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A novel free-standing polymeric composite membrane for osmotic energy generation applications

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Abstract: A novel free-standing polymeric composite membrane was developed to simultaneously achieve high energy density and mechanical robustness for osmotic energy generation. The composite membrane is composed of a poly(vinyl alcohol) (PVA) gel down layer and a thin graphene/sulfonated poly(ether ether ketone) (SPEEK) top layer. The PVA layer offers excellent mechanical stability and flexibility and high water permeability, and the SPEEK thin film allows cations to pass through by diffusion. As a result, the composite membrane manages to achieve a high power density of ca. 5.89W/m² under a salinity gradient of 50 (0.5 M|0.01 M, NaCl). Furthermore, the energy generation device can maintain the high power output for 4 days or under 300P pressure, indicating excellent long-term stability and mechanical durability. The excellent comprehensive performance is attributed to that down PVA gel and top thin graphene/SPEEK layer both exhibit good ion transport behavior, ion selectivity and membrane stability in saline solution. The work provides a new strategy to design and prepare high-performance membrane for energy harvesting devices.

Key words: Graphene/SPEEK, PVA gel, free-standing, energy conversion, mechanical robustness.

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33 1. Introduction

34 The use of fossil fuels is arguably one of the major causes of current climate
35 change, altering Earth's ecosystems and causing a series of environmental problems^[1].
36 Since nuclear power facing negative public opinion, researchers are turning their
37 attention to develop renewable and sustainable energy sources that could be safe,
38 reproducible and ecological, such as solar, wind and hydro power^[2, 3]. During last
39 decades, the osmotic energy generation (*aka.* blue energy or salinity gradient energy)
40 is considered an environmental friendly and low-carbon technology for sustainable
41 power generation^[4-6]. Driven by the Gibbs free energy of high concentration seawater
42 and freshwater mixing, the counter ions preferentially pass through the ion-selective
43 channels within the semipermeable membrane, thereby directly generating electricity^[7].
44 From above respect, the membrane properties, such as water permeability, ion transport
45 behavior, ion selectivity and membrane stability in saline solution are the keys to
46 osmotic energy generation technology.

47 Generally, the membrane is composed of porous down layer and a thin top layer^[8].
48 The porous down layer mainly acts as supporting substrate, providing good water
49 permeability and good membrane stability, such as porous polymer film^[9], porous
50 anodic aluminum oxide (AAO)^[10-11], mesoporous carbon^[12] and silica membranes^[13, 14].
51 The thin top layer is based on polymer, carbon or other inorganic materials, which acts
52 as ion transporting and ion selective layer^[2]. Although these inorganic rigid supporting
53 substrate exhibit high water permeability and ion transport behavior, yet, it also show
54 low ion selectivity, leading to a relatively low power density ($< 5.0 \text{ W m}^{-2}$). Furthermore,
55 compared with these down and top inorganic rigid layer, polymeric layer can be easily
56 assembled into energy harvesting devices due to high processability and high flexibility.
57 So, recently, all-polymeric membrane is more promising for application energy
58 harvesting devices. For example, Jiang et al reported an organic heterogeneous
59 membrane composed of one layer of functional polyelectrolyte hydrogel membrane and
60 one layer of supporting porous aramid nanofiber (ANF) membrane by a sequential
61 blade-casting method^[9]. The resulting membrane achieved a power density of 5.06 W
62 m^{-2} . Zhang et al reported the fabrication of a composite membrane composed of a
63 porous PET substrate and a top layer made from polystyrene-*b*-poly(4-vinylpyridine)
64 (PS-*b*-P4VP). The maximum power output on external electrical load is as high as 0.35
65 W m^{-2} ^[15]. Using the same substrate, Xu et al employed TEMPO oxidized cellulose
66 nanofibers to prepare the top layer. The resulting membrane achieved a power density

67 of 0.96 W m^{-2} [16]. Zhang et al. reported a mechanically strong MXene/Kevlar nanofiber
68 composite membrane for salinity power generation, in which the power density reached
69 *ca.* 4.1 W m^{-2} [17]. These polymeric composite membranes are based on hydrophobic
70 polymer substrate with few pores, indicating a good mechanical stability in saline
71 solution and under water pressure. However, these hydrophobic polymer substrates
72 exhibit low water permeability and ion transport behavior, leading to a low power
73 density. To overcome above problems, two strategy are generally used. Firstly, a free-
74 standing polymeric GO/CNFs composite membrane was developed, in which the
75 substrate was removed. The power density was improved to be 4.19 W m^{-2} [18].
76 Secondly, a hydrophilic polymer substrate (e.g. SPSF) was developed, in which a high
77 power density of *ca.* 7 W m^{-2} was obtained [19]. However, the two membranes shows
78 poor mechanical stability and long-term durability in saline solution and under water
79 pressure. Therefore, it is a still high challenge to fabricate membranes with high power
80 density, mechanical stability and long-term durability.

81 In this study, a novel free-standing polymeric membrane is developed for robust
82 osmotic energy generation, which is composed of thin top graphene/SPEEK layer and
83 down PVA layer. The incorporation of ultra-thin two-dimension (2D) graphene into
84 SPEEK thin top layer can improve the cation transportation and the mechanical
85 properties of the composite membrane. Furthermore, the down PVA layer was prepared
86 by a new process, providing water permeability, ion transport behavior, ion selectivity
87 and stability. As a result, the free-standing SPEEK-G/PVA composite membrane
88 displays exceptional mechanical stability, tunable ion flux and enhanced energy power
89 density. This study thus opens up a new avenue for the development of membrane
90 technologies for low-carbon and sustainable energy production.

91 **2. Experimental**

92 2.1 Material

93 PVA (1799, Macklin), PEEK (Aldrich), H_2SO_4 (98%), graphene was purchased
94 from Chang Zhou Xi Ju Chemical Company. NaCl, KCl, ethanol (99%) and methanol
95 (99%) were purchased from Tian Jin Damao Chemical Company.

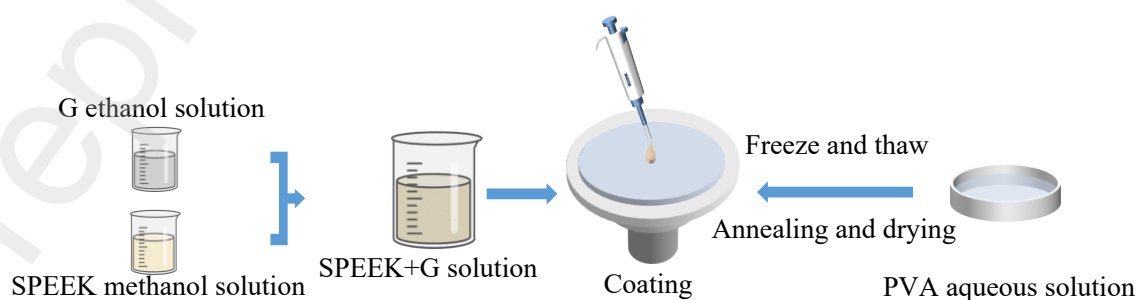
96 2.2 Preparation of graphene nanosheets

97 The graphene was prepared by a facile two-steps method as following. Firstly, the
98 expanded graphite (EG) was prepared by bubbling expansion method. 30g KMnO_4 was
99 added to 180mL concentrated sulfuric acid in the ice bath. Natural graphite (30g) was
100 added to above solution under mechanical stirring at room temperature for 1 h. Then,

101 30g Na₂CO₃ was added to above mixture under mechanical stirring. H₃PO₄ (420mL)
102 was added into above mixed system under mechanical stirring for 5 h. Thereafter, the
103 products were washed and filtered, forming EG. Secondly, 10g EG were added to
104 500mL NaOH solution (pH=14). The mixture was mechanically agitated for 2 h at
105 15,000 rpm using the FA 40 high shear dispersing emulsifier (Fluko), forming graphene
106 dispersion solution. Graphene is modified with PVP and dried to give a graphene
107 powder.

108 2.3 Preparation of free-standing composite membranes

109 The free-standing composite membranes was prepared by three-step method as
110 shown in following Scheme 1. Firstly, sulfonated PEEK (SPEEK) was synthesized to
111 improve the hydrophilicity of PEEK. In a 500 mL bottle flask, 5g PEEK was added to
112 250g H₂SO₄ (98%), and mixture was heated to 50°C. The reaction was carried out at
113 60°C for 12 h. The products were dropped into ice-deionized water, washed repeatedly,
114 and freeze-dry to obtain SPEEK. 0.1g of SPEEK was dissolved in 10g methanol to
115 obtain a solution with a mass fraction of 1 wt%. Secondly, the free-standing PVA film
116 was prepared by molding method. A 10% PVA aqueous solution was prepared at 90°C,
117 cooled slowly at room temperature and poured into glass dishes. The glass dishes were
118 then transferred to a refrigerator at -20 °C for 2 h, and then thawed at room temperature
119 for 5 h. This process was repeated 5 times to obtain the flexible, porous PVA membrane.
120 The obtained substrate membranes were then placed in a refrigerator freezer (12 °C)
121 and slowly dried for 5 days, followed by hot pressing at 110 °C for 2 h to obtain
122 enhanced mechanical properties. Thirdly, PVP-modified graphene powder was
123 dispersed in anhydrous ethanol by sonication to obtain an ethanol dispersion of
124 graphene. The SPEEK methanol solution (1wt %) was blended with the graphene
125 ethanol dispersion in a volume ratio of 1:1 v/v. The mixture was then ultra-sonicated
126 for 2 h, and spin-coated onto the prepared PVA layer to afford a composite membrane
127 with a mixed matrix top layer.



129 Scheme 1. The preparation of free-standing composite membranes.

130 2.4 Characterization

131 Differential scanning calorimetry (DSC) measurements were performed using the
132 PerkinElmer DSC-7.

133 The ^1H NMR (400 MHz) analysis was conducted using a BRUKER AVANCE
134 400 spectrometer with DMSO- d_6 as a solvent.

135 The FT-IR spectra were recorded on a Fourier transform infrared spectrometer
136 (FTIR-IR-8400s)

137 XRD pattern was characterized by the X-ray diffractometer (XRD, Bruker).

138 The Raman spectra were characterized by using Laser Raman Spectrometer
139 (Renishaw Invia).

140 The micro-structure of membranes were characterized by Scanning electron
141 microscope (SEM, Hitachi SU8010).

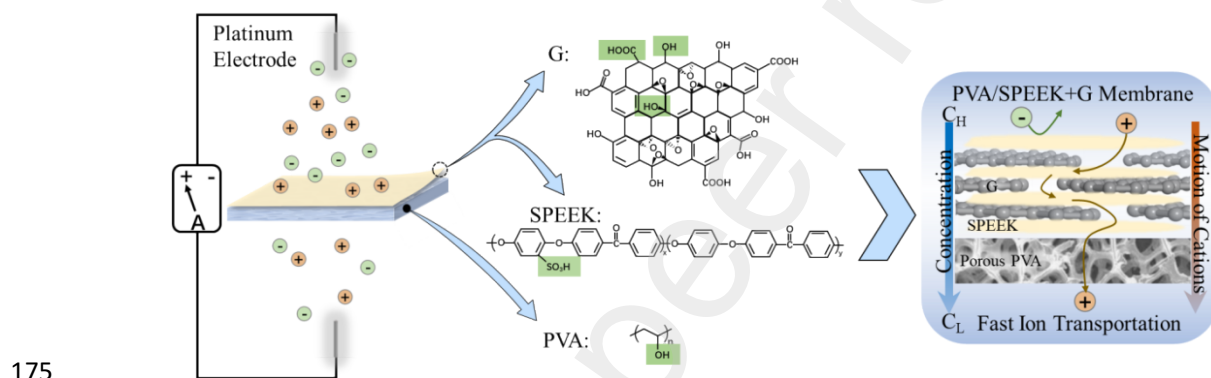
142 2.5 Salinity gradient energy conversion tests

143 The electrochemistry measurements including I-V and osmotic energy conversion
144 tests were carried out by using a Keithley 6487 semiconductor picoammeter (Keithley
145 Instruments, Cleveland, OH) in a costumed device. The tested window area was 3×10^{-8}
146 m^2 and a pair of lamellar platinum electrode was used. Asymmetric concentrations of
147 NaCl electrolyte were added into the corresponding reservoirs. We simulated the sea
148 water and river freshwater using 50-fold concentration gradient (0.5 M| 0.01 M NaCl).

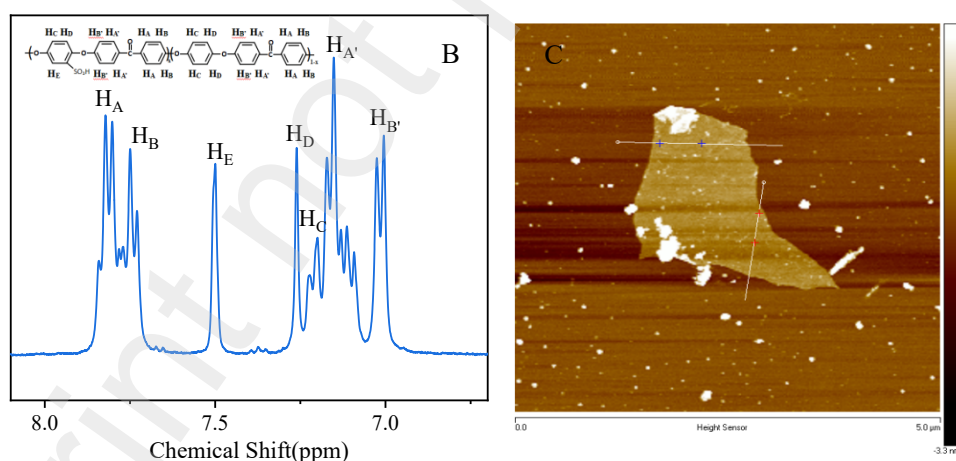
149 3. Results and discussion

150 The ion transport process in SPEEK/G/PVA assembled membranes during
151 osmotic energy generation is illustrated (Fig.1A).The osmotic power device is
152 integrated by separating two reservoirs containing different concentrations of sodium
153 chloride (NaCl) solutions with a freestanding and flexible SPEEK/G/PVA membrane
154 in which cations are mainly allowed to pass through the ion channels in composite
155 membranes along the salinity gradient. In addition to the ionizable sulfonic acid and
156 carboxylic acid groups in the membrane, the ion-screening performance of the
157 membrane also depends on the geometric channel in the membrane. The down PVA
158 hydrogel was prepared via freeze-thaw and hot pressing methods. The resultant material
159 exhibits hydrophilicity, high porosity, enhanced mechanical strength, making it an ideal
160 substrate for composite membrane fabrication^[20, 21]. The PEEK precursor was reacted
161 with H_2SO_4 at elevated temperature to obtain SPEEK with pendent sulfonic acid groups
162 along the backbone^[22]. The degree of sulfonation was determined to be 60% by NMR
163 characterization (Fig.1B). The graphene nanosheets were prepared by mechanical

164 exfoliation method, and characterized by AFM, TEM and Raman spectrometer
 165 (Fig.1C-E). As shown in Figure 1C and 1D, the prepared graphene are ultra-thin sheet
 166 structure with a thickness of ca.1.0nm. The Raman spectra of graphene samples show
 167 two characteristic bands of $1,325\text{ cm}^{-1}$ (D band) and $1,580\text{ cm}^{-1}$ (G band) (Fig.1E),
 168 corresponding to defective sp^3 -type carbon and sp^2 hybrid aromatic carbon^[23],
 169 respectively. We clearly observed the 2D band at $2,700\text{ cm}^{-1}$, indicating that the
 170 aromatic structure in the stripped graphene is well preserved ^[24-26]. With the materials
 171 in hand, we then fabricate the SPEEK-G/PVA composite membrane to simultaneously
 172 achieve mechanical robustness and enhanced membrane performance. Specifically,
 173 SPEEK solution and graphene dispersion were mixed at a ratio of 1:1 (v/v), and the
 174 mixture was then coated onto the PVA hydrogel via spin-coating.



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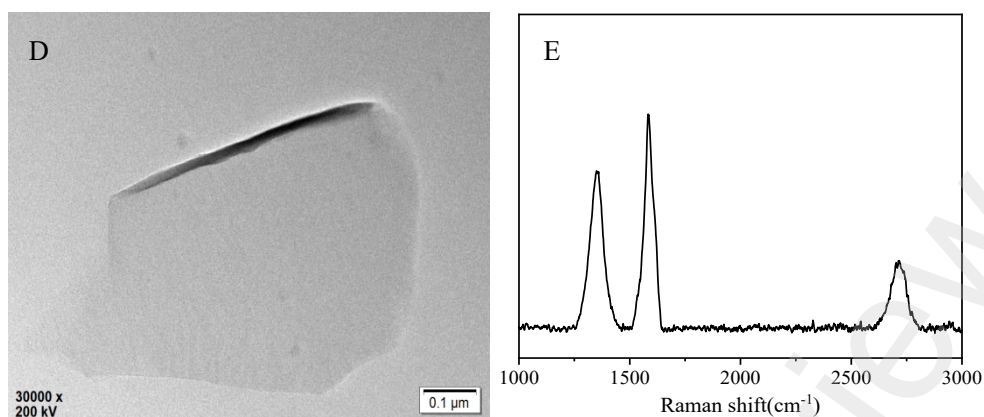
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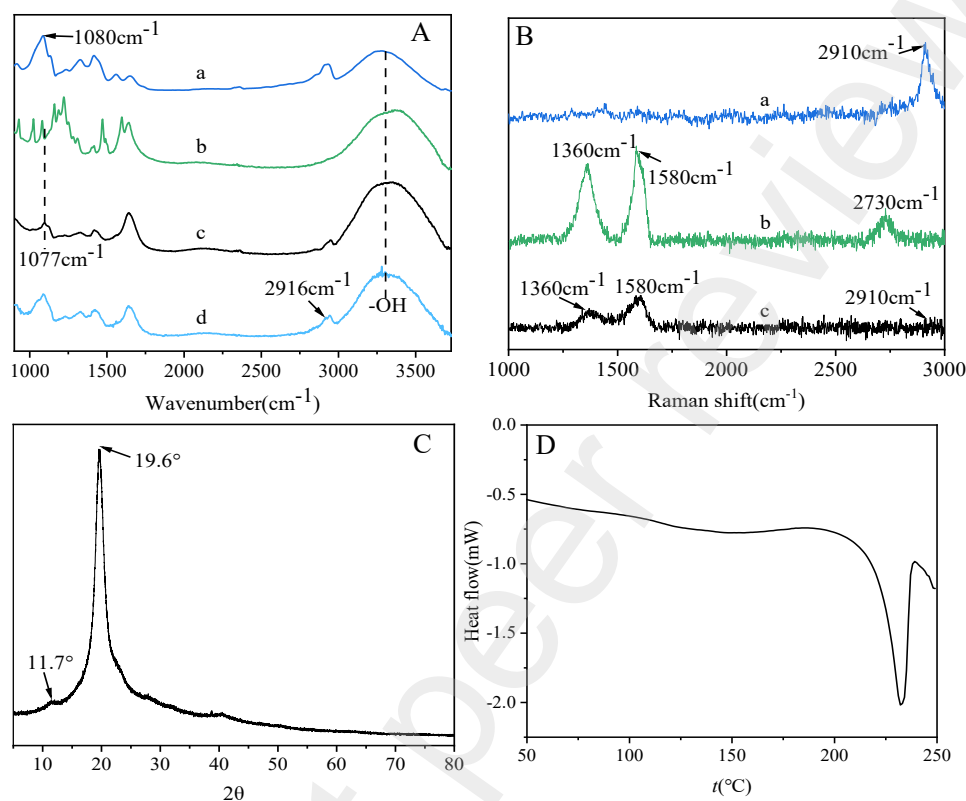
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183 Fig.1. (A) Schematic diagram of power generation of composite membrane and
 184 composite membrane with its chemical composition, (B) ^1NMR analysis of SPEEK,
 185 (C) AFM image, (D) TEM image and (E) Raman spectrum of graphene nanosheets.

186 The successful preparation of SPEEK-G/PVA composite membrane was
 187 confirmed by the FT-IR, Raman and XRD measurements. Fig.2A shows the FT-IR
 188 spectra of PVA substrate, SPEEK precursor, SPEEK-G/PVA membrane and a control
 189 sample of SPEEK/PVA membrane. The absorption peaks at $3,320\text{ cm}^{-1}$ and $1,080\text{ cm}^{-1}$
 190 can be assigned to O-H stretching of PVA (Fig.2A-a). The absorption peaks at $1,077\text{ cm}^{-1}$
 191 1 and $1,223\text{ cm}^{-1}$ were assigned to the symmetric and asymmetric stretching vibrations
 192 of O=S=O groups of SPEEK, respectively (Fig.2A-b). The absorption peaks at
 193 $1,470\text{ cm}^{-1}$ and $1,593\text{ cm}^{-1}$ were assigned to the symmetric and asymmetric stretching
 194 vibrations of C=C groups of SPEEK, respectively. The absorption peak at 1010 cm^{-1}
 195 was assigned to S=O stretching vibrations of SPEEK. Compared to the spectrum of
 196 SPEEK/PVA membrane (Fig.2A-c), we observed two absorption peaks at $1,740\text{ cm}^{-1}$
 197 and $2,916\text{ cm}^{-1}$ from the spectrum Fig.2A-d, which can be assigned to COOH and C-H
 198 stretching vibrations of graphene, respectively. These results indicate the successful
 199 preparation SPEEK-G/PVA membrane. Fig.2B shows the Raman spectra of SPEEK-
 200 G/PVA membrane. In addition, we observed two new absorption peaks at $1,360\text{ cm}^{-1}$
 201 and $1,580\text{ cm}^{-1}$, which can be assigned to characteristic D and G bands of graphene. This
 202 result further proves the presence of graphene in SPEEK top layer. Fig.2C shows the
 203 XRD spectra of SPEEK-G/PVA composite membrane. It clearly showed two peaks at
 204 $2\theta = 11.7$ and 19.7° , which are assigned to top SPEEK-G layer and the support PVA
 205 layer, respectively. Within the top layer, the interlayer distance of nanosheets is
 206 determined to be 1.12 nm. For the PVA substrate, the peak at $2\theta = 19.7^\circ$ indicates the

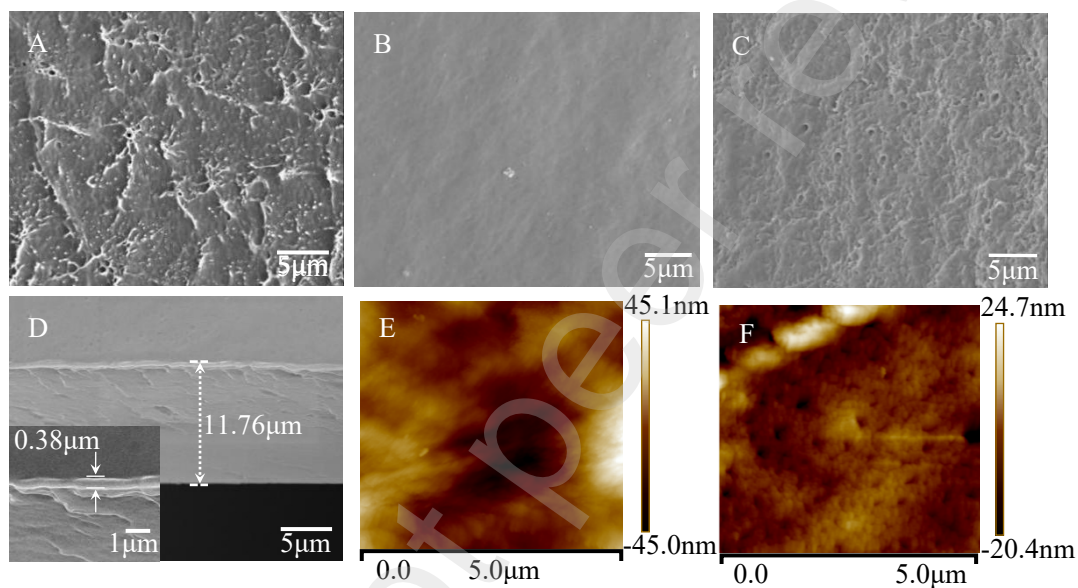
207 formation of PVA crystalline domains, which enhance the mechanical properties of the
 208 substrate. The crystalline density of PVA layer was further determined to be 49.43%
 209 by the DSC measurement (Fig.2D)^[27]. The observed smaller interlayer distance and
 210 more compact structure are expected to yield better cation transportation ^[28-30].



211
 212 Fig.2. (A) FTIR of membranes (a, PVA. b, SPEEK. c, SPEEK/PVA. d, SPEEK-
 213 G/PVA). (B) Raman of membranes (a, PVA. b, SPEEK-G. c, SPEEK-G/PVA). (C)
 214 XRD pattern of SPEEK-G/PVA composite membrane. (D)DSC curve of PVA.

215 We then investigate the micro-structure of the resulting SPEEK-G/PVA
 216 membrane by SEM measurements. The incorporation of graphene nanosheets into the
 217 SPEEK matrix leads to a rough surface morphology as shown in Fig.3A. In comparison,
 218 the pure SPEEK film exhibited a smoother, and more compact structure. This is because
 219 during the solvent evaporation process, the exchange rate of solvent and air in the
 220 vertical direction is different, forming a denser layer (Fig.3B). The high porosity of
 221 PVA substrate was also revealed by the SEM image shown in Fig. 3C. The cross-
 222 section SEM images revealed an asymmetric structure of the resultant SPEEK-G/PVA
 223 membrane (Fig.3D). Of particular note, the porosity and size of pores will increase in
 224 aqueous solution due to the swelling effect. As shown in Fig 4D, the total thickness of
 225 the composite membrane is *ca.* 11.8 μm with a SPEEK-G mixed matrix top layer of

226 380 nm. The thin thickness of top layer can significantly reduce the water and/or ions
 227 trans-membrane resistance, leading to enhanced presence. No clear boundary was
 228 observed at the interface between the top SPEEK-G layer and the PVA substrate due to
 229 their excellent compatibility. The micro-structure of SPEEK-G/PVA membrane was
 230 further characterized by AFM images (Fig.3E-F). The Ra and Rq values of PVA were
 231 4.1 and 5.5nm, the Ra and Rq of SPEEK-G were 10.1 and 12.8nm, respectively. For
 232 SPEEK-G, the dark regions represent the hydrophilic domains formed by the
 233 aggregation of sulfonated SPEEK segments. These domains form transport channels
 234 for water molecules and cations as well as selectivity for anions.



235
 236 Fig.3. SEM images of (A) top SPEEK-G layer, (B) top SPEEK layer and (C) support
 237 PVA layer. (D) SEM images of Cross-section SPEEK-G/PVA composite membrane.
 238 AFM images of (E) SPEEK-G layer and (F) PVA layer.

239 We finally evaluated the membrane performance using a customized osmotic energy
 240 generation device. (Fig.4A). The osmotic power device is integrated by separating two
 241 reservoirs containing different concentrations of sodium chloride (NaCl) solutions with
 242 a freestanding and flexible SPEEK-G/PVA membrane, in which cations are allowed to
 243 pass through the ion channels in composite membranes along the salinity gradient. In
 244 addition to the ionizable sulfonic acid (of SPEEK) and carboxylic acid groups (of G-
 245 nanosheets) in the membrane, the ion-screening performance of the membrane also
 246 depends on the geometric channel in the membrane. The ion transport behaviors of
 247 SPEEK/PVA or SPEEK-G/PVA composite membranes were characterized and
 248 compared by the ionic current-voltage (I-V) property first. The linear ohmic ion

249 transport behavior over a range of NaCl electrolyte concentrations indicates the
250 asymmetric structure of the composite membrane (Fig.4B). The ionic conductance over
251 a series of NaCl concentrations is plotted as a function of electrolyte concentration
252 (Fig.4C). This result reveals the obvious charge-governed ion transport and confined
253 ion transport behaviors through the SPEEK/PVA or SPEEK-G/PVA composite
254 membrane. There is a critical concentration point at approximately 0.01 M electrolyte.
255 Above this point, the ionic conductance follows the bulk rule of linearly increasing with
256 concentration due to the thin electrical double layer (EDL)^[17, 31]. However, as the
257 concentration decreases to the critical point, a strong nonlinear relationship is observed,
258 and the ionic conductivity deviates sharply from the bulk value, reaching a plateau. This
259 interesting phenomenon induced by the overlapping EDL in the ion transport channels
260 results in ion enrichment in the confined spaces, where the ion transport behavior is
261 determined by the surface and space charges of the SPEEK/PVA or SPEEK-G/PVA
262 composite membranes, rather than determined by the bulk concentration^[4, 32]. Fig.4D
263 shows variation of different current densities with increasing load resistance for the
264 SPEEK/PVA or SPEEK-G/PVA composite membranes. The diffusion current
265 gradually decreased with the increase of load resistance, and the output power density
266 reached its peak value when the load resistance was approximately 20k Ω (Fig.4E).
267 Compared with PVA or SPEEK/PVA membranes, the SPEEK-G/PVA composite
268 membrane showed a low resistance of 20k Ω (Fig.4E) and a higher current density
269 (Fig.4D), leading to a high output power density. The maximal power densities of
270 different membranes were concluded in Fig.4F. Compared with PVA (ca.2.0W/m²) or
271 SPEEK/PVA membranes (ca.5.2W/m²), the SPEEK-G/PVA composite membrane
272 exhibited the highest power density of 5.89W/m². This is achieved by creating
273 interfacial voids between the graphene flakes and SPEEK chains (due to the
274 repulsion between -COO⁻ and -SO₃⁻ groups), which increases the fractional free volume
275 within the top layer, thereby increasing the permeation rate^[33].

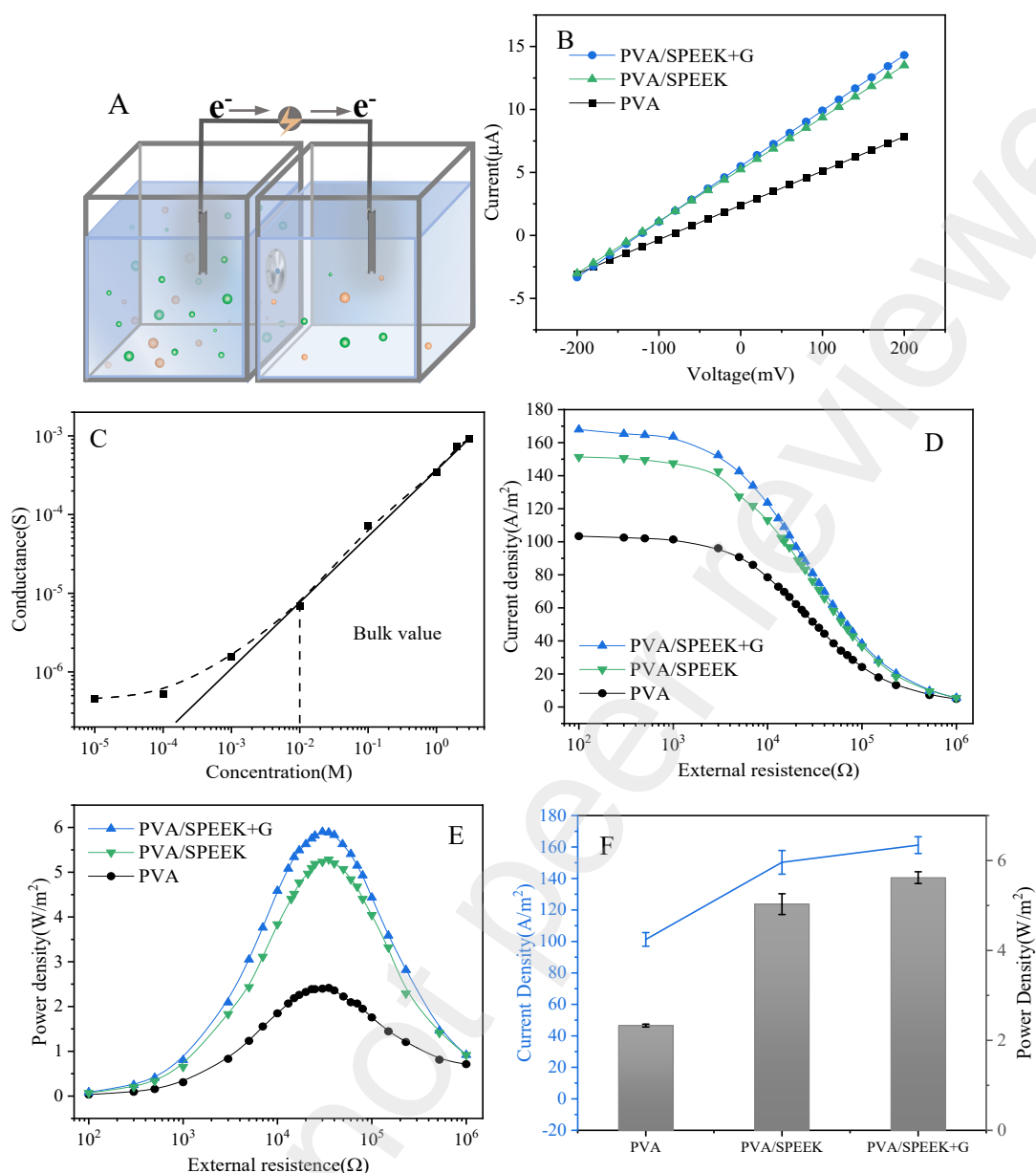
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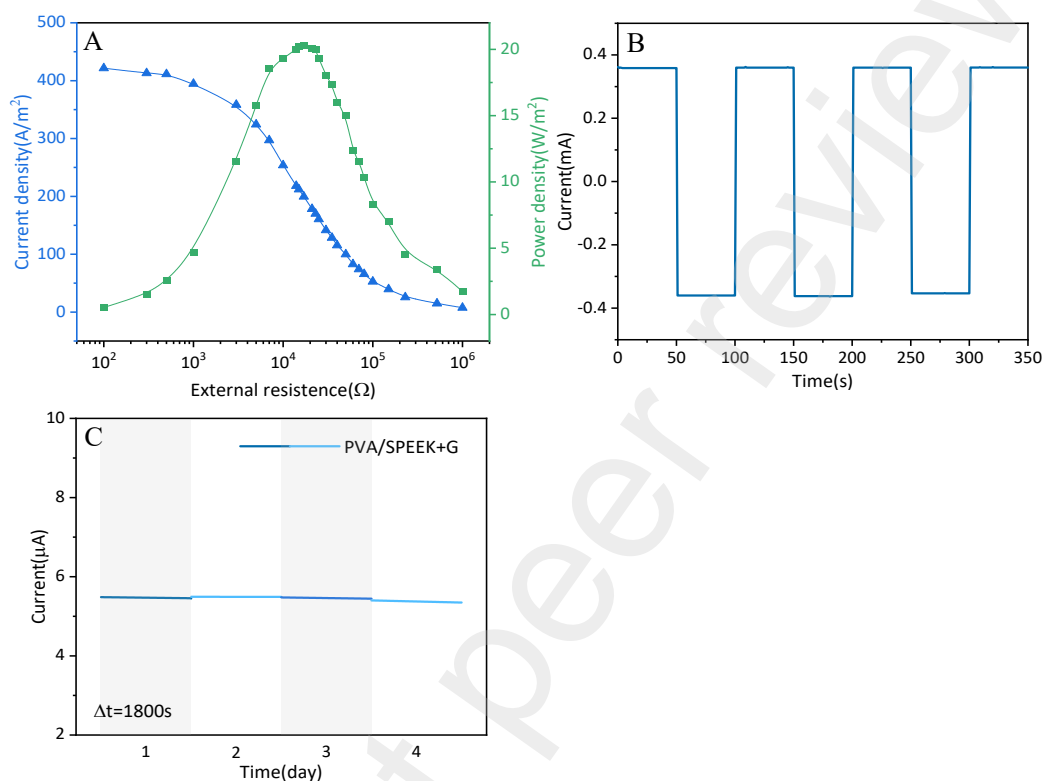
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282 Fig.4. (A) Diagram of osmotic energy generation device. (B) I-V curves of PVA,
 283 SPEEK/PVA membranes and SPEEK-G/PVA composite membrane under two
 284 configured NaCl concentration gradients. (C) Ionic conductance in a range of
 285 concentrations of neutral NaCl electrolyte. (D) The current density and (E) power
 286 density of PVA, SPEEK/PVA membranes and SPEEK-G/PVA composite membrane
 287 as a function of load resistance. (F) The Maximal current density and power density of
 288 various membranes.

289 In order to optimize the configuration, a 500-fold concentration gradient (5 M/0.01
 290 M NaCl) was adopted and the result was shown in Fig.5A. The power density increased
 291 from 5.8 to 20.3W/m² for the SPEEK-G/PVA. From Fig.5B, we can conclude that both
 292 negative and positive ionic currents are relatively constant, and each cycle can last for

11

293 50 s and repeated 7 times. In addition, we performed a 96-h energy collection test using
 294 the constructed membrane-based generator. As seen from Fig.5C, the obtained current
 295 remained stable during long-term testing. These results confirm the excellent chemical
 296 stability and long-term durability of SPEEK-G/PVA heterogeneous composite
 297 membrane.



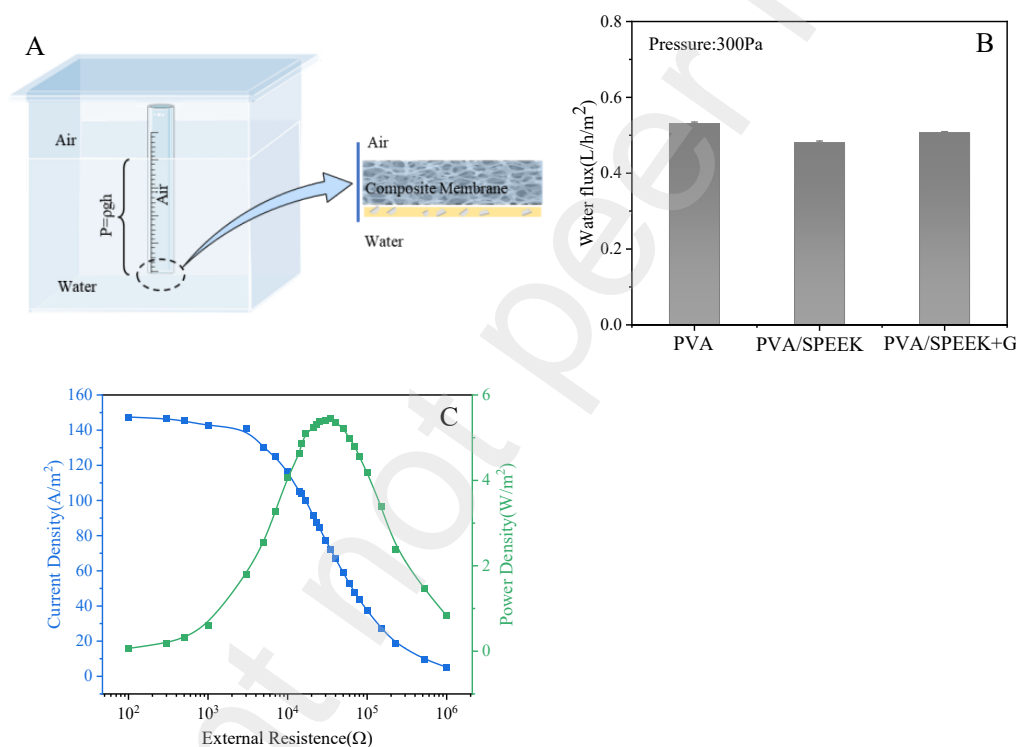
298
 299 Fig.5. (A) Power density and Current density of membranes at a gradient of 500. (B)
 300 The ionic current curve of the membrane with an alternately external bias of +2V/-2 V
 301 shows its stable ion transport property. (C) Long-term stability of the membrane-based
 302 generator.

303 The mechanical stability of the SPEEK-G/PVA composite membrane was
 304 further characterized by using a self-made setup (Fig.6A). A pressure (P , Pa) was
 305 applied to the membrane, which was determined by Eq 1:

$$306 \quad P = \rho gh \quad (1)$$

307 where ρ (g/cm³), g (9.8N) and h (cm) are the density of water, gravity and height of air,
 308 respectively. Here, the pressure applied to the composite membrane was calculated to
 309 be 300 Pa. We observed that the SPEEK-G/PVA membrane can maintain its integrity
 310 under this pressure. The water is forced through these membranes by applied pressure.
 311 Interestingly, water is not absorbed by the membrane like other PVA-based hydrophilic
 312 membranes. The result may be attributed to the high degree of crystallinity of PVA

313 substrate^[34]. The SPEEK-G/PVA membrane shows a high water flux rate of 0.51 L/m²
 314 h due to its high hydrophilicity, thin top layer and porous substrate (Fig.6B). For
 315 osmotic energy generation device, higher flux rate are highly desirable to improve ions
 316 transportation rates, increase current and power densities, and reduce fouling. The
 317 output power density and current density of SPEEK-G/PVA composite membrane after
 318 pressure treatment were characterized as a function of load resistances (Fig.6C). The
 319 diffusion current gradually decreased with the increase of load resistance, and the
 320 output power density reached its peak value when the load resistance was
 321 approximately 23k Ω . The maximum power density was calculated to be 5.7W/m²,
 322 which is identical to the value before pressure treatment. These results further prove the
 323 enhanced mechanical stability of the SPEEK-G/PVA membrane.



324
 325 Fig.6. (A) Schematic diagram of Pressure experiment. (B) Water flux of the membrane
 326 at 300Pa pressure. (C) Power density and Current density of composite membranes
 327 after Pressure experiment with a gradient of 50.

328 4. Conclusions

329 In this study, we have successfully fabricated a composite membrane containing
 330 graphene nanosheets in its top layer. Benefiting from the asymmetry in chemical
 331 composition and membrane configuration, the ions transport could be boosted and
 332 regulated as required. High performance of osmotic energy generation is attributed to

333 the successful incorporation of nanosheets, which is favorable for ion transport.
334 Moreover, as nanofillers, the addition of graphene nanosheets further enhances the
335 mechanical properties of the resulting composite membrane. Our work thus opens up a
336 new avenue for the development of membrane-based technology for practical energy
337 generation applications.

338 **Acknowledgments**

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