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1 **Asymmetric Ionic Aerogel of Biologic Nanofibrils for Harvesting Electricity from Moisture**

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14

15 **Abstract**

16 Artificial asymmetric ionic membranes have attracted great interests in harvesting electricity from
17 ubiquitous water activities, while mostly based on delicately-designed nanopores/nanochannels, either
18 to harness saline water in mimic of cytomembranes or to harness moisture with carbon nanomaterials.
19 Herein, fully biological asymmetric ionic aerogels were fabricated from biological oppositely-charged
20 nanofibrils through a facile freeze-casting method. When exposing to moisture, these nanofibrils may
21 be hydrated by capturing moisture and thus simulate the charged nanochannels for ion transport. Ion
22 dissociation and diffusion ions would induce directional movement of charges, thereby leading to a
23 potential up to 115 mV. With sustainability, biocompatibility and biodegradability, these biological
24 nanogenerators may promise a low-cost and high-efficiency electricity harvest strategy from moist air,
25 being capable of serving as self-powered wearable, biomedical and miniaturized electronic devices.

26 **Keywords:** Asymmetric ionic aerogel; Biological nanofibrils; Electricity harvest; Moisture.

27

28 **1. Introduction**

29 Porous Janus membranes, i.e., porous membranes with asymmetric properties (e.g., chemical
30 compositions, wettability, charges and porosity) on each side, have shown great potential in various
31 energy-efficient applications (e.g., emulsification [1], demulsification [2], fog harvesting [3] and
32 energy harvesting [4]), because of their super capabilities of reducing permeating resistance of specific
33 gases and liquids, and further allowing their selective mass transport. In particular, asymmetric surface
34 charges of porous membranes, which enable selective permeation of anions or cations in mimic of cell
35 membranes [5, 6], have been implemented in electrodialysis [7], ionic rectification [8], and
36 nanofiltration of charged nanomaterials [9], *etc* [10, 11]. Besides these, asymmetric ionic membranes
37 have also shown great superiority in harvesting electricity from ubiquitous waters (e.g., salinity
38 gradient [12] and moisture [13]) for applications in flexible, wearable and biomedical devices.
39 However, in most cases these asymmetric ionic membranes were based on the delicately-designed
40 nanopores/nanochannels (e.g., made of anodic aluminum oxide (AAO) [12, 14], block copolymers [4],
41 closely packing particles [15] and graphene [13]). Owing to uncontrollable and broad-range nanopores
42 sizes, biological fibrous membranes, despite having broad applications in filtration/separation
43 membranes [16, 17], have rarely been endeavored to serve as asymmetric ionic membranes, especially
44 for the purpose of harvesting energy for water activities (e.g., evaporation, diffusion and flow).

45 Within a charged nanopore/nanochannel with its radius comparable to the Debye length of the
46 ionic solution, its surface charges would produce an electric double layer, and then influence both the
47 enrichment and transport of anions and cations [18]. In order to avoid the possible presence of ionic
48 concentration polarization for selective and efficient ion transport, asymmetric ionic channels were
49 normally introduced to optimize the ion-enrichment and ion-depletion effects [19]. For example,

50 anion/cation diode-like selective transport was achieved by asymmetric ionic nanochannel membranes
51 of polyimide [20], polyamide [21], polyethylene terephthalate (PET) [22] and closely packing silica
52 nanoparticles [15]. Ionic rectification with the ratio up to hundreds was obtained with asymmetric
53 conical PET nanochannel with opposite surface charge [23]. Electricity was also harvested from
54 salinity gradient and osmotic energy of saline water, based on asymmetric ionic channels of AAO [12,
55 14], block copolymers [4], and mesoporous carbon [12].

56 Besides harvesting energy from saline water, asymmetric ionic membranes could also be
57 employed to harvest electricity from moisture. In contrast to saline water, moisture from industry,
58 natural evaporation and physiological processes (e.g., transpiration and respiration) is more ubiquitous
59 and spontaneous in the environment, and thus capable of affording a huger application potential for
60 facile and low-cost electricity generation. In most cases, the asymmetric ionic membranes were
61 produced from carbon nanomaterials (e.g., graphene oxides) with a gradient distribution of charged
62 groups (e.g., carboxyl) [13, 24-27]. When exposing to moisture, adsorption and condensation of
63 moisture occurred within the inner pores of nanomaterials [13, 24, 25, 28-30]. Ions (e.g., H^+ and H_3O^+)
64 may be dissociated with a concentration gradient, and thus generate a transmembrane electric pulse
65 [13, 25, 26, 29, 30]. Notably, electric potential arising from waterflow would also be possible during
66 this process, according to the mechanisms of stream potential [31, 32], electron drag [33], ion hopping
67 [34], polarization-induced-dissociation effect [35], and charge exchange between water molecules and
68 carbon nanomaterials [36].

69 In order to relieve environmental/cytotoxic concerns for wide use of high-cost inorganic/carbon
70 nanomaterials [28, 37, 38], sustainable biomaterials have attracted great interests in harvesting energy
71 from water activities [39]. In particular, we found that biological nanofibrils (NFs) with charged

72 surfaces may be hydrated in moisture and serve equivalently as the charged nanochannels for energy
73 harvest from moist air flow [40]. With comparison to inorganic nanomaterials and synthetic polymers
74 [41, 42], biologic nanomaterials have the advantages of abundant functional groups and facileness of
75 chemical modification. Thus, in this study asymmetric ionic aerogel was produced from 2,2,6,6-
76 tetramethylpiperidine-1-oxyl-oxidized cellulosic NFs (i.e., TEMPO-CNFs) and quaternized cellulosic
77 NFs (i.e., Quatern-CNFs) in a facile directional-freeze casting method. When exposed to moist air, the
78 asymmetric ionic aerogel could induce an open circuit potential (V_{oc}) as high as ~115 mV with a
79 maximum short circuit current (I_{sc}) of 45 nA, which is a comparable or superior overall performance
80 compared with reported moisture-driven generators (see details in Table S1). This production strategy
81 also maintained valid for other types of biological nanofibrils with oppositely charged states, such as
82 amyloid fibrils of bovine serum albumin (BSA)/chitin NFs, carboxylated silk NFs/chitin NFs, BSA
83 NFs/lysozyme NFs, TEMPO-CNFs/chitin NFs and TEMPO-CNFs/lysozyme NFs.

84 With comparison to the asymmetric ionic nanopores/channels reported in the literature, biological
85 nanofibrils were not only sustainable and low-cost, but also promising to avoid complicated procedures
86 for nanochannel production and surface treatment (e.g., plasma, laser and harsh oxidation). Their facile
87 procedures of surface chemical modification also ensured to produce asymmetric membranes with
88 opposite charges on each side, in contrast to gradient distributions of charges groups in asymmetric
89 ionic membranes of graphene oxides [13]. Thus, in addition to harvesting electricity from moist air
90 flow by using mono-component aerogels of biological nanofibrils [40], electricity could also be
91 harvested directly from more ubiquitous moist air through this bilayer type of asymmetric ionic aerogel,
92 which may promise a low-cost and high-efficiency handy power supply solution, and facilitate wide
93 applications of innovative self-powered electronic devices.

94 **2. Experimental section**

95 *2.1 Fabrication of asymmetric ionic aerogel*

96 Fabrication of silk NFs, amyloid NFs, deacetylated chitin NFs and BSA NFs was detailed in
97 Supporting Information. Aerogels were fabricated with the suspensions of these NFs. Typically, a
98 suspension of Quatern-CNFs (0.3–0.6 wt%) was poured into a mold, followed by subjecting to
99 unidirectional freezing with liquid nitrogen. Unidirectional freezing was also performed after pouring
100 another solution of Tempo-CNFs (0.3–0.6 wt%). The asymmetric bilayer aerogel (2–10 mm in
101 thickness) was obtained by freeze-drying in a freeze drier (FD-1C-50, Beijing BoYiKang) at $-55\text{ }^{\circ}\text{C}$.
102 The aerogel was laminated between two electrodes of Pt nets (purchased from Global Jinxin
103 International Technology Co., LTD , with the mesh size of 0.25 mm and diameter of Pt wires of 0.1
104 mm) with the size = 3×3 , 4×4 or $5 \times 5\text{ cm}^2$, serving as the current collectors (see details in Fig. S5).
105 The RH value was adjusted by saturated salt solutions within the enclosed environment at $25\text{ }^{\circ}\text{C}$, such
106 as RH=99% (Na_2HPO_4), RH=90% (Na_2CO_3), RH=80% (NH_4Cl), RH=70% ($\text{CO}(\text{NH}_2)_2$), RH=60%
107 (NaBr) and RH=50% ($\text{Ca}(\text{NO}_3)_2$).

108 *2.2 Sensing measurements*

109 The sensors were constructed by laminating the bilayer aerogel (diameter of 2 cm, thickness of 6 mm
110 and ratio of bilayer thickness of ~ 1) within the Pt electrodes. For finger sensing, the sensor was fixed
111 on a glass slide. And an index finger slowly approached to the sensor at ambient RH. Both the electric
112 potential (V_{oc}) and the distance between the sensor and finger were measured simultaneously. For
113 breath sensing, the sensor was integrated to a commercial aspirator (3M N95), the V_{oc} variation was
114 recorded under strenuous exercise and relaxation states. For humidity sensing, the sensor was fixed on
115 one hydroponic *Alocasia genus* outdoors (Qingdao in North China: East longitude $\sim 120^{\circ}$ and North

116 latitude $\sim 36^\circ$). The V_{oc} value was recorded from 8 o'clock to 20 o'clock (Apr. 26th, 2019), together
117 with the temperature, RH and solar density.

118 *2.3 Characterization*

119 Transmission electron microscopy (TEM) and field emission scanning electron microscopy (FESEM)
120 were performed on Hitachi H-7650 (Hitachi, Japan) and JEOL 7401 (JEOL, Japan), respectively. Zeta
121 potential was recorded on Zetasizer Nano ZSE (Malvern Instruments Ltd., England). Elemental
122 analysis was carried out on an Elementar Analysensysteme GmbH Vario EL Cube elemental analyser.
123 Open circuit voltage and resistance in real time were recorded using a digital multimeter (MS8265,
124 Mastech Ltd. Dongguan, China). Short-circuit current is recorded in real time using a digital nanometer
125 (JX-A04, Jianxin Ltd. Dongguan, China). Relative humidity values were measured by a digital RH
126 meter (S-WS05, Shenxinhui Electronics Co., Ltd. Shenzhen, China).

127 **3. Results and discussion**

128 *3.1 Design of asymmetric ionic nanofibrous aerogel as biological generator*

129 Bio-macromolecules and their assemblies are characteristic of abundant functional groups and hereby
130 opt to be chemically modified for different surface charges and charge densities [43-45]. Being one of
131 the most fundamental building blocks of natural biomaterials, biological NFs with negative or positive
132 surface charges could be extracted from naturally abundant biomass and/or synthesized through
133 supramolecular self-assembly (Fig. 1a-1c & Fig. S1-S2) [40, 46]. For instance, CNFs with negative
134 and positive charges were exfoliated mechanically from hardwood via TEMPO-mediated oxidization
135 (i.e., TEMPO-CNFs) [47] and 2,3-epoxypropyl trimethylammonium chloride cationization (i.e.,
136 Quatern-CNFs) [48], respectively (Fig. 1a-1d); Negatively charged silk NFs (i.e., carboxylated silk
137 NFs) were exfoliated mechanically from *Bombyx mori* cocoons through a NaClO oxidization method

138 (Fig. S2) [49]; And positively charged amyloid NFs were synthesized via supramolecular assembly of
139 lysozyme at pH \sim 2 and 60 °C (i.e., lysozyme NFs) (Fig. S2) [50]. Negatively charged amyloid NFs
140 were synthesized via a poor-solvent-induced fibrillation of BSA molecules (i.e., BSA NFs) (Fig. S2)
141 [49]. All these NFs had the diameter of <10 nm and the aspect ratio of $>10^2$ (Fig. 1b & Fig. S1-S2).
142 Among these biological NFs, charged CNFs have been studied in details, because they are one type of
143 the most abundant biological materials in nature, and have seen diverse applications in catalysts,
144 electro-optical films, nanofiber-reinforced composites, microelectronics, *etc* [45, 51]. Their surface
145 charge densities and ζ -potential could be tuned precisely, e.g., 0.5~1.39 mmol g⁻¹ carboxyl groups and
146 -25~-43 mV of ζ -potential for TEMPO-CNFs, and 0.5~1.28 mmol g⁻¹ quaternary ammonium groups
147 and 30~54 mV of ζ -potential for Quatern-CNFs (Fig. S1).

148 Owing to their highly charged surfaces, these CNFs (~ 3.5 mg mL⁻¹) maintained colloiddally stable
149 at the nematic states (inset of Fig. 1b). After directionally freezing the dispersion of TEMPO-CNFs
150 with liquid nitrogen, another layer of Quatern-CNFs dispersion was casted onto its top. Then fibrous
151 bi-layered aerogel with oriented structure was produced through a freeze-drying process (Fig. 1e &
152 S3). Hierarchical porosities were further revealed with the oriented microscale pores (i.e., the channel
153 width 1–10 μ m) and nanoscale pores (i.e., the size <100 nm). The aerogel porosity varied within
154 99.2–99.6% by tuning the CNFs concentrations in their dispersions from 3 to 6 mg ml⁻¹ (Fig. S4).

155 The humidity-induced nanogenerator was constructed by laminating the bilayer of cellulosic
156 aerogel (e.g., 3/3 mm/mm thick for TEMPO-CNFs/Quatern-CNFs; 2 cm in diameter) between two
157 parallel Pt nets as current collectors (mesh size ~ 0.25 mm) (Fig. 1e-1f & S5). At an environmental
158 relative humidity (RH) of $\sim 99\%$, V_{oc} increased dramatically to a maximum value as high as ~ 115 mV
159 at ~ 20 min, and then decreased gradually to vanishment within ~ 30 min (Fig. 1g). With alternately

160 switching moisture between On and Off, a variational period of V_{oc} was observed. This power
161 generation ability could be cyclically repeated without severe decay (Fig. 1g & S6). In addition, an I_{sc}
162 up to 45 nA was also aroused by the moisture, following the variation route similar to that of V_{oc} (Fig.
163 S6 & S7).

164 3.2 Suggested mechanism of the biological generator

165 Further investigation showed that low RH (e.g., <50%) produced negligible V_{oc} , while the higher RH
166 $\geq 50\%$ promoted the V_{oc} value progressively up to maximum value of ~ 115 mV at RH $\sim 99\%$ (Fig. 2a
167 & S8). These phenomena confirmed that water played a vital role in this electricity-generation process.
168 To be noted, biological NFs not only had the ultrathin diameter of < 10 nm and large specific surface
169 area, but also had the contents of hydrophilic groups (e.g., hydroxy, carboxyl in TEMPO-CNFs and
170 quaternary ammonium in Quatern-CNFs) higher than those of carbon nanomaterials used for moisture-
171 induced electricity generation [13, 24, 25, 28, 29]. When exposing to moist air, these fibrous aerogels
172 could easily capture moisture and immobilize water molecules via hydrogen bonding (e.g., TEMPO-
173 CNFs-O \cdots H-OH and Quatern-CNFs-N \cdots H-OH). And inevitably capillary condensation occurred
174 within the nanoscale pores of the aerogel according to Kelvin's equation [52]:

$$175 \quad \ln \frac{P}{P_0} \sim \frac{\gamma}{r} \quad (1)$$

176 where P_0 and P are the saturation vapor pressures of water near planar surface and concave meniscus,
177 respectively; r is the curvature radius of the water surface (being negative for concave meniscus); and
178 γ is the surface tension of water. For the bilayer aerogel with the hydrophilic group concentration of
179 ~ 0.9 mmol g^{-1} (i.e., TEMPO-CNFs with the carboxyl content of ~ 0.89 mmol g^{-1} and Quatern-CNFs
180 with the quaternary ammonium group of ~ 0.91 mmol g^{-1} , and thickness ratio of 1), the moisture uptake
181 capacity increased dramatically with the increasing RH, and got a maximum value up to ~ 0.9 g g^{-1}

182 (Fig. 2b & S9). And thus a bilayer hydrated shell would form on the surfaces of these NFs: an inner
 183 layer with immobilized water molecules and an out layer with free water molecules (Fig. 2d). Polar
 184 groups of the CNFs could release a large amount of counter ions (e.g., H^+ , Na^+ and Cl^-), and built an
 185 electric double layer (EDL) [36, 53]. Therefore, an ion conductive network would form within the
 186 hydrated surface and channels of the fibrous aerogels [54]. Correspondingly, the internal resistance
 187 sharply decreased from ~ 100 to $0.8\text{ M}\Omega$ when RH increased from 55 to 99% (Fig. 2b).

188 Due to the bilayer structure of the aerogel, cations were mainly produced within the TEMPO-CNF
 189 aerogel layer, while anions were produced mainly within the Quatern-CNF aerogel layer. Driven by
 190 the osmotic pressure, directional movement of net charges induced the potential (i.e., V_{oc}). And the
 191 consumption of the free ions osmosis and net charge transfer led to an evanescent V_{oc} (Fig. 2c). When
 192 switched to a depressed RH (RH <10%) the released ions would go back to the surfaces of NFs, and
 193 thereby produced a recyclable V_{oc} generation under “On/Off” moisture stimuli (Fig. 1f).

194 3.3 Structural optimization of asymmetric ionic aerogel nanogenerator

195 Besides the RH value, the content of charged groups on biological NFs can also play a prominent role
 196 in the device performance. V_{oc} increased obviously with an increasing concentration of charged groups
 197 as exhibited in Fig. 3a. According to Nernst equation for a concentration difference cell [55]:

$$198 \quad V \sim \frac{RT}{F} \left(\left| \ln \frac{a_2^+}{a_1^+} \right| + \left| \ln \frac{a_2^-}{a_1^-} \right| \right) \quad (2)$$

199 where the R, T and F represent the gas constant, temperature and Faraday’s constant; a_2^+ and a_1^+
 200 refer to the activities of cations in the Quatern-CNFs side and interface of the two sides, respectively,
 201 while a_2^- and a_1^- refer to the activities of anions in the TEMPO-CNFs side and interface of the two
 202 sides, respectively. Thus, more dissociable groups would increase the number of counter ions, and thus
 203 enhance the output voltage. However, the aerogels with excessive dissociable groups (e.g., >1 mmol

204 g^{-1}) led to a slight decrease in V_{oc} at high RH values (e.g., 99%) (Fig. 3a), due to the structural collapse
205 under hydration (Fig. S10).

206 The V_{oc} value could also be tuned by the geometric structures of the fibrous aerogels (Fig. 3b-3e).
207 A larger device area seemingly led to a higher I_{sc} value (Fig. 3c). With the constant device thickness
208 (i.e., 6 mm) and dissociable group contents (e.g., $\sim 0.9 \text{ mmol g}^{-1}$ for carboxyl groups in TEMPO-CNFs
209 and quaternary ammonium in Quatern-CNFs), the thickness ratio of the bilayer was optimal at $\sim 1:1$,
210 owing to the nearly equal amounts of free charges. Thus the aerogel generator could be optimized with
211 the porosity of $\sim 99.3\%$, the aerogel thickness of $\sim 6 \text{ mm}$, and the bilayer thickness ratio of $\sim 1:1$ (Fig. 3b-
212 3e). Furthermore, these nanogenerators could also be connected in series or in parallel for high V_{oc} or
213 I_{sc} (Fig. 3f & Fig. S11).

214 *3.4 Electricity-generation performance of asymmetric ionic aerogel nanogenerator*

215 The electricity generated by this biological diode generator could be conveniently accumulated and
216 stored with the conventional solutions. As shown in Fig. 4a, commercial capacitors (e.g., capacitance
217 3.3 mF) were charged with the diode generator, being able to serve as power supply for daily
218 appliances such as lighting a red LED with a driven voltage $\sim 1.5 \text{ V}$ (Fig. S12 & Video S1). Since
219 moisture widely exists in nature (e.g., evaporation of waters and transpiration of plants) and in industry
220 (e.g., drying and water cooling), the biological nanogenerators enable a variety of applications. For
221 instance, the generator was capable of a self-powered electrical humidity sensor with a sensitivity as
222 high as $2.35 \text{ mV/RH}\%$ (Fig. 4b), being superior to most of the humidity sensors in the literature, such
223 as porous carbon humidity sensor ($\sim 2 \text{ mV/RH}\%$), polymer nanowire sensor ($\sim 1.3 \text{ mV/RH}\%$),
224 graphene oxide hydrovoltaic sensor ($\sim 0.7\text{--}1 \text{ mV/RH}\%$), graphene oxide/poly(sodium 4-
225 styrenesulfonate) composite dielectric sensor ($0.0375 \text{ mV/RH}\%$) and polyaniline piezoresistive sensor

226 (0.64 mV/RH%) [24, 25, 27, 41, 56, 57]. Because of the distance-determined moisture distribution
227 near the human skin, the generator could also detect the distance away from the skin, which may
228 promise diverse applications like touchless control and contact warning (Fig. 4c & Fig. S13) [58].

229 The biological nanogenerator could also be powered by some physiological processes, e.g.,
230 transpiration and perspiration, rendering huge potentials for self-powered health monitoring devices.
231 When integrated with a commercial respirator (like 3M N95), the generator could detect the dynamic
232 characteristics of breathing (e.g., frequency and intensity). As shown in Fig. 4d, the frequency of the
233 V_{oc} pulses coincided with the breath before and after strenuous exercise with a breathing frequency of
234 20 and 38 min^{-1} . Moreover, this biologic generator could also be installed near plants to monitor and
235 quantify their transpiration process which releases >99% of water consumed by plants into air [59]. As
236 shown in Fig. 4e & S14, the electrical signal of this generator above one hydroponic *Alocasia genus*
237 was collected on daytime of Apr. 26 th, 2019 (Qingdao in North China: East longitude $\sim 120^\circ$ and
238 North latitude $\sim 36^\circ$), which reflected the intensity of plant transpiration in real time. Furthermore, the
239 biological generator could be fully degraded in natural soil leachate within 25 days (Fig. S15), once
240 again demonstrating the nanogenerator ideal for next generation wearable electronic devices.

241 **4. Conclusion**

242 In this study, asymmetric ionic aerogels of biological NFs enabled the electric energy harvest from
243 moisture variation. Biological NFs were not only sustainable and low-cost, but also promising in
244 abundant functional groups and facileness of chemical modification. Asymmetric ionic aerogels were
245 fabricated of carboxylated and quaternized cellulosic NFs through a facile directional-freeze casting
246 method. When exposing the asymmetric aerogels to moisture, these NFs could capture water from air
247 and formed ion conductive networks with hydrated nanochannels. Ion dissociation and diffusion would

248 lead to directional movement of charges, thereby producing a potential across the aerogel. The
249 generators of asymmetric ionic aerogels could also be fabricated by other biological NFs pairs such as
250 BSA NFs/deacetylated chitin NFs, carboxylated silk NFs/deacetylated chitin NFs, BSA NFs/lysozyme
251 NFs, TEMPO-CNFs/deacetylated chitin NFs and TEMPO-CNFs/lysozyme NFs (Fig. S16).
252 Combining sustainability, biocompatibility and biodegradability, these biological nanogenerators may
253 promise a low-cost and high-efficiency handy power supply strategy, as well as capable of serving as
254 self-powered wearable, biomedical and miniature electronic devices.

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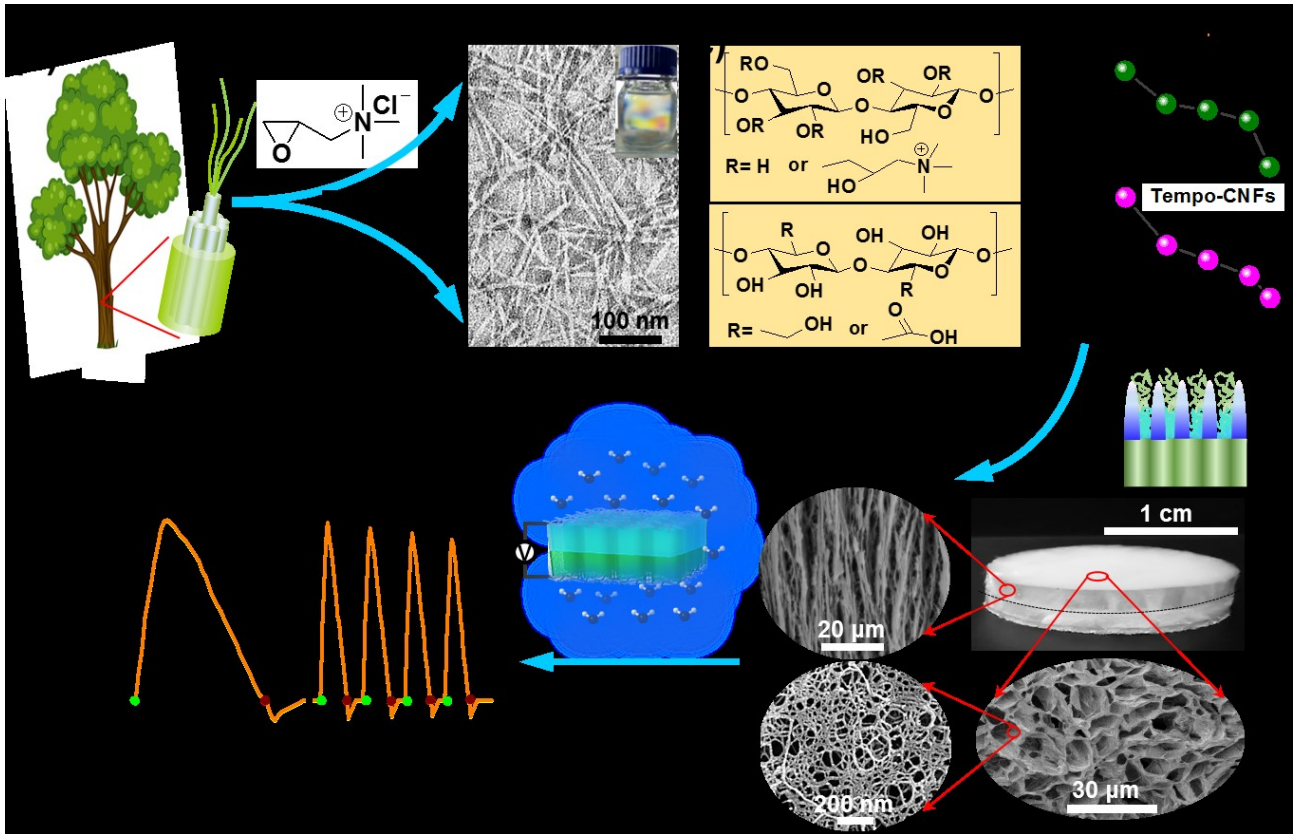
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348 **Fig. 1.** Synthesis pathway of asymmetric ionic nanofibrous aerogel as biological generator. (a)

349 Schematic illustration of synthesizing oppositely charged CNFs from wood via mechanical exfoliation.

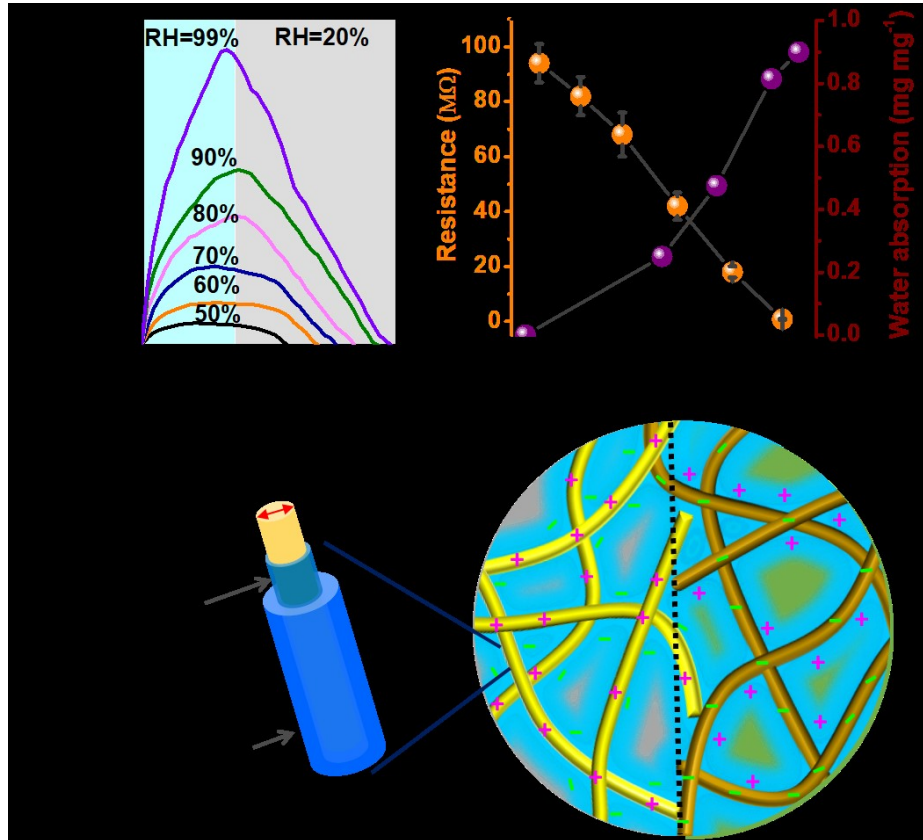
350 (b) Typical TEM image of negatively charged TEMPO-CNFs. (c-d) Chemical structures (c) and Zeta

351 potentials (d) of Quatern-CNFs (top) and TEMPO-CNFs (bottom). (e) Optical and SEM images of

352 asymmetric ionic aerogel fabricated by directional freezing and freeze drying. (f) V_{oc} generated with

353 asymmetric ionic generator under periodic moist stimuli. RH = 99%.

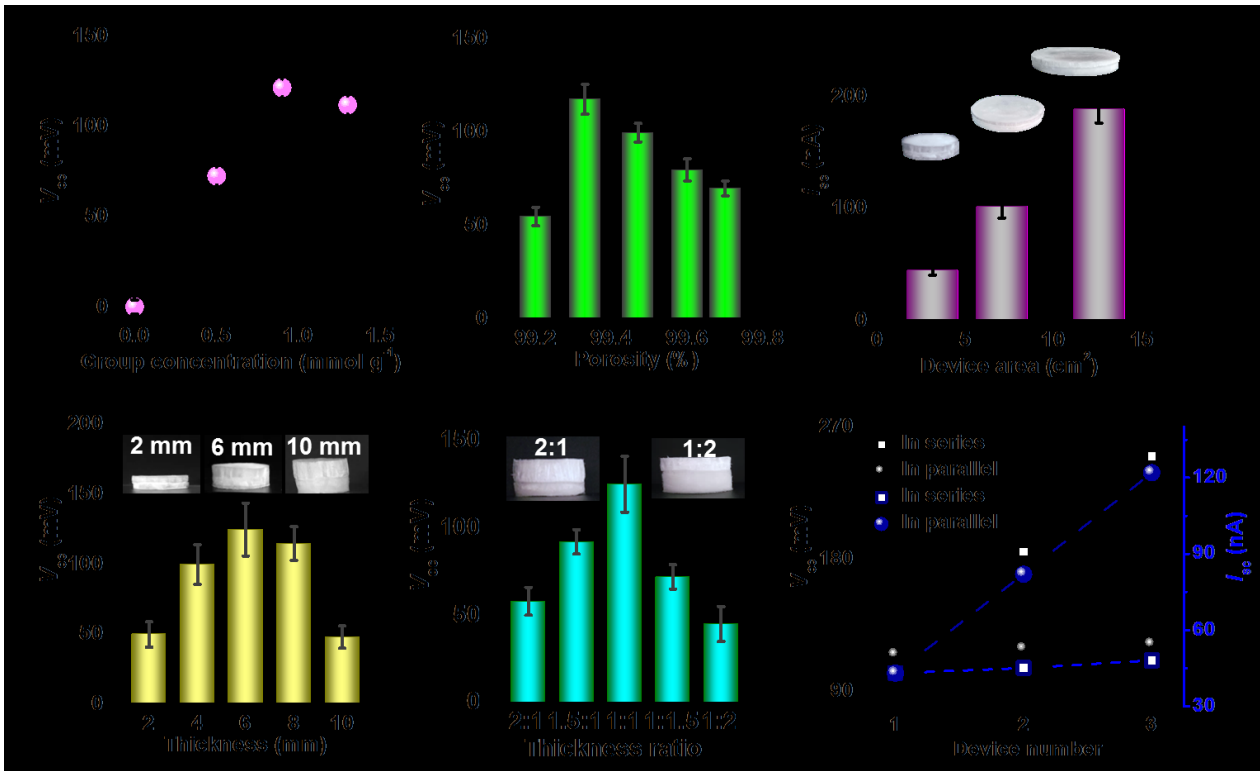
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356 **Fig. 2.** Electricity-generation mechanism of asymmetric ionic aerogel. (a) V_{oc} variation upon exposing
 357 to different RHs. (b) Capacity of water absorption and internal resistance at different RHs. Carboxyl
 358 content of TEMPO-CNFs: $\sim 0.89\text{ mmol g}^{-1}$; Quaternary ammonium group of Quatern-CNFs: ~ 0.91
 359 mmol g^{-1} . Generator diameter: 2 cm; Thickness: 6 mm; Bilayer thickness ratio: ~ 1 ; RH=99%. (c)
 360 Schematic illustration of voltage induced by directional movement and neutralization of free ions
 361 within hydrated charged nanochannels.

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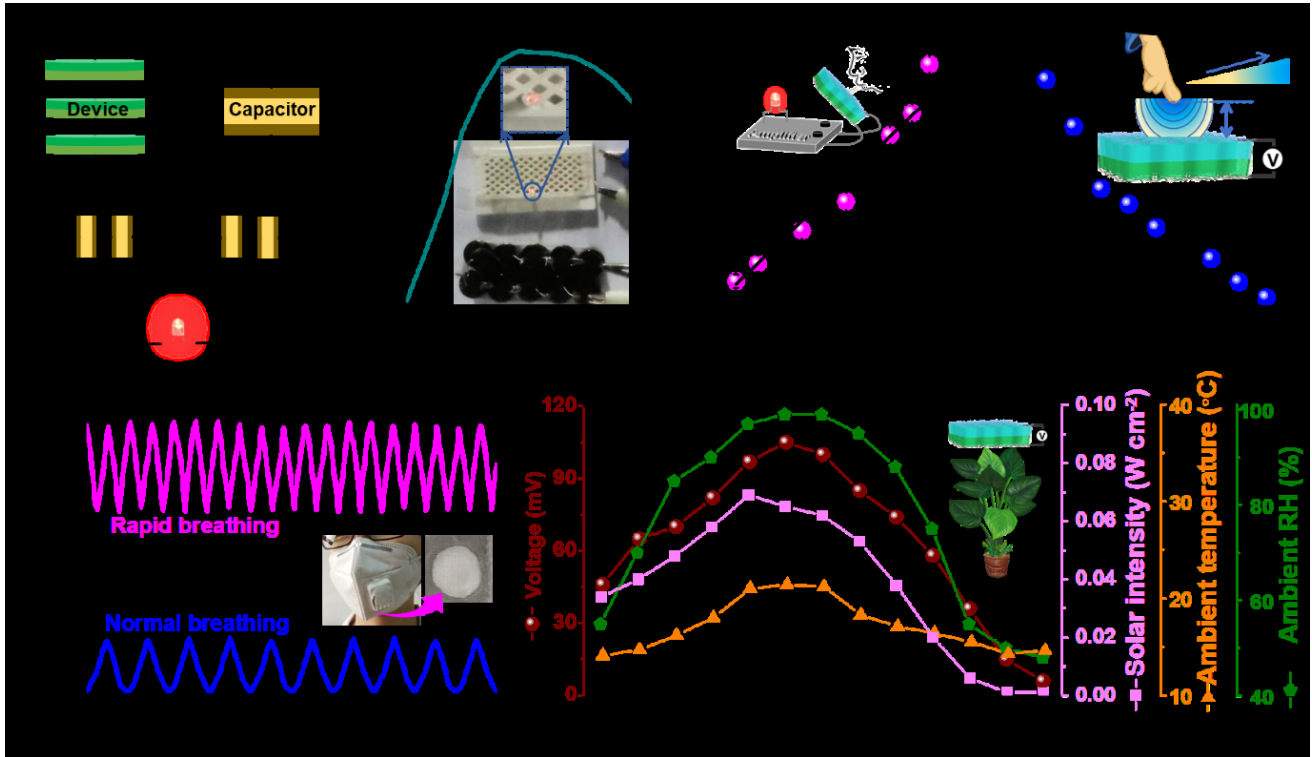
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Fig. 3. Structural optimization of asymmetric ionic aerogel nanogenerator. (a) Effect of charged group content on equilibrium V_{oc} . (b) Effect of aerogel porosity on V_{oc} . (c) Effect of aerogel area on V_{oc} . (d) Effect of aerogel thickness on V_{oc} . (e) Effect of thickness ratio of TEMPO-CNFs/Quatern-CNFs layers on V_{oc} . (f) V_{oc} and I_{sc} of generators in series and parallel. Generator diameter: 2 cm; Thickness: 6 mm; Thickness ratio: ~1; RH =99%.



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370 **Fig. 4.** Electricity-generation performance of asymmetric ionic aerogel nanogenerator. (a) Charging
 371 commercial capacitors with biological generator in series and parallel (Left) and discharging curve
 372 (Right). The inset shows a commercial red LED was powered by capacitors. (b) Asymmetric ionic
 373 aerogel nanogenerator serving as electrical humidity sensor. (c) Asymmetric ionic aerogel
 374 nanogenerator to sense finger distance. (d) V_{oc} variation when exposing to respiration (N, Frequency)
 375 settled on commercial aspirator. (e) V_{oc} variation when exposing to transpiration hanged above an
 376 *Alocasia macrorrhiza* at natural conditions (Beijing Time 8-20 o'clock, Qingdao in North China,
 377 Daytime on Apr. 26th, 2019). Generator diameter: 2 cm; Thickness: 6 mm; Thickness ratio: ~1.