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## **Electronic Supporting Information (ESI)**

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

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#### **1. Supplementary Introduction** 32

#### 33 1.1. Internal concentration polarization (ICP) and structural parameter (S)

### 34



- 35 36

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

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Internal concentration polarization (ICP) is a very unique phenomenon that takes place in 38 39 osmotically-driven membrane processes. The cause of ICP is that the support layer of FO 40 membrane functions as an unstirrable boundary layer to the diffusion of draw solute (inside 41 membrane support layer). As a result, the osmotic difference across selective layer (effective 42 osmotic driving force,  $\Delta \pi_{eff}$ , as shown in Figure S1) is reduced to be much lower than the 43 osmotic difference between feed solution bulk and draw solution bulk (apparent osmotic 44 driving force,  $\Delta \pi_{bulk}$ , as shown in Figure S1), regardless of whichever membrane orientation 45 (i.e. FO mode or PRO mode) is. Taking FO mode (support layer facing draw solution, which is 46 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 47

48 layer is being diluted. This causes the osmotic pressure at the top surface of support layer 49  $(\pi_{D,eff})$ , as shown in Figure S1) to become lower than that at the bottom surface of support 50 layer ( $\pi_{D,m}$ , as shown in Figure S1). The diffusion of draw solute from bottom surface to top 51 surface inside support layer serves as the compensation to restore  $\pi_{D,eff}$ . Unfortunately, 52 conventional support layers are made of tortuous 1D architecture, which severely hinders 53 this compensated diffusion of draw solute and thus generates a remarkable osmotic gradient 54  $(\pi_{D,m} - \pi_{D,eff})$  between bottom surface and top surface of support layer. As a result,  $\Delta \pi_{eff}$  is 55 significantly reduced from  $\Delta \pi_m$  (the osmotic difference between membrane surfaces, as 56 shown in Figure S1). This means  $\Delta \pi_{eff}$  is much lower than  $\Delta \pi_{bulk}$  because  $\Delta \pi_m$  is equaling to or 57 smaller than  $\Delta \pi_{bulk}$  depending on the extent of external concentration polarization (ECP).

58

59 Many previous studies on FO technology have observed the phenomenon that the water flux 60 of FO process is much smaller than theoretical prediction based upon RO performances of 61 membrane, and they figured out ICP is the main reason for this phenomenon.<sup>1-3</sup> The 62 governing equation for water flux at FO mode has been developed by previous studies,<sup>4, 5</sup> as 63 adapted into equation S1 for the quantitative analysis of ICP.

64 
$$J_w = A \Delta \pi_{eff} = A (\pi_{D,eff} - \pi_{F,m}) = A (\pi_{D,m} \exp(-J_w K) - \pi_{F,m})$$
 (S1)

where *A* is water permeability of FO membrane selective layer,  $\Delta \pi_{eff}$  is effective osmotic driving force,  $\pi_{D,eff}$  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 (*i.e.* FO membrane top surface),  $\pi_{D,m}$  is the osmotic pressure of draw solution at support layer bottom surface (*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.

$$71 K = \frac{s}{D} (S2)$$

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.

74 
$$S = \frac{\tau \times t}{\varepsilon}$$
 (S3)

75 where  $\tau$ , t, and  $\varepsilon$  are the tortuosity (dimensionless,  $\geq 1$ ), thickness, and porosity 76 (dimensionless, 0 ~ 1) of support layer.

77

Based upon equation S1~S3,  $exp(-J_wK)$  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  $\Delta \pi_{eff}$ , the severer ICP effect, and the smaller  $J_w$  will be.

83

84 Moreover, unlike ECP, ICP cannot be mitigated through increasing the flow velocity or 85 turbulence on membrane surface. Therefore, ICP is a more stubborn problem to FO 86 processes. The address of this issue mainly relies on the innovation of membrane structure 87 especially the structure of support layer, in other words, the minimization of S value. Based 88 upon equation S3, the decrease of support layer thickness (t) or the increase of support layer 89 porosity ( $\varepsilon$ ) can reduce S value. However, the mechanical integrity of FO membrane will be 90 inevitably compromised. Hence, a very smart way to minimize S value is through reducing 91 the tortuosity ( $\tau$ ) of support layer.

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96 **1.2.** The physical meaning of tortuosity (τ)



98red curve: real water path (/)99Figure S2. Concept illustration on the tortuosity of support layer. (a) Support layer with100segregated pores. (b) Support layer with interconnected pores, wherein the light green101pores indicate the new pores formed to connect those originally segregated pores.

102

103 The physical meaning of structural parameter (*S*) is the average distance for draw solute 104 molecule to take when traveling through support layer from its top surface to bottom 105 surface.<sup>3</sup> In other words, *S* represents the thickness of boundary layer that is caused by 106 support layer for hindering the diffusion of draw solute. As mentioned in equation S3, *S* is 107 directly proportional to the tortuosity ( $\tau$ ) and thickness (*t*) of support layer while inversely 108 proportional to the porosity ( $\varepsilon$ ) of support layer.

109

Briefly, the tortuosity ( $\tau$ ) of support layer equals to the ratio of / 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.

114 
$$\tau = \frac{l}{t}$$
(S4)

116 The tortuosity is negatively correlated with pore interconnectivity (the higher pore 117 interconnectivity, the lower tortuosity). Figure S2 compares the tortuosity of support layer 118 between two architectures (support layer thickness is the same): architecture of segregated 119 pores and architecture of interconnected pores. Figure S2a illustrates that the pores in 120 conventional support layer is isolated (low interconnectivity). Water molecules have to 121 follow the tortuous path inside each segregated channel and thus take a long pathway when 122 permeating through the support layer from its top surface to bottom surface. As a result, I 123 value is big and hence  $\tau$  value is high for architecture of segregated pores. In contrast, Figure 124 S2b illustrates that new channels (as marked by light green color) are formed to connect 125 those previously segregated pores to form an interconnected architecture. Water molecules 126 can find a short pathway when permeating through this interconnected architecture. As a 127 result, / value is small and hence  $\tau$  value is low for architecture of interconnected pores.

128

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.

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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.

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S7

### 140 **1.3.** Systematic comparison between this study and previous reports on GO-polymer

- 141 support layer for FO membrane
- 142

# 143Table S1. A systematic comparison between this study and previous reports on GO-144polymer support layer for FO membrane.

Articles	Overall assessment	Rationale	Scope and contents	Significant novelties
This study	This is a very novel, in-depth, comprehensive, and systematic study to:	This study is based on the deep understanding of 3D membrane architecture and	Scope This is a very comprehensive study to systematically	This study achieves fundamental contributions of milestone significance to
	<ul> <li>explore new 3D architecture with 2D nanomaterials via a facile and economic approach for breaking the intrinsic ICP bottleneck on FO processes.</li> <li>discover the mechanism for the formation of 3D architecture.</li> </ul>	<ul> <li>its effect to break</li> <li>ICP bottleneck on</li> <li>FO, as well as the structure, property, and potentiality of 2D nanomaterials.</li> <li>[1]. 3D architecture is the fundamental solution to solve ICP problem.</li> <li>[2]. Graphene-</li> </ul>	<ul> <li>investigate :</li> <li>[1]. the transformation of polymer matrix architecture from 1D to 3D under different conditions.</li> <li>[2]. the formation mechanism of 3D architecture.</li> <li>[3]. the role of GO nanosheets in architecture</li> </ul>	synthetic membrane and 2D nanomaterials, which include: [1]. For the first time, an entirely 3D architecture <i>i.e.</i> GO- polymer 3D architecture is created via a facile and economic phase- inversion
	<ul> <li>[3]. uncover the role of 2D nanosheets in forming 3D architecture.</li> <li>[4]. investigate structure-function relationships for the transformation of membrane architecture under different</li> </ul>	<ul> <li>based 2D</li> <li>nanomaterial</li> <li>s offer great</li> <li>opportunities</li> <li>to form</li> <li>advanced</li> <li>structures.</li> <li>[3]. There is no</li> <li>previous</li> <li>report to</li> <li>synthesize</li> <li>GO-polymer</li> <li>3D</li> <li>architecture</li> <li>via phase-</li> </ul>	transformation <u>Main content</u> [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%).	<ul> <li>[2]. For the first time, a new theory <i>i.e.</i> GO- induced microregional phase inversion is developed to reveal the mechanism for forming this 3D architecture.</li> </ul>
	conditions.	<ul> <li>inversion process for tackling ICP issue.</li> <li>[4]. This can be a good opportunity to leverage</li> </ul>	<ul> <li>[2]. the effect of polymer concentration.</li> <li>[3]. the effect of different solvents.</li> <li>[4]. the effect of GO lateral size (basal</li> </ul>	[3]. For the first time, the unique role of GO nanosheets in forming this 3D architecture is unveiled: GO is

		GO's 2D structure characteristic s from a new perspective, achieve a new 3D architecture via facile and economic process, and further understand 3D architecture formation mechanism.	<ul> <li>plane area).</li> <li>[5]. the comparison with using PVP or PEG as hydrophilic additive.</li> <li>[6]. Material characterizations.</li> <li>[7]. Membrane separation properties.</li> <li>(additional note: FO membrane selective layer is hydrogel).</li> </ul>	<ul> <li>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.</li> <li>[4]. This study sheds new light on 2D nanomaterials for developing high performance filtration membranes.</li> </ul>
Wang, et. al., J. Membr. Sci., 2015, 475, 281- 289. <sup>6</sup>	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). <u>Remarks</u> • No mention of the concept 3D	<ul> <li>[1]. "Recently, the modification of hydrophobic polymer has attracted considerable attention" (quoted directly from introduction section).</li> <li>[2]. "carbon nitride materials have the potential to enhance the composite substrate</li> </ul>	Scope         [1]. "Taking advantage of its special architecture and physicochemical properties of CN/rGO" (quoted directly from introduction section).         Main content         [1]. the effect of rGO/polymer ratio (only ranging from 0% to 1%).	[1]. "The results suggest that functionalizati on of FO membranes with the CN/rGO nanosheets is a promising approach for high performance FO membrane development" (quoted directly from conclusion section).

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	<ul> <li>architecture.</li> <li>No exploration on 3D architecture formation mechanism.</li> <li>No exploration on the role of 2D nanosheets in forming 3D architecture.</li> </ul>	wettability" (quoted directly from introduction section).	<ul> <li>[2]. Material characterizations.</li> <li>[3]. Membrane separation properties.</li> <li><b>Remarks</b> <ul> <li>No exploration of high incorporating ratio (no data for incorporating ratio &gt;1%).</li> </ul> </li> <li>(additional note: FO membrane selective layer is polyamide).</li> </ul>	
Park <i>et. al.,</i> <i>J. Membr.</i> <i>Sci.</i> , 2015, 493, 496- 507. <sup>7</sup>	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).	[1]. "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).	Scope         [1]. "GO nanosheets were used as fillers to modify the polysulfone (PSf) support of TFC-FO membranes" (quoted directly from introduction section).         Main content         [1]. the effect of rGO/polymer ratio (only ranging from 0% to 1%)	[1]. "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
	Remarks•No mention of the concept 3D architecture.•No exploration on 3D architecture formation mechanism.	[2]. "These unique dimensional and surface properties of GO nanosheets offer great potential for making composite	<ul> <li><u>078 to 178</u>].</li> <li>[2]. Material characterizations.</li> <li>[3]. Membrane separation properties.</li> </ul>	conclusion section) .
	<ul> <li>No exploration on the role of 2D nanosheets</li> </ul>	<i>materials"</i> (quoted directly from introduction	<ul> <li>No exploration of high incorporating ratio (no data for</li> </ul>	

in forming 3D architecture.	section).	incorporating ratio >1%).	
		(additional note: FO membrane selective layer is <u>polyamide</u> ).	

### 147 Notes on Table S1.

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(1) This article is the first study that creates an entirely new membrane architecture *i.e.* "GOpolymer 3D interconnected porous architecture", develops a new theory *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.

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154 (2) Categorical differences also exist in the objectives and scope of research: previous 155 reports used GO or its derivative as an "additive" at relatively low incorporating ratio 156 (GO/polymer ratio:  $\leq$ 1%) for the basic purpose of modifying polymer matrix;<sup>6, 7</sup> while this 157 study utilizes GO as an essential membrane building-block in high incorporating ratio 158 (GO/polymer ratio: up to 6.67%) to qualitatively change phase inversion process and thus 159 discovered the new architecture *i.e.* 3D interconnected porous architecture at the 160 incorporating ratio beyond previous reports scope (GO/polymer ratio: 3.33%).

161

(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.

167	(4) Additionally, the material for selective layer is different: polyamide in previous reports,
168	while hydrogel macromolecule in this study. In view of membrane selective layer, this study
169	and previous reports synthesize different kinds of membrane.
170	
171	(5) In order to avoid any misinterpretation of previous reports, the statements and
172	viewpoints describing previous reports are quoted directly from the Abstract, Introduction,
173	and Conclusion sections (as shown in "italic" style) of their articles.
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### **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,<sup>8</sup> with the detailed synthetic protocol recorded in our previous study.<sup>9</sup> Polyethersulfone (PES, weight averaged molecular weight  $Mw \approx 63$  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, ≥99.8%, Sigma-Aldrich), or 1-methyl-2-pyrrolidone (NMP, ≥99.9%, Sigma-Aldrich) was used separately as the solvent of dope solution. Polyvinyl alcohol (PVA,  $Mw \approx 93$  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 (Na<sub>2</sub>SO<sub>4</sub>, decahydrate, ≥99.0%, Sigma-Aldrich) was employed as the draw solute (draw solute and salt are interchangeable in this manuscript). Deionized water (DI water, 18 M $\Omega$  cm) was obtained from a Millipore Q ultrapure water system.

S13

### 215 **2.2.** The detailed composition of various dope solutions prepared for the synthesis of

216 support layer

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218	Table S2. The	detailed comp	osition of	various dope solu	utions investiga	ated in this paper.
	Dope solution <sup>a)</sup>	GO/polymer [%]	GO conc. [wt%]	Polymer conc. <sup>b)</sup> [wt%]	Solvent <sup>c)</sup> [wt%]	Research aims
	Conventional	0.00	0.00	15	85	
		0.33	0.05	15	84.95	
		0.67	0.10	15	84.90	
		1.00	0.15	15	84.85	To investigate the
	GO-polymer	1.33	0.20	15	84.80	effect of
	composite	2.00	0.30	15	84.70	GO/polymer ratio
		3.33	0.50	15	85.50	
		5.00	0.75	15	84.25	
		6.67	1.00	15	84.00	
	Conventional	0.00	0.00	17.5	82.5	
	GO-polymer composite	3.33	0.58	17.5	82.0	To investigate the
	Conventional	0.00	0.00	20	80	concentration
	GO-polymer composite	3.33	0.67	20	79.5	
	Conventional	0.00	0.00	17.5	82.5 (DMAc) <sup>d)</sup>	
	GO-polymer composite	3.33	0.58	17.5	82.0 (DMAc)	To investigate the
	Conventional	0.00	0.00	17.5	82.5 (NMP) <sup>e)</sup>	solvents
	GO-polymer composite	3.33	0.58	17.5	82.0 (NMP)	

<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-

- 222 methyl-2-pyrrolidone.
- 223
- 224
- 225



228 Figure S3. Optical photos of as-prepared GO-polymer composite dope solution. 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%.

### 247 **2.3. Characterizations**

248 Transmission electron microscope (TEM, JEOL JSM 2010-H) was used to characterize the 249 morphology of as-synthesized GO nanosheets. For TEM sample preparation, sonicated GO 250 solution was dripped onto 400-mesh carbon coated copper grids and then dried in room 251 temperature. Atomic force microscope (AFM, Park XE-100) was used to characterize the 252 topography of as-synthesized GO nanosheets and membranes in non-contact mode, with 253 silicon wafer as the substrate to immobilize the sample. Dynamic light scattering (DLS, 254 Mastersizer 2000) was employed to characterize the lateral sizes of GO nanosheets. Filed 255 emission scanning electron microscope (FESEM, JEOL JSM 7600F) was used to characterize 256 membrane architectures under accelerating voltage of 5 kV. Membrane samples were 257 immediately fractured after flash-frozen in liquid nitrogen to obtain cross-sections. All FESEM 258 samples were coated by gold for 20 s using a Cressington 108auto sputter coater. Attenuated 259 total reflection-Fourier transform infrared spectroscopy (ATR-FTIR, Perkin Elmer 2000, ZnSe 260 crystal method) was used to analyze the functional groups of membrane surface with the 261 samples freeze-dried overnight before scanning. X-ray diffraction (XRD) patterns were 262 investigated by a Bruker AXS D8 Advance diffractormeter with a Cu K $\alpha$  radiation source. 263 Contact angle was determined on an optical goniometric equipment (AST VCA Optima) using 264 sessile drop technique. The contact angle data was recorded at the initial moment when DI 265 water (3 µl) fully wet membrane surface, and reported as the average of 9 random 266 measurements. The samples for thermogravimetric analysis (TGA, Perkin Elmer TGA 7) were 267 heated from 30 °C to 900 °C at the temperature ramp of 10 °C/min. TGA experiments were 268 conducted under the purging gas of air or pure nitrogen gas separately.

269

### 271 **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.*<sup>10</sup> 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.

279

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

281 The rejection of neutral solid solute by support layer is determined through measuring the 282 solute concentration in permeate and retentate at the same filtration time. In detail, 200 283 ppm aqueous solution of PEG or PEO was utilized as the feed solution at time 0. A custom-284 built cross-flow filtration module was employed to circulate the feed solution on the top 285 surface of support layer under 1 bar transmembrane hydraulic pressure difference ( $\Delta P$ ) at 23 286 ± 2 °C. The crossflow rate was kept as 1.0 L/min. And a plastic spacer (SEPA CF spacer, 17 mil) 287 was placed on top of support layer to generate flow turbulence. Total organic carbon (TOC, 288 Shimadzu TOC-VCSH) was used to measure solute concentration in both permeate and retentate at 90<sup>th</sup> min of filtration. And the rejection of neutrally charged solid solute by as-289 290 synthesized support layer was determined according to equation S5.

291 
$$Rejection = \left(1 - \frac{c_p}{c_R}\right) \times 100\%$$
 (S5)

where  $C_P$  is the concentration of solid solute in permeate while  $C_R$  is the concentration of solid solute in retentate.

295 (2) To determine the Stokes diameter of solid solute

296 Stokes diameter of neutrally charged solid solute can be calculated by Stokes-Einstein

equation, with the specific calculation method demonstrated in equation S6 and S7.

298

$$300 d_{s,peg} = 3.346 \times 10^{-2} \times M_{peg}^{0.557} (S6)$$

301 where  $d_{s,peg}$  is the Stokes diameter of PEG in the unit of nm;  $M_{peg}$  is the molecular weight of 302 PEG in the unit of Dalton.

- 303
- 304 For PEO,

$$305 \quad r_{s,peo} = 2.088 \times 10^{-2} \times M_{peo}^{0.587} \tag{S7}$$

306 where  $d_{s,peo}$  is the Stokes diameter of PEO in the unit of nm;  $M_{peg}$  is the molecular weight of 307 PEO in the unit of Dalton.

308

309 (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 assynthesized 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.<sup>11</sup>

316 Rejection = 
$$erf(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{x} e^{-\frac{u^2}{2}} du$$
 (S8)

$$317 \qquad x = \frac{\ln d_s - \ln \mu_s}{\ln \sigma_s} \tag{S9}$$

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.

$$322 \quad Rejection = E \times (lnd_s) + F \tag{S10}$$

- 323 where *E* is the slope and *F* is the intercept, respectively.
- 324

325 From this linear fitting on log-normal probability paper, mean solute diameter ( $\mu_s$ ) can be 326 calculated as  $d_s$  corresponding to rejection = 50%, while  $\sigma_s$  can be determined from the ratio 327 of  $d_s$  at rejection = 84.13% to  $d_s$  at rejection = 50%. Furthermore, by ignoring the 328 dependence of solute rejection on the hydrodynamic interaction between solutes and 329 pores,<sup>12</sup> the mean pore diameter ( $\mu_P$ ) can be regarded the same as solute mean pore 330 diameter ( $\mu_s$ ), and geometric standard deviation ( $\sigma_P$ ) of membrane (as-synthesized support 331 layer) can be regarded the same as solute geometric standard deviation ( $\sigma_s$ ). Based upon the 332 obtained  $\mu_P$  and  $\sigma_P$ , the pore size distribution of a pore-flow membrane (as-synthesized 333 support layer) can be expressed as the following probability density function.

334 
$$\frac{df(d_p)}{dd_p} = \frac{1}{d_p ln \sigma_p \sqrt{2\pi}} \exp\left[-\frac{(ln d_p - ln \mu_p)^2}{2(ln \sigma_p)^2}\right]$$
(S11)

335 where 
$$d_P$$
 is the pore size of membrane (as-synthesized support layer).

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## **3. Supplementary Results and Discussion**

**3.1.** Demonstration of the three dimensional coordinate system

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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.

### 352 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.

_	5.		Perpendicular	Perpendicular	ln xz
Ierm	Dimension	GO-induced	to z axis	to xz plane	plane
	growing in the direction	NLSI	NL - I	Nucl	Mara
z-axis channei	from top to bottom	NOT	NOT	NOT	Yes
	growing in the direction	Ma a	No	Net	No.5
x-axis channei	from right to left	Yes	Yes	NOT	Yes
	growing in the direction	Vac	Vec	Vac	Net
y-axis channel	from front to back	res	res	res	INOT

- 370 3.2. The existence of GO nanosheets in as-synthesized FO membrane of GO-polymer 3D
- 371 architecture



373 Figure S5. FESEM and XRD characterizations of GO-polymer composite support layer. (a) 374 High-magnification FESEM image on the bottom surface of GO-polymer composite support 375 layer. The blue line highlights the embedded GO nanosheets, showing that GO sheets can be 376 embedded at in-plane orientation (parallel to membrane surface) in GO-polymer composite 377 support layer. (b) Additional high-magnification FESEM image on the bottom surface of GO-378 polymer composite support layer. The blue line highlights the embedded GO nanosheets, 379 showing that GO sheets can be embedded at non-in-plane orientation (inclined to 380 membrane surface) in GO-polymer composite support layer. The preferential orientation of 381 embedded GO nanosheets in GO-polymer composite support layer is recommended in 382 future study. The above two FESEM images provide eye-visible evidences for the existence of 383 GO nanosheets in as-synthesized GO-polymer composite support layers. Besides, image (b) 384 demonstrates that some embedded GO nanosheets experience certain curling with wrinkles 385 formed at the surfaces and edges. (c) XRD patterns of GO, GO-polymer composite support 386 layer, and conventional polymer support layer (GO/polymer ratio: 0.00%). As marked by the 387 grey line, the XRD pattern of GO has a characteristic peak at  $2\vartheta = 11.6^\circ$  (corresponding to interlayer spacing of ~0.74 nm).<sup>13</sup> This characteristic peak is observed in the XRD pattern of 388 389 GO-polymer composite support layer but absent in the XRD pattern of conventional polymer 390 support layer, which corroborates the existence of GO nanosheets in GO-polymer composite 391 support layer. It's worthwhile to note that GO-polymer composite support layer in this figure 392 are synthesized at GO/polymer ratio of 6.67% with 15 wt% polymer and 84 wt% DMF.



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Figure S6. Thermogravimetric analysis (TGA) results. (a) Graphite and as-synthesized GO nanosheets. (b) As-synthesized support layer of conventional 1D architecture (the dope solution contains 15 wt% polymer and 85 wt% DMF with GO/polymer ratio of 0.00%) and support layer of GO-polymer 3D architecture (the dope solution contains 15 wt% polymer and 84.5 wt% DMF with GO/polymer ratio of 3.33%).

### 400 Additional Discussion on Figure S6

401 Figure S6a shows that as-synthesized GO nanosheets have lower thermal stability compared 402 to its parent material *i.e.* graphite (SP1, Bay Carbon, USA). Under nitrogen gas, graphite 403 maintains 100% mass without any loss despite the increase of temperature from 30 °C to 404 900 °C. In contrast, as-synthesized GO nanosheets undergo weight loss along with the 405 elevation of temperature, with only 40% weight left at 900 °C. Particularly, the slow loss of 406 weight from 255 °C to 900 °C for GO is considered as the carbonization process, wherein 407 molecules other than carbon are removed. Under dry air, graphite does not lose any mass 408 until temperature elevated to 730 °C. And at 900 °C the weight left for graphite is 51%. In 409 contrast, GO undergoes 10% weight loss from 30 °C to 100 °C, which is due to the 410 evaporation of absorbed water or any other volatile molecules. The weight loss from 250 °C 411 to 600 °C is 32% and attributed to thermal decomposition of oxygenic groups as well as carbon lattice.<sup>13</sup> At 680 °C, nearly 0% mass is left for as-synthesized GO nanosheets. 412

414 As shown in Figure S6b, the TGA analysis results substantiate the presence of GO nanosheets 415 in the support layer of GO-polymer 3D architecture. Generally, support layer of GO-polymer 416 3D architecture possesses slightly higher thermal stability compared with conventional 417 support layer of 1D architecture. Under nitrogen gas, the decomposition is started at ~460 °C 418 for both support layers, and the weight loss rate of conventional support layer is constantly 419 higher than support layer of GO-polymer 3D architecture. At 900 °C, the weight left is 33% 420 for conventional support layer of 1D architecture and 36% for support layer of GO-polymer 421 3D architecture. The 3% higher weight left is attributed to the incorporated GO nanosheets. 422 Interestingly, the GO/polymer ratio to fabricate the support layer of GO-polymer 3D 423 architecture is 3.33% (the GO nanosheets concentration and polymer concentration in dope 424 solution are 0.5 wt% and 15 wt%, respectively). Under dry air, the weight loss curve turns to 425 be steep as temperature exceeds 580 °C for both support layers due to the oxidation and 426 lysis of polymer chain. At 900 °C, 0.0 wt% mass is left for conventional support layer of 1D 427 architecture while 0.7 wt% mass is left for support layer of 3D architecture. The higher 428 weight fraction left for support layer of 3D architecture is ascribed to the embedment of GO 429 nanosheets in polymer matrix. 430 431 432 433

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440 Figure S7. ATR-FTIR spectrum of as-synthesized support layer under different GO/polymer 441 ratios. As-synthesized conventional support layer (1D architecture) has several characteristic infrared (IR) bands: 1578 cm<sup>-1</sup> (C-C bond in benzene ring of polymer *i.e.* PES), 1487 cm<sup>-1</sup> (C=C 442 443 bond in benzene ring of PES), 1325 cm<sup>-1</sup> (asymmetric stretching of CSO2C group), 1300 cm<sup>-1</sup> (asymmetric stretching of O=S=O groups), 1244 cm<sup>-1</sup> (C-O vibrations of the aromatic ether 444 bond), 1153 cm<sup>-1</sup> (symmetric stretching of O=S=O groups), and 1107 cm<sup>-1</sup> (C-O vibrations of 445 446 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<sup>-1</sup> (O-H stretching 447 of hydroxyl groups on GO nanosheets), 1733 cm<sup>-1</sup> (C=O stretching of carboxyl groups on GO 448 449 nanosheets), 1627 cm<sup>-1</sup> (C=C stretching of unoxidized graphitic carbon), which proves that 450 the incorporation of GO nanosheets equips as-synthesized support layer with various 451 oxygen-containing functional groups. Therefore, FTIR results also substantiate the 452 embedment of GO nanosheets in as-synthesized GO-polymer composite support layer. 453

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**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.



483 484 Figure S9. Supplementary FESEM images on the architecture of as-synthesized support 485 layers under GO/polymer ratio below 1.33% (inclusive). The GO/polymer ratio is (a) 0.00 486 wt%, (b) 0.67%, and (c) 1.33%, while polymer concentration and solvent in dope solution are 487 kept as 15 wt% and DMF, respectively. The red circles on Figure S9b, S9c mark some typical 488 new channels emerged in the dimensions (y-axis and x-axis) perpendicular to z-axis 489 dimension.



492 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%. 

- 510 3.4. The effect of polymer concentration upon the formation of GO-polymer 3D
- 511 architecture
- 512



514 Figure S11. The effect of polymer concentration upon the formation of GO-polymer 3D 515 architecture. (a) 0.00% GO/polymer ratio, 15 wt% polymer, and 85 wt% DMF. (b) 3.33% 516 GO/polymer ratio, 15 wt% polymer, and 84.5 wt% DMF. (c) 0.00% GO/polymer ratio, 17.5 517 wt% polymer, and 82.5 wt% DMF. (d) 3.33% GO/polymer ratio, 17.5 wt% polymer, and 82 518 wt% DMF. (e) 0.00% GO/polymer ratio, 20 wt% polymer, and 80 wt% DMF. (f) 3.33% 519 GO/polymer ratio, 20 wt% polymer, and 79.5 wt% DMF. The red circles on Figure S11b, S11d, 520 and S11f highlight some typical new channels emerged in the dimensions (y and x axes) 521 perpendicular to z axis.

522

### 523 Additional discussion on Figure S11.

- 524 To verify the universality of GO-induced transformation from 1D architecture to 3D
- 525 architecture, the effects of polymer concentration and solvent are also investigated, with the
- 526 corresponding results displayed in Figure S11 and Figure S12, respectively.

528 Figure S11 demonstrates the effect of polymer concentration upon the formation of GO-529 polymer 3D architecture. Figure S11a, S11c and S11e serve as the control group (GO/polymer 530 ratio is 0.00%) for polymer concentration of 15 wt%, 17.5 wt% and 20 wt%, respectively, 531 whose z-axis channel wall is all found to be nonporous at micrometer-scale. As highlighted by 532 the red circles on Figure S11d and S11f, GO-induced new channels along y axis (and x-axis) 533 that perforate z-axis channel at micrometer sale are also formed under polymer 534 concentration of 17.5 wt% and 20 wt%. However, it's worthy to note that the pore area 535 perforated by y-axis (and x-axis) channel with respect to a unit area of xz cross-section plane 536 gets decreased along with the increase of polymer concentration from 15 wt% to 20 wt%, as 537 compared among Figure S11b, S11d and S11f. The explanation to this phenomenon is 538 elaborated as follows. The increase of polymer concentration results in the increase in 539 absolute viscosity of dope solution, which makes z-axis channel wall to be thicker as 540 evidenced by the comparison among Figure S11a, S11c, and S11e. However, thicker wall 541 provides bigger resistance to the perforation by new channels grown along y and x axes, and 542 consequently, the pore interconnections in y-axis and x-axis dimensions get decreased.

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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

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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 82.5 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.

### 561 Additional discussion on Figure S12

The solvent of dope solution has been revealed to influence phase inversion process to a significant extent.<sup>14</sup> 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.

- 567 Figure S12 demonstrates the effect of solvent upon the formation of GO-polymer 3D
- 568 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 sale 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.



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 containing microregions and GO-absent microregions, which stimulates the spread of fingering displacement from original 1 dimension (z axis) to 3 dimensions (x, y and z 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 3) consequently, the formed finger-like channels are only grown in 1 dimension (along z axis) but segregated in the other 2 dimensions (x and y axes). (b) Dynamic process Figure S13. Dynamic process of GO-induced phase inversion and conventional phase inversion. (a) Dynamic process of conventional phase inversion, wherein (a-1) the fingering displacement proceeds to the depth near GO-containing microregion, the existed GO nanosheets generate viscosity differences in x and y axes between GOfilm is cast from conventional dope solution and immediately immersed in the nonsolvent (DI water); (a-2) viscous fingering displacement proceeds merely along z axis; (a603 **3.7** The relationship between GO's lateral size (basal plane area) and the properties of GO-

604 induced new channels in the dimensions perpendicular to membrane thickness dimension

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607 Figure S14. The relationship between GO lateral size and the properties of GO-induced 608 new channels in the dimensions perpendicular to thickness dimension. (a-1) AFM image of 609 relatively large GO nanosheets, which are prepared by routine bath-sonication (Branson, 70 610 Watts, 1.5 hours at 20 °C), (a-2) DLS characterization result for the size distribution of GO 611 nanosheets, (a-3) GO-polymer architecture synthesized with relatively large GO nanosheets 612 (the optimized 3D architecture in this study). (b-1) AFM image of relatively small GO 613 nanosheets, which are prepared by routine bath-sonication plus probe-sonication (Vibra 614 CellTM, 750 Watts, 1.5 hours at 20 °C). (b-2) DLS characterization result for the size 615 distribution of GO nanosheets, (b-3) GO-polymer architecture synthesized with relatively 616 small GO nanosheets. In the dope solution to fabricate support layers, GO/polymer ratio is 617 3.33%, polymer concentration is 15 wt%, and solvent is DMF.

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### 619 Additional discussion on Figure S14.

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621 It has been reported that the lateral size (basal plane area) of GO nanosheets exfoliated

622 from graphite oxide is related to the intensity and time of ultra-sonication (Perreault et al.,

623 ACS Nano, 2015, 9, 7226).<sup>15</sup> A bath-sonication (Branson, 70 Watts, 1.5 hours at 20 °C) was

624 employed as the routine protocol to prepare the GO solutions for various dope solutions as

- 625 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<sup>™</sup>, 750 Watts, 1.5 hours at 20 °C) to produce GO 627 628 nanosheets in relatively small sizes. AFM imaging displays that probe-sonication at high 629 intensity is effective to produce GO nanosheets with smaller lateral sizes (Figure S14a-1, 630 S14b-1). DLS characterization results reveal that the average size (mass median diameter,  $d_{50}$ ) 631 of GO nanosheets is reduced from 2.8 µm to 0.8 µm after probe-sonication (Figure S14a-2, 632 S14b-2). This means the average basal plane area of routinely-prepared GO nanosheets is 633 estimated to be ~11 times larger than that of probe-sonicated GO nanosheets 634 (2.82/0.82=12.3). Figure S14a-3 and S14b-3 display GO-polymer architecture synthesized 635 with GO nanosheets of different average sizes, which indicate there is a positive correlation 636 between GO's lateral size and GO-induced new channels in x-axis and y-axis dimensions 637 (perpendicular to thickness dimension). In particular, at ~30% relative depth, large y-axis (x-638 axis) channel with pore size exceeding 15 µm can be produced by incorporating relatively 639 large GO nanosheets (as marked by red circle in Figure S14a-3). In contrast, y-axis (x-axis) 640 channel with pore size exceeding 15 µm is not formed by incorporating relatively small GO 641 nanosheets, and the y-axis (x-axis) channels at ~30% relative depth are typically < 5  $\mu$ m in 642 size (as marked by the red circle in Figure S14b-3). Moreover, FO water flux of the 643 membrane with GO-polymer support layer synthesized by relatively large GO nanosheets (the optimized 3D architecture in this study) is 18.3  $\pm$  1.5 L m<sup>-2</sup> h<sup>-1</sup>, which is evidently higher 644 645 than FO water flux of the membrane with GO-polymer support layer synthesized by relatively small GO nanosheets  $(14.1 \pm 1.2 \text{ Lm}^{-2} \text{ h}^{-1})$ . In addition, structural parameter of GO-646 647 polymer support layer synthesized by relatively large GO nanosheets is  $166 \pm 13 \mu m$ , which is 648 considerably lower than the structural parameter of GO-polymer support layer synthesized 649 by relatively small GO nanosheets (221  $\pm$  19  $\mu$ m).

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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.

656 Moreover, this result is consistent with our developed new theory i.e. "GO-induced 657 (microregional) phase inversion". The driving force to produce new channels in the 658 dimensions perpendicular to membrane thickness dimension is the viscosity difference 659 between "GO-containing microregions" and "GO-absent microregions". GO nanosheets with 660 large basal plane generate higher viscosity difference between microregions, and thus 661 produce the new channels (x-axis channels and y-axis channels) in large size. On the contrary, 662 GO nanosheets with small basal plane generate lower viscosity difference between 663 microregions, and thus produce the new channels in small size. And if the viscosity 664 difference between microregions becomes smaller than a certain threshold value, the 665 microregional viscosity difference may not be sufficient to perforate the wall of z-axis 666 channels, leading the channel formation in new dimensions (and also the formation of 667 curvaceous channel wall structure) to become less evident.

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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).

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675	In the future, a systematic study on the relationship between GO lateral size and the
676	properties of GO-induced new channels (formed in the dimensions perpendicular to
677	thickness dimension) is recommended.
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699 **3.8.** The investigation on using PVP or PEG as hydrophilic "additive" in dope solution 700



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702 Figure S15. The effect of different additives in dope solution on FO membrane architecture 703 and performances. (a) Illustration on GO-polymer composite dope solution and GO-induced 704 phase inversion. GO-containing microregions and GO-absent microregions are formed in GO-705 polymer composite dope solution. The red arrows indicate GO-induced phase inversion 706 proceeds in 3 dimensions. (b) Illustration on dope solution with PVP or PEG as additive and 707 its phase inversion process. There is no microregional difference formed at micrometer scale 708 for the dope solution with PVP or PEG. The red arrow indicates conventional phase inversion 709 proceeds merely in one dimension. (c) Membrane with GO-polymer composite has 3D 710 interconnected porous architecture, wherein plenty of new pores are formed perforating 711 the wall of z-axis channels. (d, e) Membranes synthesized by the dope solution with PVP (d) 712 or PEG (e) have conventional 1D tortuous architecture. (f) Water flux at FO mode (draw 713 solution is 0.5 M Na<sub>2</sub>SO<sub>4</sub> and feed solution is DI water). (g) Structural parameter of support 714 layers. For c ~ g, the incorporating ratio is the same for GO, PVP, and PEG: GO/PES = PVP/PES 715 = PEG/PES = 3.33%; PES concentration is 15 wt%; and solvent is DMF.  $M_W$  of PVP and PEG is 716 55 kDa and 40 kDa, respectively. Error bar is presented based upon the statistics of 5 717 independent membrane samples for each condition.

719 Additional discussion on Figure S15.

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721 In order to further explore the mechanism for forming "3D interconnected porous 722 architecture", our established new theory *i.e.* "GO-induced (microregional) phase inversion" 723 is verified by using different hydrophilic additives in dope solution. Widely-used hydrophilic additives polyvinyl pyrrolidone (PVP) and polyethylene glycol (PEG) are employed for 724 725 preparing the dope solution at the same incorporating ratio (PVP/PES = PEG/PES = GO/PES = 726 3.33%, each dope solution contains only one additive). Membrane synthesis follows the 727 same procedure as detailed in "Experimental" section. The results are presented in Figure 728 S15. Figure S15d and S15e display that the FO membrane with PVP or PEG in dope solution 729 has conventional 1D tortuous architecture: segregated pores (channels) are merely grown in 730 z-axis dimension (membrane thickness dimension). In contrast, FO membrane with GO-731 polymer composite has 3D interconnected porous architecture: plenty of new channels in 732 micrometer size are formed in the dimensions perpendicular to membrane thickness 733 dimension, which perforate the wall of z-axis channels (Figure S15c). Moreover, Figure S15f 734 shows that FO water flux is merely increased by 7~14 % through using PVP or PEG as additive, 735 compared to pristine membrane (control group, dope solution without any additive). In 736 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 737 738 only reduced by 3~7% through using PVP or PEG as additive, compared to pristine 739 membrane. In contrast, the S value of membrane with GO-polymer 3D architecture is 42% 740 lower than that of pristine membrane. These results indicate GO nanosheets have a 741 remarkable superiority in reducing ICP extent compared to PVP or PEG when used as the 742 "additive" (membrane building-block) in dope solution (at the same incorporating ratio of 743 3.33%).

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745 Our established new theory i.e. "GO-induced (microregional) phase inversion" is further 746 elaborated here. Figure S15a and S15b illustrate the differences in phase inversion process 747 for comparing GO-polymer composite dope solution and the dope solution with PVP or PEG 748 as hydrophilic additive. As shown in Figure S15a, rather than "dissolved" in the solvent of 749 dope solution, GO nanosheets are dispersed in the dope solution. The dispersions of GO 750 nanosheets form "GO-containing microregions" and "GO-absent microregions" inside dope 751 solution at micrometer scale. "GO-containing microregions" have relatively high viscosity 752 while "GO-absent microregions" have relatively low viscosity. The viscosity differences 753 between "GO-containing microregions" and "GO-absent microregions" function as the 754 driving force to stimulate new phase inversion (viscous fingering) process in the dimensions 755 perpendicular to membrane thickness dimension. As a result, new channels are formed 756 perforating the wall of conventional 1D pore (fingerlike channel) during the phase inversion 757 process, resulting in the formation of 3D interconnected porous architecture. The essence of 758 GO's "2D structure characteristics" is (1) GO's nanometer-sized thickness enable its stable 759 dispersion in dope solution, and (2) GO's micrometer-sized basal plane enables the 760 generation of sufficient viscosity differential to produce new pores at micrometer scale. In 761 contrast, Figure S15b demonstrates that PVP or PEG is dissolved in the solvent to form the 762 dope solution homogenous at micrometer scale, rather than forming "microregion of 763 relatively high viscosity" and "microregion of relatively low viscosity" at micrometer scale. 764 The lack of microregional differential in the dope solution with PVP or PEG causes its phase 765 inversion process to merely proceed in one dimension. As a result, conventional 1D tortuous 766 architecture are formed when using PVP or PEG as hydrophilic additive.

768	In sum, our developed new theory <i>i.e.</i> "GO-induced (microregional) phase inversion" can
769	well explain why conventional 1D tortuous architecture is formed when using PVP or PEG as
770	hydrophilic additive. These results also imply that it's GO's 2D structure characteristics,
771	rather than GO's hydrophilicity, play the dominant role in stimulating the transformation of
772	polymer architecture from 1D tortuous to 3D interconnected.
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**3.9.** Supplementary information on the effect of GO/polymer ratio upon top surface 793 structure of as-synthesized support layers



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.





812 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
- 832 architecture and FO membrane of conventional 1D architecture.



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. 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<sub>2</sub>SO<sub>4</sub>) 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.

e of conventi rane with GO-	nembran r FO memb	Inds for FO H stands fo	n). P-H sta ion). GO/P-	triacetate, wove	ne (cellulose - d by conventic	I FO membrai ver synthesize	or commercial HT	ote: HTI-CTA stands for the standard standa	No
1.77 ± 0.19	84.2 ± 2.6	91.1 ± 2.2	191 ± 25	$1.88 \pm 0.48$	17.1 ± 1.8	92.7 ± 1.5	$1.99 \pm 0.14$	GO/P-H 6.67	
1.67 ± 0.17	84.9 ± 2.9	91.4 ± 2.7	179 ± 21	$1.22 \pm 0.33$	$17.8 \pm 1.6$	93.5 ± 1.2	2.01 ± 0.15	GO/P-H 5.00	
<u>1.55 ± 0.13</u>	85.5 ± 2.8	91.2 ± 2.8	<u>166 ± 13</u>	0.79 ± 0.26	<u>18.3 ± 1.5</u>	94.8 ± 1.2	1.94 ± 0.17	GO/P-H 3.33	
1.80 ± 0.17	84.1 ± 2.5	90.8 ± 3.1	<b>194 ± 18</b>	0.85 ± 0.30	15.8 ± 1.2	94.6 ± 1.1	1.70 ± 0.15	GO/P-H 2.00	
$1.94 \pm 0.19$	83.5 ± 1.9	90.3 ± 2.6	209 ± 22	0.67 ± 0.25	$14.9 \pm 1.5$	95.1 ± 1.1	$1.63 \pm 0.13$	GO/P-H 1.33	
2.37 ± 0.23	83.2 ± 2.8	89.5 ± 2.6	254 ± 26	$0.54 \pm 0.21$	$12.3 \pm 1.4$	95.3 ± 0.9	$1.35 \pm 0.11$	GO/P-H 1.00	
2.66 ± 0.27	82.8 ± 3.1	89.1± 2.3	286 ± 24	$0.48 \pm 0.16$	$10.5 \pm 1.3$	95.6 ± 0.8	$1.10 \pm 0.08$	GO/P-H 0.67	
2.69 ± 0.23	82.2 ± 2.7	88.8 ± 2.5	290 ± 25	$0.41 \pm 0.13$	9.8 ± 0.9	96.0 ± 0.7	0.98 ± 0.09	GO/P-H 0.33	
<b>2.64 ± 0.26</b>	82.0 ± 2.5	88.6 ± 2.8	285 ± 26	$0.70 \pm 0.16$	$10.6 \pm 1.2$	95.2 ± 1.3	$1.12 \pm 0.10$	P-H	
3.65 ± 0.31	41.5 ± 2.8	52.5 ± 11	455 ± 43	1.25 ± 0.29	4.8 ± 0.7	97.0 ± 1.0	$0.40 \pm 0.07$	HTI-CTA	
	[%]	[µm]	Parameter [µm]	at FO mode [g m <sup>-2</sup> h <sup>-1</sup> ]	FO mode [L m <sup>-2</sup> h <sup>-1</sup> ]	Na <sub>2</sub> SO <sub>4</sub> [%]	Permeability [L m <sup>-2</sup> h <sup>-1</sup> bar <sup>-1</sup> ]		
Tortuosity	Porosity	Thickness	Structural	Reverse salt flux	Water flux at	Rejection of	Water	Membrane	

857 3.11. Supplementary information on the effect of GO/polymer ratio upon the properties of as-synthesized FO membranes

Table S3. Properties of as-synthesized FO membranes.

concentration and solvent in dope solution are kept as 15 wt% and DMF, respectively. composite support layer (support layer synthesized by GO-induced phase inversion), while the number stands for GO/polymer ratio (%). Particularly, GO/P-H 3.33 stands for as-synthesized FO membrane of 3D architecture (optimized). For all synthesized support layers, polymer ional 1D polymer

S45

nembrane 5 M draw plications	2) The best in mpared at 0 ngineering appropriate	mparison. ( $z$ nd $J_S$ are conn ndant for er	lected for the cor O mode. (4) $J_W$ ar awater that is abu	process are se on is fixed as F mparable to sea	hase-inversion brane orientation .5 M NaCl is con	cated by p . (3) Mem essure of 0	that are fabric he comparison the osmotic pro	ranes (support layers) study is selected for t data is not available (	Note: (1) Memb from each peer solute unless the
madzadeh <sup>19</sup>	N.A.	390	7.35	18.8	0.5 M NaCl	DI water	polyamide	TiO <sub>2</sub> /PSf ratio: 0.60%	TFC
$Wang^6$	3.2	163	4.1	21	0.5 M NaCl	DI water	polyamide	rGO/PES ratio: 0.50%	TFC
Park <sup>7</sup>	2.85	191	3.5	19	0.5 M NaCl	DI water	polyamide	GO/PSf ratio: 0.25%	TFC
Ma <sup>18</sup>	4.1	340	11	20	0.5 M NaCl	DI water	polyamide	zeolite/PSf: 0.5%	TFC
Huang <sup>17</sup>	4.6	1220	ω	10	1.5 M NaCl	DI water	polyamide	nylon 6,6 MF (BLA020)	TFC
Ren <sup>16</sup>	N.A.	533	4	15	1.0 M NaCl	DI water	polyamide	N.A.	HTI-TFC
Ren <sup>16</sup>	N.A.	465	1	8	1.0 M NaCl	DI water	СТА	СТА	HTI-CTA
this study	3.65	455	1.25	4.8	0.5 M Na <sub>2</sub> SO <sub>4</sub>	DI water	СТА	CTA	HTI-CTA
this study	2.64	285	0.70	10.6	0.5 M Na <sub>2</sub> SO <sub>4</sub>	DI water	hydrogel	PES	1D architecture
this study	1.55	166	0.79	18.3	0.5 M Na <sub>2</sub> SO <sub>4</sub>	DI water	hydrogel	GO/PES ratio: <b>3.33%</b>	3D architecture
Reterence	Tortuosity	structural parameter (µm)	Keverse salt flux <i>J<sub>s</sub></i> at FO mode (g m <sup>-2</sup> h <sup>-1</sup> )	Water flux $J_W$ at FO mode (L m <sup>-2</sup> h <sup>-1</sup> )	draw solution	teed solution	selective layer	support layer	membrane
reports	nd previous	this study a	nbrane between	nces of FO mer	ation performa	and separa	ic parameters	comparison on intrins	Table S4. The

3.12. The comparison on intrinsic parameters and separation performances of FO membrane between this study and previous reports

S46

membrane (thin-film composite); PES stands for polyethersulfone; PSf stands for polysulfone; N.A. stands for not available.

#### 871 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.

876

877 With respect to the specific innovations, support layer tortuosity ( $\tau$ , negatively correlated 878 with pore interconnectivity) is reduced by 41% (from 2.64 to 1.55) as the result of GO-879 induced transformation from conventional 1D tortuous architecture to 3D interconnected 880 porous architecture. This decrease of tortuosity is the major contributor to the decrease of 881 support layer structural parameter (S) by 42% (from 285 μm to 166 μm), which directly 882 indicates the substantial mitigation of ICP (ICP is exacerbated exponentially along with S, as 883 aforementioned in equation S1 and S2). As a result, FO water flux is significantly enhanced by 73% from 10.6 L m<sup>-2</sup> h<sup>-1</sup> to 18.3 L m<sup>-2</sup> h<sup>-1</sup> correspondingly. 884

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886 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 887 888 development (via phase inversion process). This is because (1) S and  $\tau$  are the direct 889 indicators for support layer structure characteristics, which can be utilized to quantitatively 890 analyze the innovation of support layer architecture, and (2) S and  $\tau$  are the intrinsic 891 properties of FO membrane support layer, which are independent on FO operating 892 conditions (e.g. draw solution, feed solution, hydrodynamic conditions on membrane 893 surfaces, etc.) and FO membrane selective layer properties. To our best knowledge (not 894 limited within the data of Table S4), the tortuosity (1.55) and structural parameter (166  $\mu$ m)

S47

895 of our GO-polymer 3D architecture are among the lowest (best) value in the literature on 896 phase inversion fabricated support layers. In particular, support layer tortuosity of our GO-897 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.*;<sup>6</sup>  $\tau$ : 898 2.85, from Park et al.<sup>7</sup>). This is consistent with our finding that a new architecture *i.e.* "GO-899 900 polymer 3D interconnected porous architecture" is created. As discussed previously in 901 Supplementary Introduction, structural parameter equals to tortuosity × thickness / porosity. 902 The increase of support layer porosity or the decrease of support layer thickness can reduce 903 S value, however, membrane mechanical integrity will be inevitably compromised. Therefore, 904 the decrease of tortuosity is a smart way to reduce structural parameter for the 905 minimization of ICP. In other words, given at the same S value, the lower tortuosity allows 906 the membrane support layer to possess higher thickness or lower porosity, which will 907 benefit the mechanical strength and practical processing of membrane. In short, to our best 908 knowledge, the  $\tau$  (1.55) and S (166  $\mu$ m) of our GO-polymer 3D architecture is among the 909 lowest (best) value in the literature on phase inversion fabricated support layers.

910

911 In addition, it is worthwhile to note that FO water flux  $(J_W)$  and reverse salt flux  $(J_S)$  are not 912 the intrinsic properties of FO membrane, because these two parameters are dependent on 913 many other external conditions including (1) membrane selective layer separation properties 914 (water permeability and salt permeability), (2) the type and diffusivity of draw solute, (3) the 915 osmotic pressure of draw and feed solutions, (4) fouling extent of membrane, (5) the 916 hydrodynamic conditions on membrane surfaces (related to external concentration polarization), (6) the differences in membrane test equipments and methods, and so on.<sup>20</sup> 917 918 Noteworthily, this study focuses on the innovation of FO membrane support layer

919	architecture. And this study chooses to test commercial HTI FO membrane (cellulose acetate,
920	CTA) at the same operating conditions for comparison purpose. This type of membrane is
921	extensively studied worldwide in FO domain and its properties are well understood.
922	Particularly, the structural parameter (S) of this membrane tested by Ren and McCutcheon
923	( <i>Desalination</i> , 2014, 343, 187) is reported as 465 $\mu$ m, <sup>16</sup> which is quite comparable to the S
924	value reported by our study (455 $\mu$ m). Therefore, HTI CTA FO membrane is suggested as the
925	reference for the indirect comparisons among different reports if applicable. For example, in
926	Ren and McCutcheon's study (Desalination, 2014, 343, 187; the data at 0.5 M NaCl is not
927	available), the $J_W$ of HTI TFC membrane (15 L m <sup>-2</sup> h <sup>-1</sup> ) is 87.5% higher than HTI CTA
928	membrane (8 L m <sup>-2</sup> h <sup>-1</sup> ) at 1.0 M NaCl at FO mode; while in our study, the $J_W$ of membrane
929	with GO-polymer 3D architecture (18.3 L m <sup>-2</sup> $h^{-1}$ ) is 281% higher than HTI CTA membrane
930	(4.8 L m <sup>-2</sup> h <sup>-1</sup> ) at 0.5 M Na <sub>2</sub> SO <sub>4</sub> at FO mode. In short, this study states prudentially that GO-
931	induced support layer architecture transformation from conventional 1D tortuous to 3D
932	interconnected porous leads to the significant increase of FO flux $(J_W)$ for as-synthesized
933	membrane by 73% to 18.3 L m <sup>-2</sup> h <sup>-1</sup> , which is 2.8 times higher than the $J_W$ of HTI CTA FO
934	membrane under the same operating conditions.
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