S value of membrane with GO-polymer 3D architecture is 42% lower than that of pristine membrane. These results indicate GO nanosheets have a remarkable superiority in reducing ICP extent compared to PVP or PEG when used as the “additive” (membrane building-block) in dope solution (at the same incorporating ratio of 3.33%).
Our established new theory i.e. “GO-induced (microregional) phase inversion” is further elaborated here. Figure S15a and S15b illustrate the differences in phase inversion process for comparing GO-polymer composite dope solution and the dope solution with PVP or PEG as hydrophilic additive. As shown in Figure S15a, rather than “dissolved” in the solvent of dope solution, GO nanosheets are dispersed in the dope solution. The dispersions of GO nanosheets form “GO-containing microregions” and “GO-absent microregions” inside dope solution at micrometer scale. “GO-containing microregions” have relatively high viscosity while “GO-absent microregions” have relatively low viscosity. The viscosity differences between “GO-containing microregions” and “GO-absent microregions” function as the driving force to stimulate new phase inversion (viscous fingering) process in the dimensions perpendicular to membrane thickness dimension. As a result, new channels are formed perforating the wall of conventional 1D pore (fingerlike channel) during the phase inversion process, resulting in the formation of 3D interconnected porous architecture. The essence of GO’s “2D structure characteristics” is (1) GO’s nanometer-sized thickness enable its stable dispersion in dope solution, and (2) GO’s micrometer-sized basal plane enables the generation of sufficient viscosity differential to produce new pores at micrometer scale. In contrast, Figure S15b demonstrates that PVP or PEG is dissolved in the solvent to form the dope solution homogenous at micrometer scale, rather than forming “microregion of relatively high viscosity” and “microregion of relatively low viscosity” at micrometer scale. The lack of microregional differential in the dope solution with PVP or PEG causes its phase inversion process to merely proceed in one dimension. As a result, conventional 1D tortuous architecture are formed when using PVP or PEG as hydrophilic additive.
In sum, our developed new theory i.e. “GO-induced (microregional) phase inversion” can well explain why conventional 1D tortuous architecture is formed when using PVP or PEG as hydrophilic additive. These results also imply that it’s GO’s 2D structure characteristics, rather than GO’s hydrophilicity, play the dominant role in stimulating the transformation of polymer architecture from 1D tortuous to 3D interconnected.
Figure S16. The effect of GO/polymer ratio upon the roughness of support layer top surface. Polymer concentration and solvent in dope solution to synthesize support layers are kept as 15 wt% and DMF, respectively.
The effect of GO/polymer ratio upon pore size distribution of support layer top surface. Polymer concentration and solvent in dope solution to synthesize support layers are kept as 15 wt% and DMF, respectively. The results are calculated based upon solute transport technique with the protocol aforementioned in Supplementary Experimental Details. Filtration experiments were conducted under transmembrane hydraulic pressure difference ($\Delta P$) of 1 bar.
3.10. The comparison on top surface structure between FO membrane of GO-polymer 3D architecture and FO membrane of conventional 1D architecture.

These two FESEM images reveal that there is no evident difference in top surface structure between FO membrane of conventional 1D architecture and FO membrane of 3D architecture: both top surfaces are dense, compact, nonporous, and defect-free at nanometer scale that is effective to reject draw solute (Na$_2$SO$_4$) and small molecules. Furthermore, experimental results also indicate that both salt rejection at RO mode and reverse salt flux ($J_s$) at FO mode are in the same level respectively between FO membrane of conventional 1D architecture and FO membrane of GO-polymer 3D architecture. Therefore, it is reasonable to conclude that the improvement in FO water flux is because of GO-induced transformation of support layer interior architecture from conventional 1D tortuous to 3D interconnected porous, not due to any difference in hydrogel selective layer.

Figure S18. High-magnification FESEM image on the top surface of as-synthesized FO membrane with (a) conventional 1D architecture and (b) GO-polymer 3D architecture.
particular, GO-P/P stands for as-synthesized FO membrane or 3D architecture (optimized), for all synthesized support layers, polymer and GO/polymer ratio (%).

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Note: H1-CFA stands for commercial H1 FO membrane (cellulose triacetate, woven). P stands for GO membrane of conventional ID. FO mode of synthesized FO membranes.

Table S3. Properties of as-synthesized FO membranes.
The comparison on intrinsic parameters and separation performances of FO membrane between this study and previous reports.

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<th>Reverse flux (L m⁻² h⁻¹)</th>
<th>Selective layer</th>
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Note: (1) Membranes (support layers) that are fabricated by phase-inversion process are selected for the comparison. (2) The best membranes from each peer study is selected for the comparison. (3) Membrane orientation is fixed as FO mode. (4) J_W and J_S are compared at 0.5 M draw solute unless the data is not available (the osmotic pressure of 0.5 M NaCl is comparable to seawater that is abundant for engineering applications). (5) HTI-CTA stands for commercial HTI FO membrane (cellulose triacetate, woven); HTI-TFC stands for commercial HTI FO membrane (thin-film composite); PES stands for polyethersulfone; PSf stands for polysulfone; N.A. stands for not available.

Table S4. The comparison on intrinsic parameters and separation performances of FO membrane between this study and previous reports.
Additional discussion on Table S4

The significant novelties that are achieved for the first time by this study include: (1) creating an entirely new 3D architecture, (2) developing a new theory for architecture formation mechanism, and (3) discovering the unique role of GO nanosheets in forming this 3D architecture.

With respect to the specific innovations, support layer tortuosity ($\tau$, negatively correlated with pore interconnectivity) is reduced by 41% (from 2.64 to 1.55) as the result of GO-induced transformation from conventional 1D tortuous architecture to 3D interconnected porous architecture. This decrease of tortuosity is the major contributor to the decrease of support layer structural parameter ($S$) by 42% (from 285 $\mu$m to 166 $\mu$m), which directly indicates the substantial mitigation of ICP (ICP is exacerbated exponentially along with $S$, as aforementioned in equation S1 and S2). As a result, FO water flux is significantly enhanced by 73% from 10.6 L m$^{-2}$ h$^{-1}$ to 18.3 L m$^{-2}$ h$^{-1}$ correspondingly.

Moreover, in Table S4, the comparisons on support layer structural parameter ($S$) and tortuosity ($\tau$) are highlighted between this study and a number of reports on FO membrane development (via phase inversion process). This is because (1) $S$ and $\tau$ are the direct indicators for support layer structure characteristics, which can be utilized to quantitatively analyze the innovation of support layer architecture, and (2) $S$ and $\tau$ are the intrinsic properties of FO membrane support layer, which are independent on FO operating conditions (e.g. draw solution, feed solution, hydrodynamic conditions on membrane surfaces, etc.) and FO membrane selective layer properties. To our best knowledge (not limited within the data of Table S4), the tortuosity (1.55) and structural parameter (166 $\mu$m)
of our GO-polymer 3D architecture are among the lowest (best) value in the literature on phase inversion fabricated support layers. In particular, support layer tortuosity of our GO-polymer 3D architecture ($\tau$: 1.55) is remarkably smaller (better) than that of previous reports using GO as the additive to fabricate GO-polymer support layer ($\tau$: 3.2, from Wang et al.; $\tau$: 2.85, from Park et al.). This is consistent with our finding that a new architecture i.e. “GO-polymer 3D interconnected porous architecture” is created. As discussed previously in Supplementary Introduction, structural parameter equals to tortuosity $\times$ thickness / porosity. The increase of support layer porosity or the decrease of support layer thickness can reduce $S$ value, however, membrane mechanical integrity will be inevitably compromised. Therefore, the decrease of tortuosity is a smart way to reduce structural parameter for the minimization of ICP. In other words, given at the same $S$ value, the lower tortuosity allows the membrane support layer to possess higher thickness or lower porosity, which will benefit the mechanical strength and practical processing of membrane. In short, to our best knowledge, the $\tau$ (1.55) and $S$ (166 μm) of our GO-polymer 3D architecture is among the lowest (best) value in the literature on phase inversion fabricated support layers.

In addition, it is worthwhile to note that FO water flux ($J_w$) and reverse salt flux ($J_s$) are not the intrinsic properties of FO membrane, because these two parameters are dependent on many other external conditions including (1) membrane selective layer separation properties (water permeability and salt permeability), (2) the type and diffusivity of draw solute, (3) the osmotic pressure of draw and feed solutions, (4) fouling extent of membrane, (5) the hydrodynamic conditions on membrane surfaces (related to external concentration polarization), (6) the differences in membrane test equipments and methods, and so on. Noteworthily, this study focuses on the innovation of FO membrane support layer
architecture. And this study chooses to test commercial HTI FO membrane (cellulose acetate, CTA) at the same operating conditions for comparison purpose. This type of membrane is extensively studied worldwide in FO domain and its properties are well understood. Particularly, the structural parameter ($S$) of this membrane tested by Ren and McCutcheon (Desalination, 2014, 343, 187) is reported as $465 \, \mu m^{16}$ which is quite comparable to the $S$ value reported by our study ($455 \, \mu m$). Therefore, HTI CTA FO membrane is suggested as the reference for the indirect comparisons among different reports if applicable. For example, in Ren and McCutcheon’s study (Desalination, 2014, 343, 187; the data at 0.5 M NaCl is not available), the $J_W$ of HTI TFC membrane ($15 \, \text{L m}^{-2} \text{h}^{-1}$) is $87.5\%$ higher than HTI CTA membrane ($8 \, \text{L m}^{-2} \text{h}^{-1}$) at 1.0 M NaCl at FO mode; while in our study, the $J_W$ of membrane with GO-polymer 3D architecture ($18.3 \, \text{L m}^{-2} \text{h}^{-1}$) is $281\%$ higher than HTI CTA membrane ($4.8 \, \text{L m}^{-2} \text{h}^{-1}$) at 0.5 M Na$_2$SO$_4$ at FO mode. In short, this study states prudentially that GO-induced support layer architecture transformation from conventional 1D tortuous to 3D interconnected porous leads to the significant increase of FO flux ($J_W$) for as-synthesized membrane by $73\%$ to $18.3 \, \text{L m}^{-2} \text{h}^{-1}$, which is $2.8$ times higher than the $J_W$ of HTI CTA FO membrane under the same operating conditions.
4. Supplementary References


