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Interfacial Solar Evaporation by a 3D Graphene Oxide Stalk for Highly Concentrated Brine Treatment

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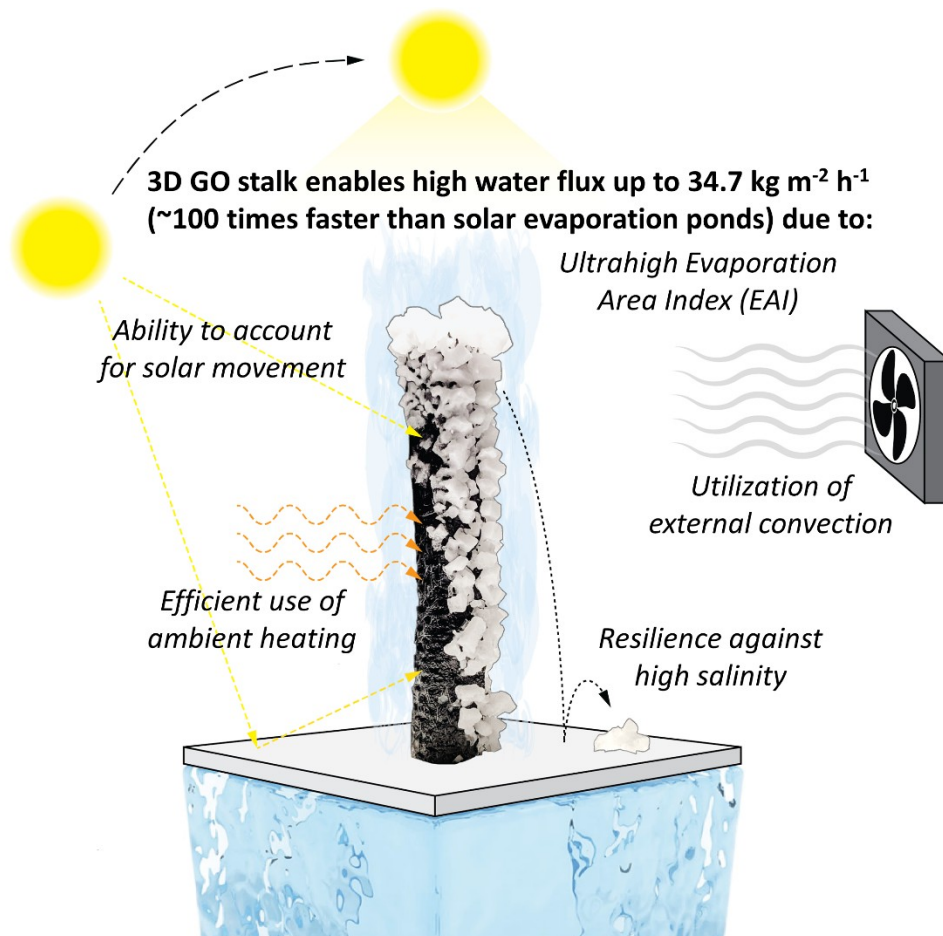
20 **Abstract**

21 In this work, we demonstrate a 3D Graphene Oxide (GO) stalk that operates near the capillary
22 wicking limit to achieve an evaporation flux of $34.7 \text{ kg m}^{-2} \text{ h}^{-1}$ under 1-sun condition. This flux
23 represents nearly a 100 times enhancement over a traditional solar evaporation pond. Interfacial
24 solar vapor generation traditionally uses 2D evaporators to vaporize water using sunlight, but
25 their low evaporative water flux limit their practical applicability for desalination. Some recent
26 studies using 3D evaporators demonstrate potential, but the flux improvement has been marginal
27 because of low evaporation area index (EAI), which is defined as the ratio of total evaporative
28 surface area to projected ground area. By using a 3D GO stalk with an ultrahigh EAI of 70, we
29 achieved nearly a 20× enhancement over 2D GO evaporator. The 3D GO stalk also demonstrated
30 additional advantages including omni-directional sunlight utilization, higher rates with external
31 forced convection (wind), and scaling resistance with highly saline brines (17.5 wt%). This
32 performance makes the 3D GO stalk extremely well-suited for the development of a completely
33 passive and low-cost technology for zero liquid discharge in brine management applications.

34

35 **KEYWORDS:** interfacial solar vapor generation, 3D evaporator, solar desalination, zero liquid
36 discharge, evaporation area index, graphene oxide

37



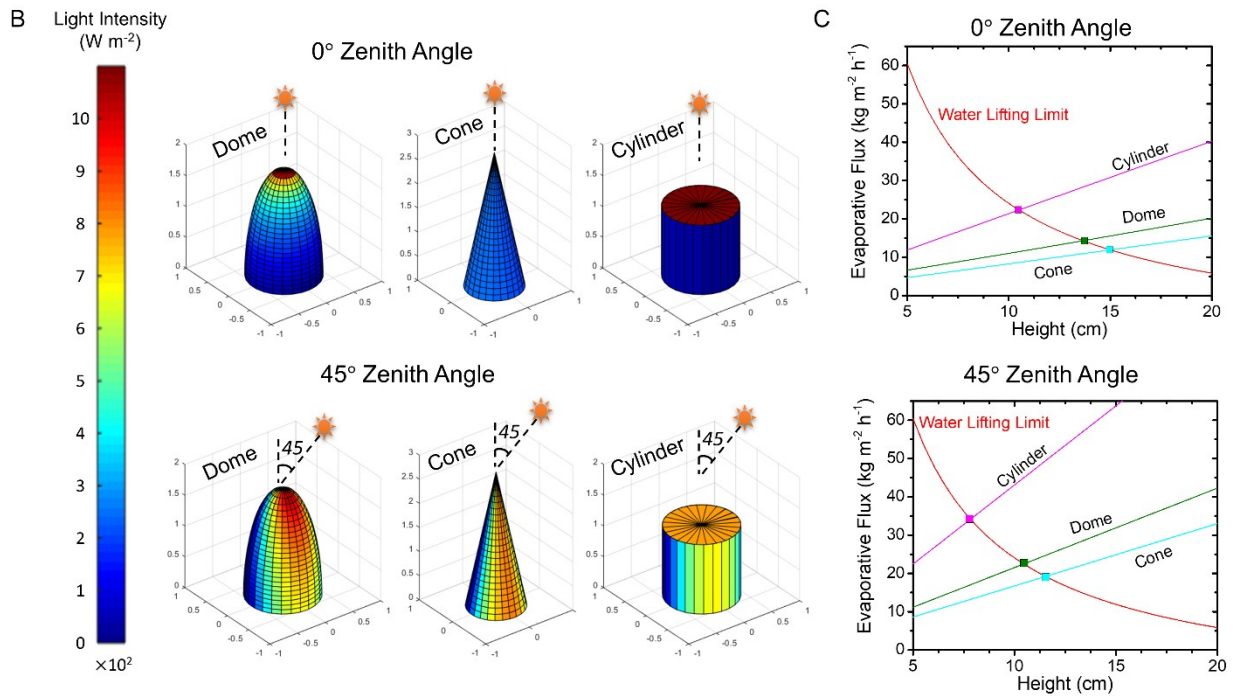
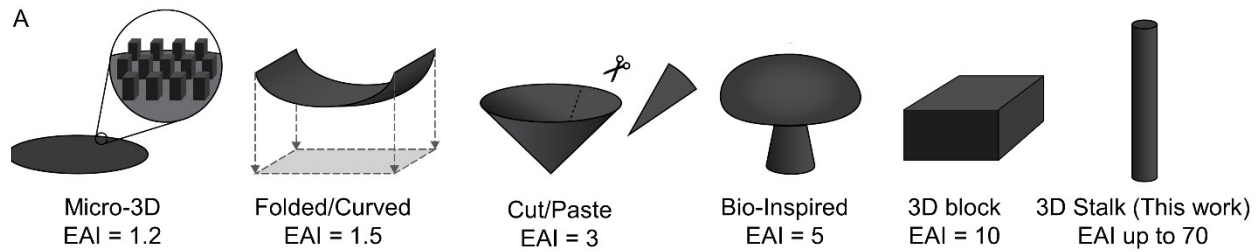
40 INTRODUCTION

41 Global water security is being threatened by rapidly increasing water demand, primarily driven by
42 industrial expansion and population growth.¹ Concurrently, overexploitation, pollution, and
43 climate change are decreasing traditional water availability,² which is estimated to cause an
44 additional 1.8 billion people to fall into water stress in the next 30 years.³ Expanding to
45 alternative water supplies typically involves advanced treatment, often by reverse osmosis (RO).
46 However, RO requires large capital investment, technical expertise, established supply chains, and
47 a reliable supply of high-grade energy to operate.⁴ Furthermore, the significant brine produced
48 by RO has to be properly managed, which severely limits where RO can be affordably
49 implemented.⁵

50 Interfacial solar vapor generation is an emerging approach to sustainably desalinate water
51 using sunlight, while being capable of producing zero liquid waste.^{6,7} Traditionally, interfacial
52 solar evaporation is achieved using flat, two-dimensional (2D) materials that float at the air-water
53 interface, where water is wicked into the material's porous structure, photothermally heated by
54 sunlight, and efficiently evaporated.⁸ Although optimization of material properties, heat
55 localization, and water replenishment rates have led to extremely high reported solar-vapor
56 conversion efficiencies, evaporative fluxes from 2D evaporators are still too low, typically
57 between 1.5 to 3.0 kg m⁻² h⁻¹,⁹⁻¹¹ to meet the demands of most water treatment applications.

58 Recently, 3D evaporators have been explored to increase the water production
59 performance.¹² As the name suggests, these 3D structures utilize capillary pumping to supply
60 water to additional surfaces for evaporation. This enables 3D evaporator to achieve evaporation
61 area index (EAI) values (ratio of total area available for evaporation relative to projected ground

62 area) that are greater than 1. Figure 1A summarizes some 3D geometries that have been reported
63 in the literature, including hierarchical structures that contain microscopic 3D features to increase
64 the EAI to around 1.2,^{13,14} curved and folded 2D sheets that lead to an increased EAI of around
65 1.5,¹⁵⁻¹⁷ 2D sheets that were intentionally converted into 3D geometries to obtain an EAI up to 3
66 by means of cutting and pasting,¹⁸⁻²⁰ and more recently bio-inspired²¹⁻²³ and other 3D
67 evaporators²⁴⁻²⁶ structures that result in EAI values of 5-15. The evaporative water flux of these
68 3D evaporators were higher than most 2D counterparts, but they have remained less than 5 kg m^{-2}
69 h^{-1} , with only a few 3D evaporators achieving higher EAI values^{27,28} that are able to marginally
70 exceed this threshold. Therefore, there is a knowledge gap on whether it is possible to engineer a
71 3D evaporator to achieve a substantially higher EAI to significantly improve water flux.



72

73 **Figure 1.** Comparison of different 3D evaporator geometries, and their corresponding EAI

74 values, light absorption, and water evaporative flux. A) Comparison of 3D evaporator geometries

75 being reported in the literature¹³⁻²⁶ and their corresponding EAI values. B) Light intensity

76 irradiated onto three 3D geometries (cone, dome, and cylinder) with solar zenith angles of 0°

77 (noon position) and 45° under 1-sun conditions. C) Comparison of the projected evaporative flux

78 of the three different 3D geometries with a set projected area and increasing height. The

79 maximum rate achievable depends on how rapidly water can be replenished to the highest

80 evaporative interface, denoted as the “Water Lifting Limit”. The evaporative flux of each 3D

81 evaporators will depend on the incident angle of solar radiation, therefore two solar zenith angles,
82 0° (top) and 45° (bottom), have been studied.

83
84 To address this challenge, we analyzed three geometries (dome, cone, and cylinder)
85 through mathematical modeling to facilitate the design of 3D evaporators. After finding the
86 optimal geometry being cylinder, we synthesized a cylindrical, 3D GO stalk that effectively
87 absorbs solar light and takes full advantage of capillary pumping to achieve significant increases
88 in EAI and evaporative surface area. We investigated this 3D design in comparison with a 2D
89 control to evaluate the potential advantages of 3D evaporators, including water flux enhancement,
90 omni-directional light absorption, utilization of wind-induced convection, and scaling resistance
91 with high-salinity brine. These findings are especially relevant as the field transitions from
92 material synthesis to technology design, with the 3D GO stalk showing promise to reduce the
93 spatial footprint of brine evaporation and potentially achieve zero-liquid-discharge (ZLD).

94

95 **MATERIALS AND METHODS**

96 **Light Intensity Analysis and Flux Prediction to Obtain Optimal Geometry.** To determine the
97 best 3D geometry to pursue, the evaporative performance of three different 3D geometries
98 (domes, cones, and cylinders as illustrated in Figure 1B) were investigated as a function of height.
99 The diameter of the projected area (base) of the dome, cone and cylinder remains constant at 1
100 cm, while the height was changed in the range of 5 – 20 cm. Using MATLAB, the 3D geometries
101 were constructed by rendering the 3D surfaces into 2D subunits, each with a specific direction
102 and inclination angle (Figure S1A and S1B). At selected light incident angle (Zenith Angle) of 0°
103 or 45° , the light intensity being irradiated onto the 3D geometry surfaces was analyzed. Using

104 empirical data collected on the evaporative flux of the 2D material as a function of light intensity
105 (Figure S1C), the evaporative flux of each 2D subunit was estimated. By summing up the
106 evaporation contributions of each 2D subunit, the total evaporative flux of the 3D geometry is
107 determined. The detailed procedure used in the light intensity and flux analysis can be found in
108 the Supplementary Note 1 in the SI.

109 **Material Preparation.** The 3D GO stalk was synthesized using a procedure adapted from our
110 previous work.⁶ As shown in Figure 3A, a GO coating solution was prepared by mixing 17.5 mg/
111 mL graphene oxide (GO) suspended in water, 0.035 M NaOH, 1,4-butanediol diglycidyl ether
112 (BDGE) and triethylenetetramine (TETA) at a volume ratio of 248 : 12.4 : 27 : 10, while keeping
113 all chemicals on ice. The GO coating solution was sonicated with a probe sonicator (Q500
114 Sonicator, Qsonica, Newtown, CT) at 40% amplitude for 4 minutes. Approximately 2.0 mL of the
115 GO coating solution was applied to a cotton humidifying filter (0.75-cm in diameter, 15-cm in
116 height), which served as the substrate for the 3D GO stalk. The GO-coated stalk was immediately
117 submerged in liquid nitrogen until completely frozen and then transferred to a freeze-dryer
118 (FreeZone 1, Labconco, Kansas City, MO) and kept at a temperature of -50°C and a pressure less
119 than 0.2 mbar for more than 12 hours. The stalk was then placed in an oven at 100°C to crosslink
120 GO and BDGE-TETA for 24 hours. The crosslinked 3D-GO stalk was then soaked in deionized
121 water to dissolve chemical residual for 24 hours, dried in a 60°C oven, and stored in air at room
122 temperature. Synthesis of the 2D GO evaporator followed the same procedure, except that the
123 substrate used was a filter paper coupon (4.7-cm in diameter) and approximately 0.34 mL of the
124 GO coating solution was coated on each coupon.

125 **Material Characterization.** The surface morphology and pore size of the 3D-GO stalk were

126 characterized by SEM (Gemini Ultra-55, Zeiss). The light absorption spectra for the 2D- and 3D-
127 evaporators were characterized using UV-Vis-Nir spectrophotometer with an integrating sphere
128 (ASD QualitySpec Pro, Malvern Panalytical and Cary 5000, Agilent). The thermal conductivities
129 were measured using a Cut-Bar method described in Supplementary Note 6.

130 **Solar Evaporation Setup.** To prepare for a solar evaporation experiment, the 3D GO stalk was
131 placed in a 250-mL beaker filled with 200 mL of feed water. The 3D stalk was secured in place
132 by a circular extruded polystyrene (EPS) foam that fit into the top of the beaker and had a hole in
133 its center to hold the 3D stalk. Parafilm was wrapped around the edge of the beaker and the 3D
134 stalk to avoid leaking water vapor from the container. The bottom of the stalk was submerged in
135 feed water to continuously supply water to the evaporation surface under capillary action. The
136 length of the stalk above the EPS foam represents the effective height of the 3D evaporator, and it
137 was adjusted to 1, 7.5, and 13 cm to achieve evaporation area index (EAI) values of 6.3, 41, and
138 70, respectively. The EAI is defined as the ratio of total surface area for evaporation relative to the
139 projected ground area. By this definition, a 2D evaporator has an EAI of 1, whereas the EAI of a
140 cylindrical 3D evaporator would increase with height. This relationship can be described by
141 Equation 1.

$$142 \quad EAI_{cylinder} = \frac{A_{total}}{A_{project}} = \frac{\frac{\pi}{4}d^2 + \pi dh}{\frac{\pi}{4}d^2} = 1 + \frac{4h}{d} \quad \text{Equation 1}$$

143 where d is the diameter and h is the effective height of the cylindrical GO stalk. If not specified
144 the effective evaporative height of the 3D GO stalk was kept at 7.5-cm, corresponding to an EAI
145 value of 41.

146 A similar setup was used for the control evaporation experiment for 2D evaporator except

147 that the 2D GO coupon was placed flat on the EPS foam on top of a 250-mL beaker. The feed
148 water was transported to the 2D GO coupon by a water-absorbing sheet (Nalgene Versi-Dry
149 Surface Protectors, Thermo Fisher Scientific) placed underneath the 2D GO coupon.

150 **Solar Evaporation Experiments.** The solar evaporation performance of the 2D or 3D
151 evaporator was evaluated using a solar simulator (91194-1000, Newport, Irvine, CA) at an
152 intensity of 1,000 W/m² at the most elevated point of light absorption. The mass evaporated over
153 time was recorded every minute using a mass balance, while the surface temperature was
154 monitored periodically using a Ti100 infrared camera. The ambient conditions were monitored
155 using temperature-humidity sensors (DHT22, Adafruit Industries), reporting temperatures
156 between 25 – 35°C and relative humidity between 20 – 40%.

157 The evaporative flux as a function of zenith angle was measured by angling the 2D and
158 3D evaporators relative to the fixed light source by 20°, 40°, 60°, and 75°. For the 2D evaporator,
159 this was achieved by using an extended water transporter and elevating the EPS base with
160 aluminum foil. This modified base could then be angled to the specified zenith angles.

161 The evaporative flux as a function of wind speed was measured by placing a variable
162 speed fan (Thermaltake, Taipei, Taiwan) about 10-cm away from the evaporator surface. Using an
163 anemometer (Flexzion), the wind speed generated by the fan at the material surface was
164 measured to be approximately 1.3, 1.9, and 3.5 m/s.

165 The evaporative flux as a function of salinity was measured by varying the NaCl
166 concentration in the feed solution. The salinities tested included 3.5, 7.0, 10.5, 14.0, 17.5 wt %
167 NaCl, representing 1x, 2x, 3x, 4x, and 5x typical seawater salinities (3.5 wt %). A long-term
168 scaling test was run with 17.5 wt % NaCl, under 1-sun conditions for 45 hours.

170 **RESULTS AND DISCUSSION**

171 **3D-Geometric Design.** To determine the optimal geometry and guide the rational design of a 3D
172 structure for solar evaporation, a MATLAB program was developed to predict the evaporative
173 flux rates of different 3D structures under varying incident light angles. We first analyzed the
174 variation of solar intensity on the 3D structure surfaces at zenith angles of 0° (solar noon
175 position) and 45° . Analyzing the performance of 3D structures at different incident light angles is
176 important because it illustrates how the performance of the evaporator would vary throughout the
177 day because of solar movement. Although this daytime variability in performance is an integral
178 feature of all evaporators, it has not been rigorously characterized until this work.

179 As illustrated in Figure 1B, we selected three structures (dome, cone, and cylinder) as
180 they are most promising to generate high EAI values by simply increasing their height. The light
181 intensity on the surfaces of each of the 3D structures have heterogeneous distribution due to the
182 changing inclination angle of the surfaces. At a Zenith angle of 0° , the top surface of the 3D
183 cylinder receives the highest light intensity, but its side surface does not receive any direct light
184 exposure; while the light intensity on the dome and cone surfaces are more diluted and
185 distributed into a larger area. When the Zenith angle increased to 45° , all the 3D structures
186 demonstrated larger areas being exposed to relatively high light intensity.

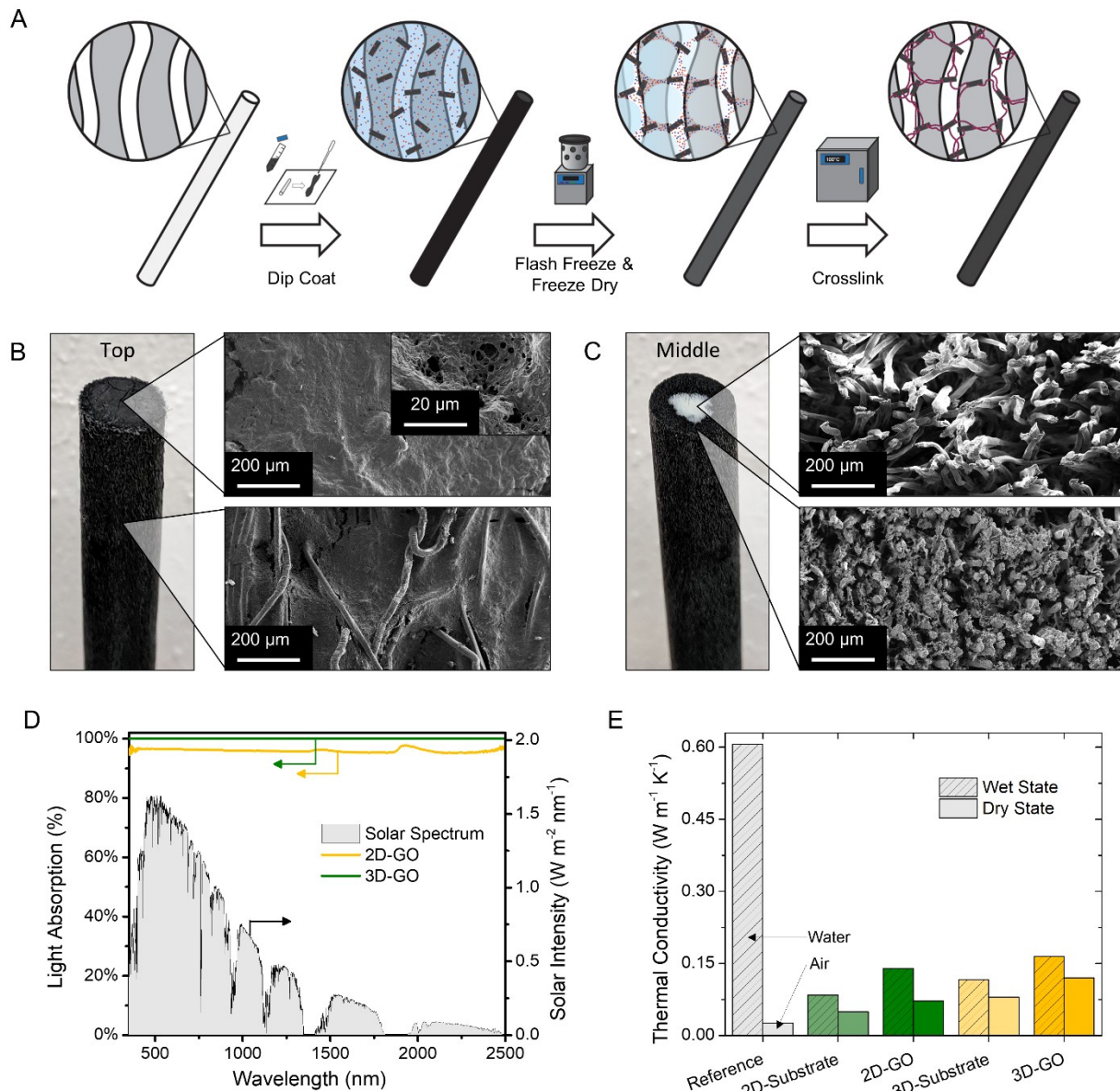
187 After translating the light intensity distribution to evaporative water flux, the total water
188 flux for each 3D structures were calculated and plotted in Figure 1C. At both 0 and 45° Zenith
189 angles, the cylindrical 3D structure demonstrated the highest water flux among the three
190 geometries being studied. The advantage of the cylinder is primarily a result of the higher EAI

191 values than that of cone or dome. For example, the EAI for the cylinder, dome, and cone at the
192 height of 5 cm is 21, 16, and 10, respectively. The increase of structure height will result in
193 further increase of EAI values and corresponding increases of evaporative water flux, as
194 illustrated in Figure 1C. However, the evaporative flux cannot increase indefinitely, as it will be
195 eventually limited by the maximum rate at which water can be lifted to the evaporative interface
196 by capillary forces. The maximum water lifting rate was calculated by assuming an internal pore
197 diameter of 100 μm and a water contact angle of 0° , and the results are plotted as the water lifting
198 limit in Figure 1C. The detailed calculation of the water lifting limit was described in the
199 Supplementary Note 2 in SI.

200 As shown in Figure 1C, the water lifting limit decreases with increasing structure height,
201 and its intersection with each flux line (for cylinder, cone and dome) represents the maximum
202 achievable evaporative flux for each geometrical design. For instance, the maximum evaporative
203 flux for a cylindrical 3D evaporator under the current design is $22 \text{ kg m}^{-2} \text{ h}^{-1}$, which was achieved
204 at a height of 10.4 cm when the solar Zenith angle is 0° . Any increase of the cylinder height
205 beyond 10.4 cm will not be able to further increase the evaporative flux due to the water lifting
206 limit. At Zenith angle of 0° , the maximum evaporative flux of the cone and dome are 14 and 12
207 $\text{kg m}^{-2} \text{ h}^{-1}$, respectively, much lower than that of the cylinder. Similarly, when the Zenith angle is
208 45° , the maximum evaporative flux of the cylinder ($34 \text{ kg m}^{-2} \text{ h}^{-1}$) is much higher than that of
209 cone and dome (22 and $18 \text{ kg m}^{-2} \text{ h}^{-1}$, respectively). This analysis indicates that a cylinder
210 represents a better 3D design than cone or dome as it will produce the highest EAI and
211 evaporative water flux. Therefore, we choose the cylindrical design as the geometry of the 3D
212 evaporator that we will investigate in the subsequent experiments. Note that the quantitative
213 prediction of maximum flux or height may differ from the real experimental data as the base and

214 pore diameters of the synthesized 3D evaporator could be different from the parameters that we
215 assumed in the calculation.

216 **Synthesis and Characterization of Cylindrical 3D Evaporator.** To synthesize a cylindrical 3D
217 evaporator, we started with a commercially available cotton stick that serves as a substrate with
218 high internal porosity, high hydrophilicity, and low thermal conductivity. To achieve ultrahigh
219 EAI, it is critical to have high internal porosity and hydrophilicity to increase the limits of water
220 replenishment rate so that water lifting does not become a limiting factor for high evaporative
221 flux. Low thermal conductivity is critical for heat localization so that the absorbed solar energy
222 can be effectively utilized for water vaporization. To enable effective solar light absorption, the
223 cotton stick was coated by crosslinked graphene oxide (GO) following the procedure illustrated in
224 Figure 2A. This creates a 3D GO stalk with a light-absorbing exterior that has sub-micrometer
225 pores (Figure 2B), while leaving the core unmodified to facilitate rapid water transport via
226 capillary wicking (Figure 2C). Based on the SEM, the pore size between cellulosic fibers in the
227 unmodified core ranges between 50 and 200 μm , whereas the GO coating provides much smaller
228 pores that can be less than 0.5 μm . The heterogeneity of these pores enables the cylindrical 3D
229 evaporator rapidly lift water through the middle of the stalk and achieve saturation, while using
230 high capillary pressure at the evaporative interface to maintain a wet state during operation.



231

232 **Figure 2.** Synthesis and characterization of the cylindrical 3D-GO stalk. A) Synthesis of the
 233 cylindrical 3D evaporator by coating GO on a cotton stick. B) Scanning electron microscopy
 234 (SEM) images of the top (with a higher magnification insert) and side of the synthesized 3D GO
 235 stalk. C) SEM images of a cross-section from the middle of the 3D GO stalk, showing the
 236 unmodified cellulose fibers at the core and GO-modified cellulose fibers toward the outer
 237 perimeter. D) Light absorption across the solar spectrum of the 2D- and 3D-GO. E) Thermal
 238 conductivity of the 2D- and 3D- substrates and GO evaporators.

239

240 In addition to having an efficient water replenishment mechanism, the 3D GO stalk
 241 demonstrates high efficiencies in broadband light absorption and heat localization that greatly

242 contribute to solar vapor generation. As shown in Figure 2D, compared to a 2D-GO control,
243 which underwent a similar synthesis process to that of the 3D-GO stalk except that a filter paper
244 was used as the supporting substrate,⁶ the 3D-GO stalk demonstrates higher and near-complete
245 absorption of light across the solar spectrum from 350 to 2500 nm. The higher absorption
246 efficiency of the 3D-GO stalk is attributed to the thickness of the GO photo-thermal material,
247 which allows for complete absorption of light that is transmitted by its top surface.

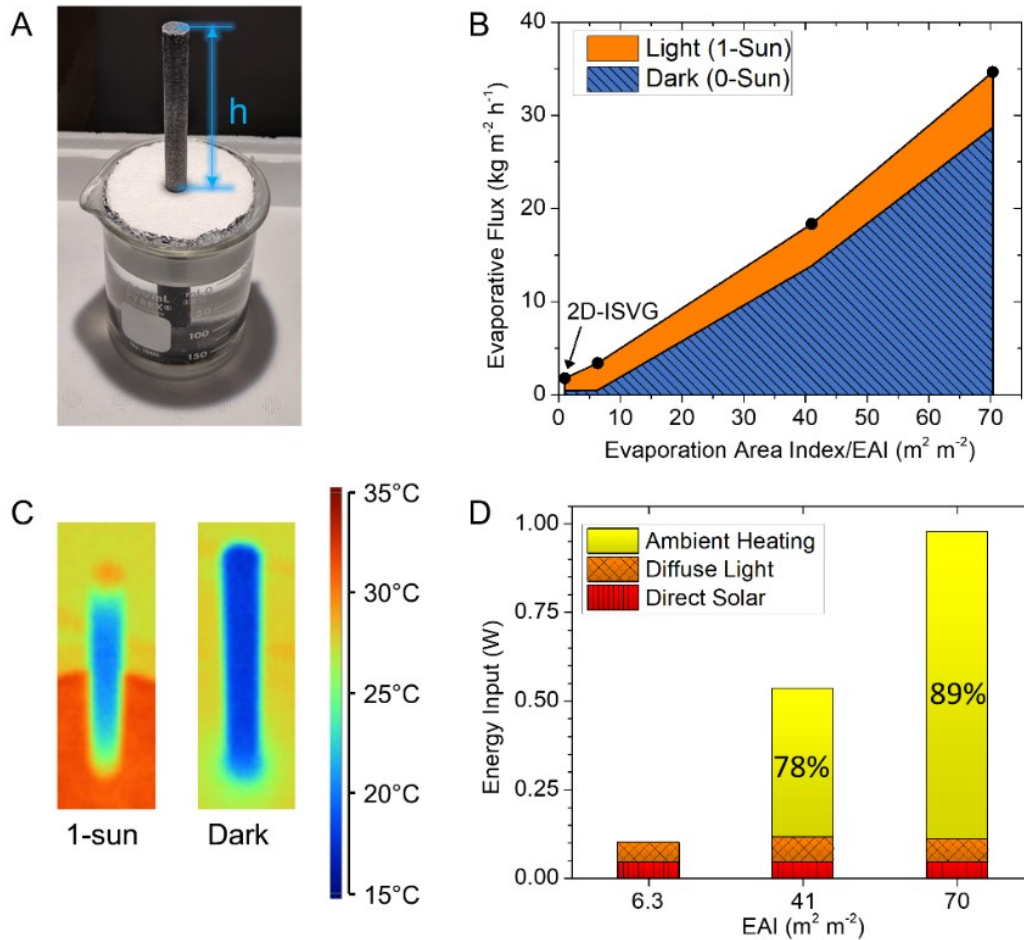
248 In traditional 2D evaporators, heat localization at the air-water interface is achieved with
249 a thermal insulation layer that minimizes conductive heat losses from the surface to the bulk
250 water. To evaluate the heat localization capability, the thermal conductivity of the evaporators, as
251 well as the unmodified substrates, was measured in both wet and dry states. Figure 2E shows that
252 introducing the GO coating increases the thermal conductivity of both the 2D- and 3D-
253 evaporators compared to the unmodified substrate. This is expected as the cross-linked GO
254 replaces air in the porous substrate. As a result, the higher thermal conductivity of the crosslinked
255 GO increases the materials' effective thermal conductivity. Similarly, the wet evaporators have
256 higher thermal conductivities in comparison to their dry counterparts as water displaces air
257 within the porous structure. The thermal conductivities of the wet 2D- and 3D-evaporators are
258 0.140 and 0.165 W m⁻¹ K⁻¹, respectively. Even though the 3D geometry results in a higher thermal
259 conductivity, the distance over which heat must be conducted before being lost to the bulk water
260 reservoir is significantly larger (1-13 cm) than traditional 2D evaporators (~200 μm). This
261 dramatically reduces the overall heat loss due to conduction and maintains the heat localization
262 that is necessary for efficient evaporation.

263

264 **Evaporation Performance of the 3D GO Stalk.** The vapor generation performance of the 3D
265 GO stalk was evaluated using the setup illustrated in Figure 3A. The bottom of the GO stalk was
266 submerged in the feed water reservoir to take in water, while the stalk above the white
267 polystyrene base provides effective area for water evaporation. By adjusting the height of the GO
268 stalk above the base to 1, 7.5, and 13 cm, we studied the performance of the GO stalk at EAI
269 values of 6.3, 41, 70, respectively. We also characterized the performance of a 2D GO evaporator,
270 which by definition has an EAI value of 1. As shown in Figure 3B, operating under 1-sun
271 conditions, increasing the EAI value beyond 1 significantly increases the evaporative flux from
272 1.8 (EAI = 1.0) to 34.7 (EAI = 70) kg m⁻² h⁻¹.

273 The flux enhancement can be attributed to both increased total surface area available for
274 evaporation and more effective utilization of energy sources (e.g., ambient heating, diffuse
275 radiation) other than the solar energy input. For example, ambient heating can serve as an
276 additional energy source due to convective heat transfer from the relatively warmer ambient
277 environment to the cooled sides of the 3D GO stalk. As demonstrated by the thermal images in
278 Figure 3C, the side surfaces of the GO stalk that are not in direct sunlight drop to a sub-ambient
279 temperature because of evaporative cooling. Similarly, the stalk under dark conditions is much
280 cooler than the ambient air, enabling heat transfer from ambient environment to the evaporation
281 surface. Comparing the evaporative performance under 1-sun and dark conditions indicates that a
282 large percentage of water flux is attributed to the evaporation taking place under dark conditions,
283 as shown in Figure 3B. The high evaporation flux under dark conditions confirms that the 3D GO
284 stalk with its large EAI is capable of effectively using ambient heating compared to other
285 geometries. Although similar behavior of drawing heat from the environment during evaporation

286 has also been observed in related works,^{15,24,29} the high aspect ratio of our 3D GO stalk capitalizes
 287 on this phenomenon, allowing the GO stalk to achieve evaporative flux rates 15-20 times what
 288 has been previously reported.



289
 290 **Figure 3.** Evaporation performance and efficiency of the 3D evaporator. A) The experimental
 291 setup for performance characterization. B) The change of evaporative flux of the 3D GO stalk in
 292 dark and light conditions as EAI value increases. C) Thermal images of the 3D GO stalk under
 293 light and dark conditions. D) Contribution to energy input from direct solar, diffuse light, and
 294 ambient heating.
 295

296 As shown in Figure 3B, the evaporative flux of the 3D GO stalk with high EAI values (40-70) are
297 more than 10 times higher than the maximum solar-to-vapor output of $1.5 \text{ kg m}^{-2} \text{ h}^{-1}$ under 1-sun
298 conditions.³⁰ This again indicates that energy sources other than direct solar are playing a very
299 important role in contributing to the high evaporative flux ($18.4 \text{ kg m}^{-2} \text{ h}^{-1}$ for the 7.5-cm stalk
300 and $34.7 \text{ kg m}^{-2} \text{ h}^{-1}$ for the 13-cm stalk). In order to understand the roles of different energy
301 sources, the total energy input (q_{input}) can be analyzed by accounting for the three primary energy
302 sources:

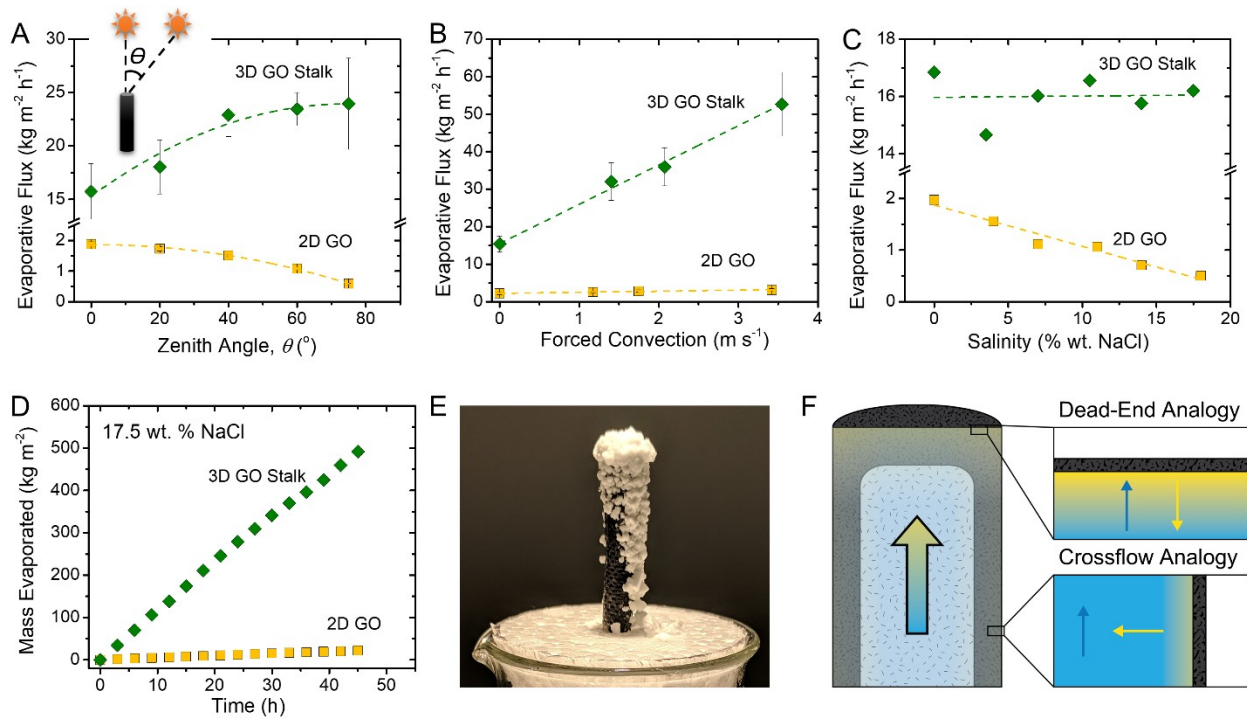
$$303 \quad q_{input} = q_{solar} + q_{diffuse} + q_{ambient} \quad \text{Equation 2}$$

304 where q_{solar} , $q_{diffuse}$, and $q_{ambient}$ are energy flows coming from direct solar radiation, diffuse
305 radiation, and ambient heating. A full description of how each of these factors were accounted
306 for can be found in Supplementary Note 3 and 4 in the SI. Through this analysis, the
307 contributions from each energy sources were calculated and plotted in Figure 3D. The amount of
308 energy from direct solar and diffuse light remains constant when the EAI value changes.
309 However, as the EAI value increases, a growing amount of energy comes from ambient heating.
310 For example, when EAI increases from 6 to 70, the energy contribution from ambient heating
311 increases from 0% to 89% of total energy input, while the contribution from direct solar
312 decreases from 44% to 4.5%. This shows that the increase in evaporative flux as the height of the
313 GO stalk increases is primarily a result of absorbing more ambient heating. Overall, the 3D GO
314 stalk is able to derive the energy for evaporation from multiple sources, enabling a dramatic
315 reduction in the spatial footprint of solar evaporation.

316

317 **3D-Enhanced Omnidirectional Light Utilization.** One major advantage of the 3D evaporator is

318 its omnidirectional light utilization as the sun moves across the sky throughout the day. Most
319 solar evaporation studies use a solar source at a fixed position, often under the optimal conditions
320 of solar noon with a zenith angle of 0° , *i.e.*, with the incident light perpendicular to the
321 evaporation surface. However, understanding the effect of solar movement is critical to predict the
322 actual performance of solar evaporators throughout the day. For 2D evaporator, an increase in the
323 zenith angle when the sun deviates from the noon position decreases the projected cross-section
324 that receives solar radiation, resulting in a decrease of evaporative flux (Figure 4A). However, the
325 3D evaporator exhibits an opposite trend, with an increase in evaporative flux as the solar angle
326 deviates from the noon position. The reason for this is that under solar noon conditions, the only
327 surface to receive direct radiation is the top of the cylindrical 3D stalk. As the zenith angle
328 increases, a greater cross-section (including a portion of the sides of the cylinder) is irradiated by
329 sunlight, resulting in a higher evaporative flux. This is a promising result for outdoor applications
330 of 3D GO evaporator, where higher performance may be achieved in the hours leading up to and
331 away from solar noon.



332

333 **Figure 4.** Enhanced evaporation performance enabled by 3D geometry. Comparison of the
 334 performance of 3D and 2D GO evaporators as a function of A) varying incident light angle, B)
 335 increasing wind speed (external forced convection rates), and C) increasing feedwater salinity. D)
 336 Mass evaporated over time with a feedwater containing 17.5 wt. % NaCl to demonstrate the
 337 constant evaporative flux observed despite scale formation. E) Scale formation on the surface of
 338 the 3D GO stalk. F) Dead-end and crossflow analogies to describe scaling behavior of the 3D-
 339 GO stalk.

340

341 **3D-Enhanced Utilization of Wind Energy** The second advantage of the 3D GO stalk is that it
 342 can extract energy from the ambient environment, thus resulting in efficient utilization of
 343 convection from the wind. To demonstrate this advantage, we used a fan to blow air at varying
 344 speeds across the 2D- and 3D-evaporators and observed significantly higher flux enhancement in
 345 the 3D evaporator than 2D. As shown in Figure 4B, when the external air flow rate increases

346 from 0 to 3.5 m s^{-1} , the evaporative flux of the 3D GO stalk increases from 15.4 to $52.7 \text{ kg m}^{-2} \text{ h}^{-1}$,
347 resulting in an increase of 241%; while the flux of 2D material only increases from 2.2 to 3.2 kg
348 $\text{m}^{-2} \text{ h}^{-1}$, an increase of merely 45%. The huge differences between the 2D- and 3D-evaporators is
349 attributed to the geometry difference that affects the formation of the airflow boundary layer. The
350 thickness of this boundary layer is important because water vapor molecules produced by the
351 evaporator must diffuse through the boundary layer before convective forces sweep them away. As
352 the rate of forced convection increases, the boundary layer thickness is compressed, decreasing
353 the distance that water molecules must diffuse and increasing the driving force for evaporation.
354 However, given that the average flow path length across the 2D evaporator is longer than that of
355 the 3D evaporator, the boundary layer is still developing (and thus thinner) over a greater portion
356 of the 3D evaporator surface area. As a result, the 3D GO stalk has a significantly higher response
357 to increases in external convection rates than the 2D GO evaporator. This result is also promising
358 because vapor accumulation near the evaporative interface is a severely limiting factor for vapor
359 production in closed systems (such as a traditional solar still) that aim to condense the water
360 vapor. Introducing external forced convection not only increases the rate of evaporation, but also
361 contribute to transporting water vapor into a separate stage for condensation if water recovery is
362 desired.

363

364 **Resilience to Mineral Scaling.** A final unexpected, but exciting advantage of the 3D GO stalk is
365 its capability of maintaining high evaporative flux when feedwater salinity increases. As shown in
366 Figure 4C, the evaporative flux of the 3D GO stalk remains almost constant at $16.0 \text{ kg m}^{-2} \text{ h}^{-1}$ over
367 the range of 0 to 17.5 wt. % NaCl, demonstrating an astonishing resilience to increasing

368 feedwater salinities which resemble brines that can currently only be treated with energy
369 intensive thermal brine concentrators. The flux of 2D GO evaporator decreases from 2 to 0.5 kg
370 $\text{m}^{-2} \text{h}^{-1}$ under these same conditions, which is expected due to the reduction in vapor pressure
371 caused by increasing feedwater salinity, consistent with what we reported in an earlier study.^{6,7} In
372 addition, the high flux of 3D GO stalk is not affected by the accumulation of salt on the
373 evaporative surface. As seen in Figure 4D, the evaporated mass of water for both 2D- and 3D-
374 evaporators increases at a relatively constant rate during the course of a continuous 45-h
375 evaporation run, despite significant salt accumulation can be observed on both 2D⁶ and 3D
376 material surfaces (Figure 4E) at such high salinity (17.5 wt. % NaCl) in feedwater. The
377 continuous high flux of the 3D stalk results in the vaporization of a total of 492 kg of water per
378 m^2 throughout the 45-h period, while under the same condition the 2D GO evaporator would only
379 vaporize 22 kg of water per m^2 . Such a high evaporation rate for a salinity that is 5 times more
380 concentrated than seawater demonstrates the potential of the 3D GO stalk for brine concentration
381 and ZLD applications.

382 To explain why the 3D GO stalk has better resistance to these high salinities compared to
383 a 2D counterpart, we illustrate the transport process in the 3D stalk using an analogy from
384 membrane filtration (Figure 4F). The evaporation process on the top surface of the stalk is
385 analogous to a dead-end filtration, which results in extreme concentration polarization because
386 the direction of water flow opposes the direction of the back-diffusion of salt, creating a higher
387 salt concentration at the evaporative interface on top of the 3D GO stalk. These high salt
388 concentrations lower the saturation vapor pressure at the evaporative interface, thus lowering the
389 driving force for evaporation and decreasing the flux. Since the evaporation on the entire 2D
390 evaporator is like dead-end filtration, its performance is prone to the negative impacts of high salt

391 concentration. However, such an effect on the performance of the 3D GO stalk is greatly
392 diminished because the top surface evaporation constitutes a small portion of the total
393 evaporative surface area (only 2.4% for this experiment). Meanwhile, the side surfaces of the 3D
394 GO stalk benefit from crossflow, where the back-diffusion of salt ions is accelerated by the
395 upward flow of water through the 3D stalk. Therefore, the reduced concentration polarization on
396 the sides may slow down the accumulation of salts and contribute to maintaining a constant
397 evaporative flux for the 3D GO stalk.

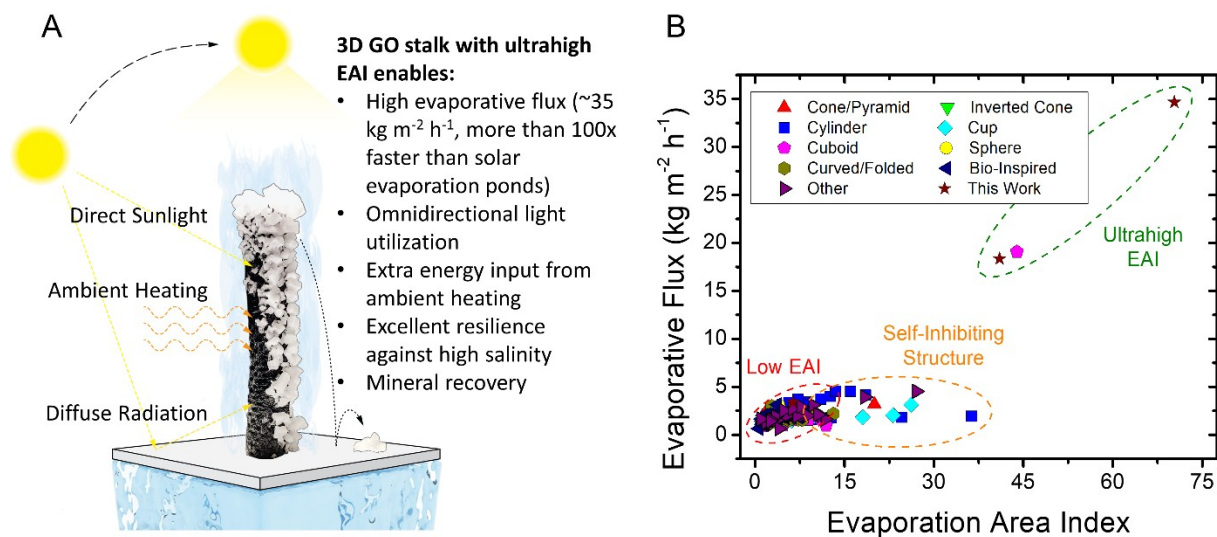
398 Furthermore, the precipitation of salt onto the surface of the 3D GO stalk (Figure 4E)
399 presents another promising opportunity in ZLD, *i.e.*, mineral recovery. As salt crystals grow on
400 the sides of the cylindrical 3D evaporator, they gradually become unstable and naturally slough
401 off the cylindrical structure. This process could be engineered into a passive salt management
402 strategy that simultaneously prevents excessive buildup of salt on the 3D structure while
403 collecting crystallized salt with valorization application.

404

405 **Technology Outlook for the 3D GO Stalk.** This study explored a variety of advantages of using
406 3D GO stalk for brine treatment in comparison with 2D evaporators. As summarized in Figure
407 5A, our cylindrical design significantly increases the EAI value, enabling high evaporative flux
408 that is about 100 times faster than a traditional evaporation pond. The flux enhancement is also
409 attributed to more efficient use of ambient heating and omnidirectional light utilization. In
410 addition, the 3D GO stalk is capable of maintaining high flux in highly concentrated brine and
411 demonstrates potential for mineral recovery. We also compared the performance of the 3D GO
412 stalk with published literature on other 3D structures. As shown in Figure 5B, this study is one of

413 two studies with EAI values greater than 30 (see Supplementary Note 5 for full details).²⁸ Most
414 structures have low evaporative fluxes (less than $5 \text{ kg m}^{-2} \text{ h}^{-1}$) due to relatively low EAI
415 values.^{15,16,20,31,32} Although some other studies demonstrate 3D evaporators with moderate EAI
416 values, they do not achieve comparable evaporative flux rates owing to self-inhibiting structures,
417 *i.e.*, their geometries prevent the diffusion of water vapor away from the evaporator, creating high-
418 humidity pockets near the evaporative interface that diminish the driving force for
419 evaporation.^{22,23,33–35}

420 The high evaporative flux combined with the passive salt management strategy
421 demonstrated in this work indicated that the 3D GO stalk has the potential to significantly reduce
422 the spatial and energy footprint of brine treatment. If paired with upstream purification steps, the
423 3D GO stalk could be used for continuous production of mineral resources for salt mining or
424 resource recovery operations. Further investigation is still needed to study the effects of crowding
425 and shading and to evaluate the fouling performance under long-term operation with realistic feed
426 streams. Nevertheless, the 3D GO stalk has demonstrated the ability to significantly reduce the
427 spatial footprint of the solar evaporation process while passively processing brines with salinities
428 as high as 17.5 wt%, bringing the field one step closer toward the development of a sustainable
429 off-grid desalination technology with ZLD and salt recovery.



430

431 **Figure 5.** Comparison of the performance of the GO stalk to other 3D evaporators. A) Summary
 432 of the advantages of 3D GO stalk. B) Comparison of our work with the evaporative flux of 3D
 433 evaporators reported through Jan 2021.^{15,18,19,21,24,27–29} The data were all obtained under 1-sun
 434 conditions. A complete reference list for all the data points is available in the Supplemental
 435 Information.

436

437 **Associated Content**

438 **Supporting Information**

439 The Supporting Information is available free of charge on the ACS Publications website. This
 440 document includes additional analysis of different 3D geometries, determination of water lifting
 441 limit, analysis of convective heat transfer for ambient heating, analysis of solar energy input from
 442 direct solar and diffuse light, compilation of 3D evaporator performance data, and thermal
 443 conductivity measurements by Cut-Bar Method.

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455

456 References

- 457 1. Leflaive, X. (2012). Water Outlook to 2050: The OECD calls for early and strategic
458 action. GWF Discuss. Pap. 1219, Glob. Water Forum, Canberra, Aust., 1–9.
- 459 2. Kundzewicz, Z.W., and Krysanova, V. (2010). Climate change and stream water quality
460 in the multi-factor context. *Clim. Change* 103, 353–362.
- 461 3. Schlosser, C.A., Strzepek, K., Gao, X., Fant, C., Blanc, É., Paltsev, S., Jacoby, H., Reilly,
462 J., and Gueneau, A. (2014). The future of global water stress: An integrated assessment.
463 *Earth's Futur.* 2, 341–361.
- 464 4. Sarai Atab, M., Smallbone, A.J., and Roskilly, A.P. (2016). An operational and economic
465 study of a reverse osmosis desalination system for potable water and land irrigation.
466 *Desalination* 397, 174–184.
- 467 5. Xu, P., Cath, T.Y., Robertson, A.P., Reinhard, M., Leckie, J.O., and Drewes, J.E. (2013).
468 Critical review of desalination concentrate management, treatment and beneficial use.
469 *Environ. Eng. Sci.* 30, 502–514.
- 470 6. Finnerty, C., Zhang, L., Sedlak, D.L., Nelson, K.L., and Mi, B. (2017). Synthetic
471 Graphene Oxide Leaf for Solar Desalination with Zero Liquid Discharge. *Environ. Sci.*
472 *Technol.* 51, 11701–11709.
- 473 7. Menon, A.K., Haechler, I., Kaur, S., Lubner, S., and Prasher, R.S. (2020). Enhanced solar
474 evaporation using a photo-thermal umbrella for wastewater management. *Nat. Sustain.* 3,
475 144–151.
- 476 8. Ghasemi, H., Ni, G., Marconnet, A.M., Loomis, J., Yerci, S., Miljkovic, N., and Chen, G.
477 (2014). Solar steam generation by heat localization. *Nat. Commun.* 5, 1–7.
- 478 9. Zhao, F., Zhou, X., Shi, Y., Qian, X., Alexander, M., Zhao, X., Mendez, S., Yang, R., Qu,
479 L., and Yu, G. (2018). Highly efficient solar vapour generation via hierarchically
480 nanostructured gels. *Nat. Nanotechnol.* 13, 489–495.
- 481 10. Liang, H., Liao, Q., Chen, N., Liang, Y., Lv, G., Zhang, P., Lu, B., and Qu, L. (2019).
482 Thermal Efficiency of Solar Steam Generation Approaching 100 % through Capillary

- 483 Water Transport. *Angew. Chemie* *131*, 19217–19222.
- 484 11. Tang, J., Zheng, T., Song, Z., Shao, Y., Li, N., Jia, K., Tian, Y., Song, Q., Liu, H., and
485 Xue, G. (2020). Realization of Low Latent Heat of a Solar Evaporator via Regulating the
486 Water State in Wood Channels. *ACS Appl. Mater. Interfaces*.
- 487 12. Zhou, J., Gu, Y., Liu, P., Wang, P., Miao, L., Liu, J., Wei, A., Mu, X., Li, J., and Zhu, J.
488 (2019). Development and Evolution of the System Structure for Highly Efficient Solar
489 Steam Generation from Zero to Three Dimensions. *Adv. Funct. Mater.* *29*, 1903255.
- 490 13. Zhang, P., Liao, Q., Yao, H., Cheng, H., Huang, Y., Yang, C., Jiang, L., and Qu, L.
491 (2018). Three-dimensional water evaporation on a macroporous vertically aligned
492 graphene pillar array under one sun. *J. Mater. Chem. A* *6*, 15303–15309.
- 493 14. Yu, Z., Cheng, S., Li, C., Li, L., and Yang, J. (2019). Highly Efficient Solar Vapor
494 Generator Enabled by a 3D Hierarchical Structure Constructed with Hydrophilic Carbon
495 Felt for Desalination and Wastewater Treatment. *ACS Appl. Mater. Interfaces* *11*, 32038–
496 32045.
- 497 15. Song, H., Liu, Y., Liu, Z., Singer, M.H., Li, C., Cheney, A.R., Ji, D., Zhou, L., Zhang, N.,
498 Zeng, X., et al. (2018). Cold Vapor Generation beyond the Input Solar Energy Limit. *Adv.*
499 *Sci.* *5*, 1800222.
- 500 16. Hong, S., Shi, Y., Li, R., Zhang, C., Jin, Y., and Wang, P. (2018). Nature-Inspired, 3D
501 Origami Solar Steam Generator toward Near Full Utilization of Solar Energy. *ACS Appl.*
502 *Mater. Interfaces* *10*, 28517–28524.
- 503 17. Liu, Z., Wu, B., Zhu, B., Chen, Z., Zhu, M., and Liu, X. (2019). Continuously Producing
504 Watersteam and Concentrated Brine from Seawater by Hanging Photothermal Fabrics
505 under Sunlight. *Adv. Funct. Mater.* *29*, 1905485.
- 506 18. Li, X., Lin, R., Ni, G., Xu, N., Hu, X., Zhu, B., Lv, G., Li, J., Zhu, S., and Zhu, J. (2017).
507 Three-dimensional artificial transpiration for efficient solar waste-water treatment. *Natl.*
508 *Sci. Rev.* *5*, 70–77.
- 509 19. Wang, Y., Wang, C., Song, X., Huang, M., Megarajan, S.K., Shaukat, S.F., and Jiang, H.
510 (2018). Improved light-harvesting and thermal management for efficient solar-driven
511 water evaporation using 3D photothermal cones. *J. Mater. Chem. A* *6*, 9874–9881.
- 512 20. Ni, F., Xiao, P., Zhang, C., Liang, Y., Gu, J., Zhang, L., and Chen, T. (2019).
513 Micro-/Macroscopically Synergetic Control of Switchable 2D/3D Photothermal Water
514 Purification Enabled by Robust, Portable, and Cost-Effective Cellulose Papers. *ACS Appl.*
515 *Mater. Interfaces* *11*, 15498–15506.
- 516 21. Xu, N., Hu, X., Xu, W., Li, X., Zhou, L., Zhu, S., and Zhu, J. (2017). Mushrooms as
517 Efficient Solar Steam-Generation Devices. *Adv. Mater.* *29*, 1606762.
- 518 22. Bian, Y., Shen, Y., Tang, K., Du, Q., Hao, L., Liu, D., Hao, J., Zhou, D., Wang, X.,
519 Zhang, H., et al. (2019). Carbonized Tree-Like Furry Magnolia Fruit-Based Evaporator
520 Replicating the Feat of Plant Transpiration. *Glob. Challenges* *3*, 1900040.
- 521 23. Xiao, P., He, J., Liang, Y., Zhang, C., Gu, J., Zhang, J., Huang, Y., Kuo, S.-W., and Chen,
522 T. (2019). Rationally Programmable Paper-Based Artificial Trees Toward Multipath
523 Solar-Driven Water Extraction from Liquid/Solid Substrates. *Sol. RRL* *3*, 1900004.
- 524 24. Shi, Y., Li, R., Jin, Y., Zhuo, S., Shi, L., Chang, J., Hong, S., Ng, K.C., and Wang, P.
525 (2018). A 3D Photothermal Structure toward Improved Energy Efficiency in Solar Steam
526 Generation. *Joule* *2*, 1171–1186.
- 527 25. Yang, Q., Xu, C., Wang, F., Ling, Z., Zhang, Z., and Fang, X. (2019). A High-Efficiency

- 528 and Low-Cost Interfacial Evaporation System Based on Graphene-Loaded Pyramid
529 Polyurethane Sponge for Wastewater and Seawater Treatments. *ACS Appl. Energy Mater.*
530 *2*, 7223–7232.
- 531 26. Lu, Y., Fan, D., Xu, H., Min, H., Lu, C., Lin, Z., and Yang, X. (2020). Implementing
532 Hybrid Energy Harvesting in 3D Spherical Evaporator for Solar Steam Generation and
533 Synergic Water Purification. *Sol. RRL* *4*, 2000232.
- 534 27. Tu, C., Cai, W., Chen, X., Ouyang, X., Zhang, H., and Zhang, Z. (2019). A 3D-Structured
535 Sustainable Solar-Driven Steam Generator Using Super-Black Nylon Flocking Materials.
536 *Small* *15*, 1902070.
- 537 28. Li, J., Wang, X., Lin, Z., Xu, N., Li, X., Liang, J., Zhao, W., Lin, R., Zhu, B., Liu, G., et
538 al. (2020). Over 10 kg m⁻² h⁻¹ Evaporation Rate Enabled by a 3D Interconnected Porous
539 Carbon Foam. *Joule* *0*.
- 540 29. Li, X., Li, J., Lu, J., Xu, N., Chen, C., Min, X., Zhu, B., Li, H., Zhou, L., Zhu, S., et al.
541 (2018). Enhancement of Interfacial Solar Vapor Generation by Environmental Energy.
542 *Joule* *2*, 1331–1338.
- 543 30. Li, X., Ni, G., Cooper, T., Xu, N., Li, J., Zhou, L., Hu, X., Zhu, B., Yao, P., and Zhu, J.
544 (2019). Measuring Conversion Efficiency of Solar Vapor Generation. *Joule* *3*, 1798–1803.
- 545 31. Xu, Y., Ma, J., Liu, D., Xu, H., Cui, F., and Wang, W. (2019). Origami system for
546 efficient solar driven distillation in emergency water supply. *Chem. Eng. J.* *356*, 869–876.
- 547 32. Li, W., Li, Z., Bertelsmann, K., and Fan, D.E. (2019). Portable Low-Pressure Solar
548 Steaming-Collection Unisystem with Polypyrrole Origamis. *Adv. Mater.* *31*, 1900720.
- 549 33. Sun, P., Zhang, W., Zada, I., Zhang, Y., Gu, J., Liu, Q., Su, H., Pantelić, D., Jelenković,
550 B., and Zhang, D. (2020). 3D-Structured Carbonized Sunflower Heads for Improved
551 Energy Efficiency in Solar Steam Generation. *ACS Appl. Mater. Interfaces* *12*, 2171–
552 2179.
- 553 34. Sui, Y., Hao, D., Guo, Y., Cai, Z., and Xu, B. (2020). A flowerlike sponge coated with
554 carbon black nanoparticles for enhanced solar vapor generation. *J. Mater. Sci.* *55*, 298–
555 308.
- 556 35. Gao, X., Lan, H., Li, S., Lu, X., Zeng, M., Gao, X., Wang, Q., Zhou, G., Liu, J.-M.,
557 Naughton, M.J., et al. (2018). Artificial Mushroom Sponge Structure for Highly Efficient
558 and Inexpensive Cold-Water Steam Generation. *Glob. Challenges* *2*, 1800035.
- 559