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1 Semicarbonized Subwavelength-Nanopore-
2 Structured Nanocellulose Paper for Application in
3 Solar Thermal Heating

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8

9 ABSTRACT

10 Recently, there has been remarkable progress in solar thermal heating by applying biomass-
11 derived carbons, which can absorb and convert solar light into thermal energy. The design of
12 subwavelength nanoporous and molecular structures of biomass-derived carbons is required for
13 suppressed reflection and enhanced absorption of solar light. However, such designs are difficult
14 because conventional biomass-derived carbons exhibit intrinsic microstructures and are prepared
15 under specific carbonization conditions. In this study, a wood cellulose nanofiber-derived carbon
16 is proposed to tailor both subwavelength nanoporous and molecular structures. Cellulose
17 nanofibers are first constructed into a paper, denoted as “nanopaper”, exhibiting subwavelength

18 nanoporous structures by tailoring the pore spaces between cellulose nanofibers. The as-prepared
19 nanopaper is then carbonized at various controlled temperatures to tailor the cellulose molecular
20 structure, *i.e.*, grow graphitic carbon domains. The graphitic carbon domains grown by
21 semicarbonization at 500 °C adequately balance solar absorption and reflection, while the
22 subwavelength nanoporous structures suppress solar reflection. Thus, the semicarbonized
23 nanopaper with tailored nanoporous and molecular structures exhibits superior solar thermal
24 heating to competitive nanocarbons, also affording thermoelectric power generation. This study
25 can guide the structural and functional design of bionanocarbons for solar thermal heating.

26

27 INTRODUCTION

28 Biomass-derived carbon materials have recently attracted increased interest owing to
29 their unique physical and chemical properties, intrinsic high-specific-surface-area porous
30 structures, and sustainability.^{1,2} The potential applications of biomass-derived carbon materials
31 include adsorption,³ separation,⁴ sensing,^{5,6} energy storage,^{7,8} and photothermal heating,⁹ among
32 which photothermal heating has recently garnered the most attention for converting renewable
33 solar light energy into heat.^{10–15} Photothermal heating is achieved using photothermal materials
34 that enable light to be absorbed and then converted into heat. Biomass-derived carbons are
35 promising photothermal materials because carbon materials absorb light over a broader
36 wavelength range (approximately 300–2500 nm) than other materials like plasmonic metal
37 nanoparticles (approximately 300–1000 nm) and metal oxide semiconductors (approximately
38 300–1500 nm),¹⁶ which is beneficial for absorbing solar light in the wavelength range of 300–

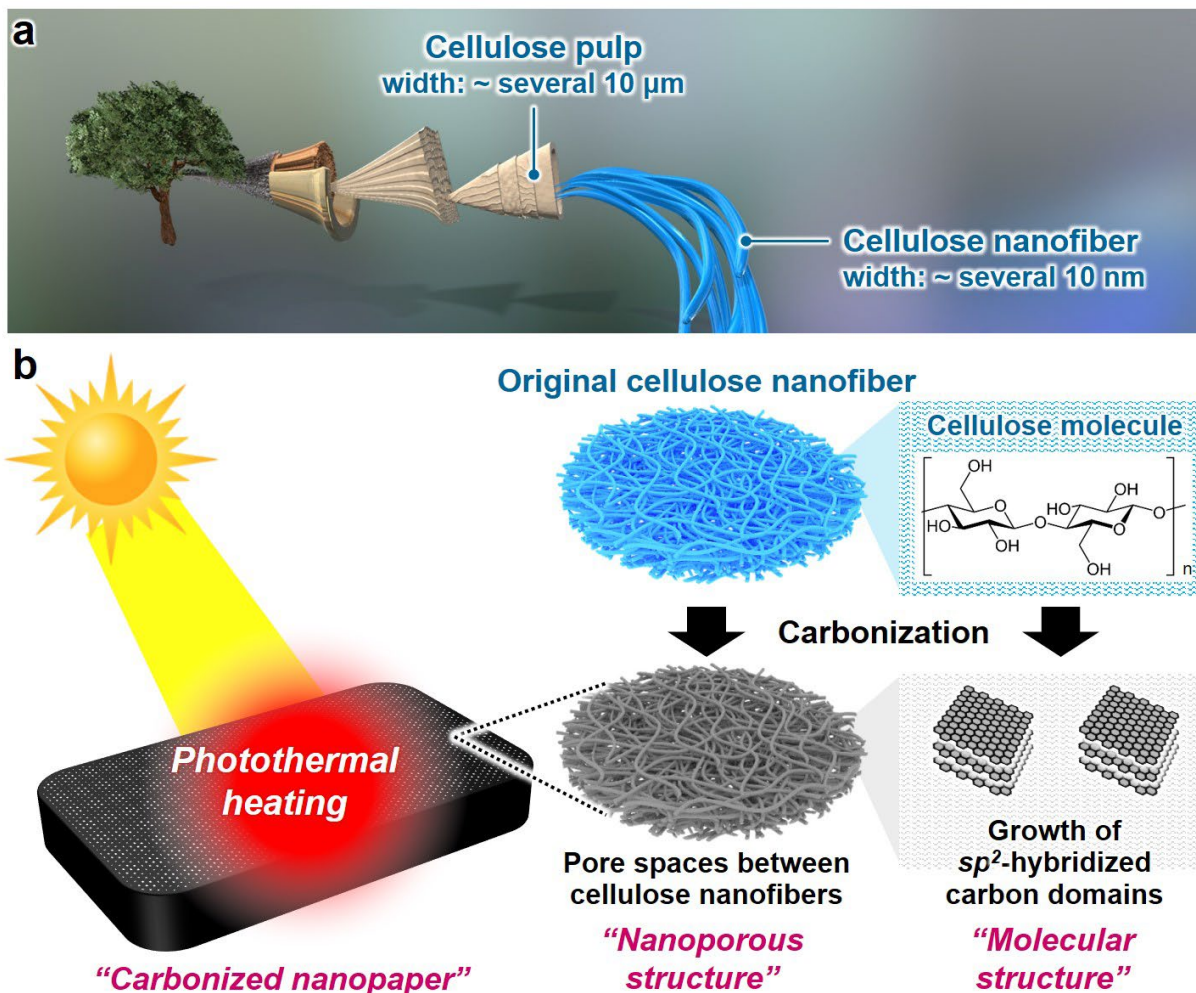
39 2500 nm (The American Society for Testing and Materials (ASTM) G173-03, Air Mass 1.5
40 Global spectrum (AM1.5G))¹⁷.

41 To use solar light energy more efficiently, photothermal materials must be structurally
42 and functionally designed to improve their solar thermal heating performances.¹⁶ For example,
43 subwavelength nanoporous structures have been extensively tailored for application as plasmonic
44 metal nanoparticles and metal oxide semiconductors to enhance light absorption by suppressing
45 light reflection to the outer surface, which is known as “light confinement.”¹⁸ For carbon-based
46 photothermal materials, their sp^2 -hybridized carbon-based molecular structures, such as the
47 distribution of the highest occupied molecular orbital (HOMO) and the lowest unoccupied
48 molecular orbital (LUMO), must also be designed because they not only affect the light-
49 absorption wavelength range but also convert absorbed light into heat via vibrational
50 relaxation.¹⁹ Therefore, tailoring both the subwavelength nanoporous and molecular structures of
51 biomass-derived carbon materials would be a rational strategy to optimize solar thermal heating.

52 Recently, various biomass-derived carbon materials, such as carbonized wood,¹⁰ cotton,¹¹
53 mushroom,¹² sugarcane,¹³ daikon,¹⁴ and agave flower stalk,¹⁵ have been reported for solar
54 thermal applications. Because these natural biomass materials inherently exhibit microstructures,
55 their carbonized derivatives also intrinsically exhibit them, thereby hindering the design of
56 subwavelength nanoporous structures. These biomass materials are carbonized to form sp^2 -
57 hybridized carbon-based molecular structures, thereby decreasing the HOMO-LUMO bandgap
58 (such as the $\pi-\pi^*$ energy gap) and thus absorbing light over a broad wavelength range. In
59 previous studies, however, these molecular structures have not been tailored to optimize solar
60 light absorption yet because the materials are frequently carbonized under specific conditions. In
61 other words, the impact of carbonization conditions on the solar light absorption of the

62 carbonized biomass materials has been insufficiently investigated. Thus, the design of biomass-
63 derived carbon materials exhibiting nanoporous and molecular structures desirable for solar
64 thermal heating applications has proven difficult.

65 Herein, a cellulose nanofiber-derived carbon material exhibiting tailored nanoporous and
66 molecular structures is proposed for effective solar thermal heating. Cellulose nanofiber, which
67 is mainly extracted from wood cell walls, has attracted significant attention as a fascinating
68 biomass nanomaterial because of its excellent physical properties, nanostructures, abundance,
69 and sustainability.²⁰⁻²² At present, cellulose nanofibers can be produced in a large-scale industrial
70 operation, and its market is estimated to reach USD 963 million by 2026.²³ Cellulose nanofibers
71 can be used as a building block to fabricate nanostructures because of its nanofiber morphology.
72 Moreover, because the cellulose sp^3 -hybridized carbon structure contains high oxygen and
73 hydrogen contents,²⁴ carbonization can be used to tune cellulose nanofiber molecular structures
74 over a wide range.²⁵ Carbonized cellulose nanofiber materials have been reported for adsorption
75 and electronic applications.²⁵⁻²⁸ To our best knowledge, however, the tailoring nanoporous and
76 molecular structures of carbonized cellulose nanofiber materials for their application in solar
77 thermal heating has been unexplored. In this study, cellulose nanofibers are fabricated into a
78 paper (hereafter denoted as “nanopaper”), exhibiting nanoporous structures by tailoring the pore
79 spaces between cellulose nanofibers and is subsequently carbonized at controlled temperatures to
80 gradually grow sp^2 -hybridized carbon domains (**Figure 1**). The carbonized nanopaper, fabricated
81 with the as-tailored nanoporous and molecular structures, exhibits excellent solar thermal heating
82 performance, which is superior even to the competitive nanocarbon materials such as carbon
83 nanotube (CNT) and graphene films.



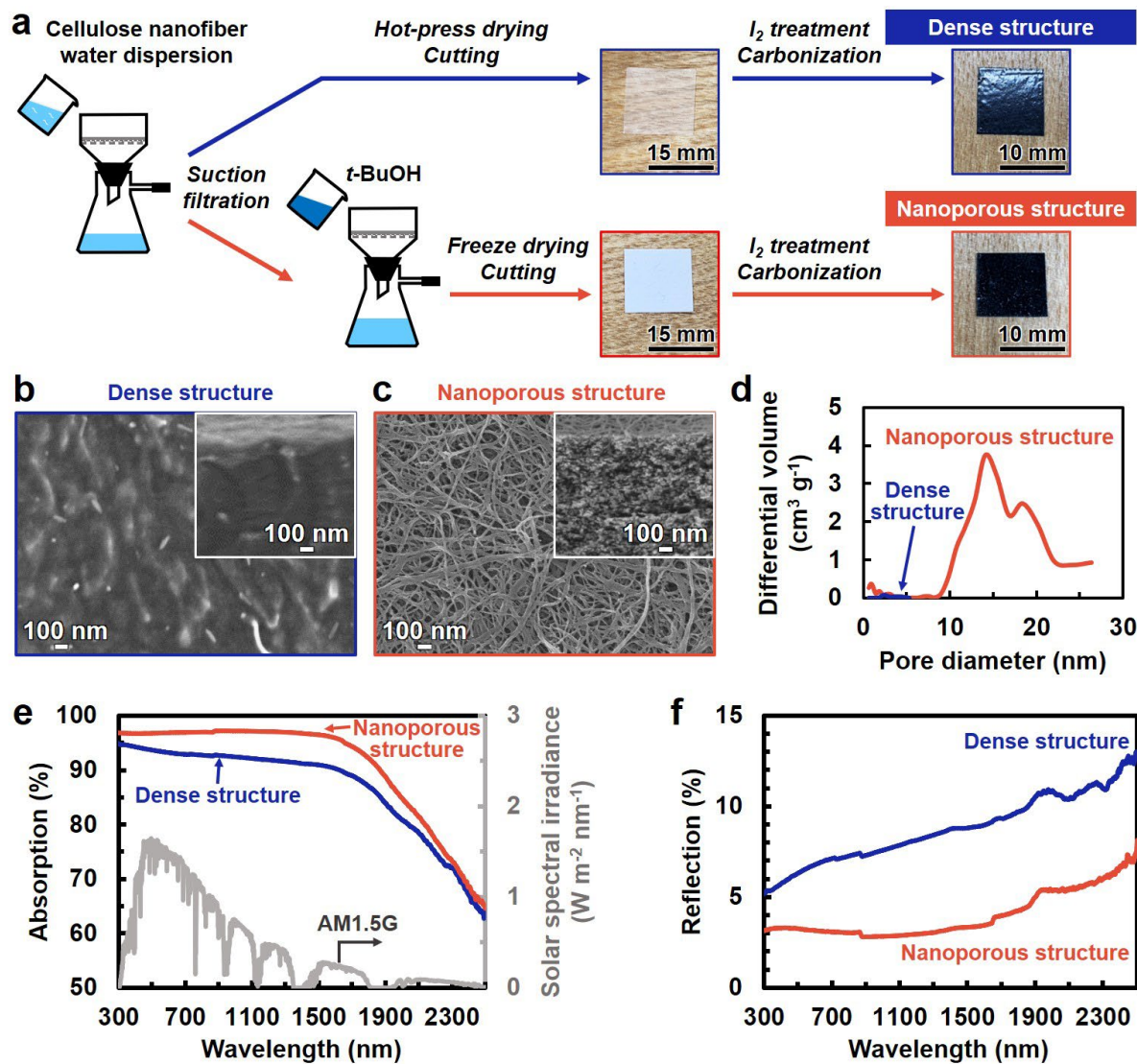
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85 **Figure 1.** Schematic illustrating the design strategy used in this study. (a) Hierarchical structure
86 from wood to cellulose pulp and cellulose nanofiber, and (b) photothermal heating by irradiating
87 carbonized cellulose nanofiber paper (*i.e.*, nanopaper) exhibiting tailored nanoporous and
88 molecular structures.

89 RESULTS AND DISCUSSION

90 **Tailoring carbonized nanopaper nanoporous structures for application to solar thermal**
91 **heating**

92 To elucidate the nanostructure impact on the light absorption and solar thermal heating
93 performances, the carbonized nanopaper nanoporous structures were first tailored based on the
94 workflow shown in **Figure 2a**. Cellulose nanofibers (width = 22 ± 8 nm) were prepared from
95 never-dried softwood bleached kraft pulp by aqueous counter collision.²⁵ Subsequently, an
96 aqueous cellulose nanofiber dispersion was dewatered, dried by hot pressing, treated with iodine
97 (I_2), and then carbonized at 500 °C to produce an approximately 55- μ m-thick carbonized
98 nanopaper exhibiting dense structures (**Figures 2b and d**) because the cellulose nanofibers had
99 aggregated during hot-press drying to evaporate high-surface-tension water (72.14 mN m^{-1} at
100 25 °C).²⁹ To suppress cellulose nanofiber aggregation, the water was exchanged for low-surface-
101 tension (19.96 mN m^{-1} at 25 °C)²⁹ *tert*-butyl alcohol (*t*-BuOH) prior to freeze drying, the I_2
102 treatment, and then carbonizing the nanopaper. The as-prepared approximately 180- μ m-thick
103 carbonized nanopaper exhibited 3D nanoporous structures, which had been derived from the
104 pore spaces between the layered cellulose nanofibers (**Figure 2c**). The nitrogen adsorption
105 analysis using the Brunauer-Emmett-Teller (BET) theory and the Density Functional Theory
106 (DFT) method indicated that the carbonized nanopaper exhibiting nanoporous structures contains
107 mesopores (**Figure 2d**), while field-emission scanning electron microscopy (FE-SEM) images
108 suggested that it also contains macropores smaller than approximately 100 nm (**Figure 2c**). The
109 I_2 pretreatment was performed to maintain the nanoporous structures of the nanopaper after
110 carbonization, because the simple carbonization of the nanopaper deteriorates the morphology of
111 cellulose nanofibers.²⁵ Although high-temperature treatment of cellulose removes carbon and
112 hydrogen as a hydrocarbon gas and weakens its carbon frameworks, the I_2 pretreatment could
113 overcome this problem; carbon removal during the high-temperature treatment was successfully
114 suppressed by the I_2 treatment,²⁵ possibly owing to the preferential formation of HI.³⁰



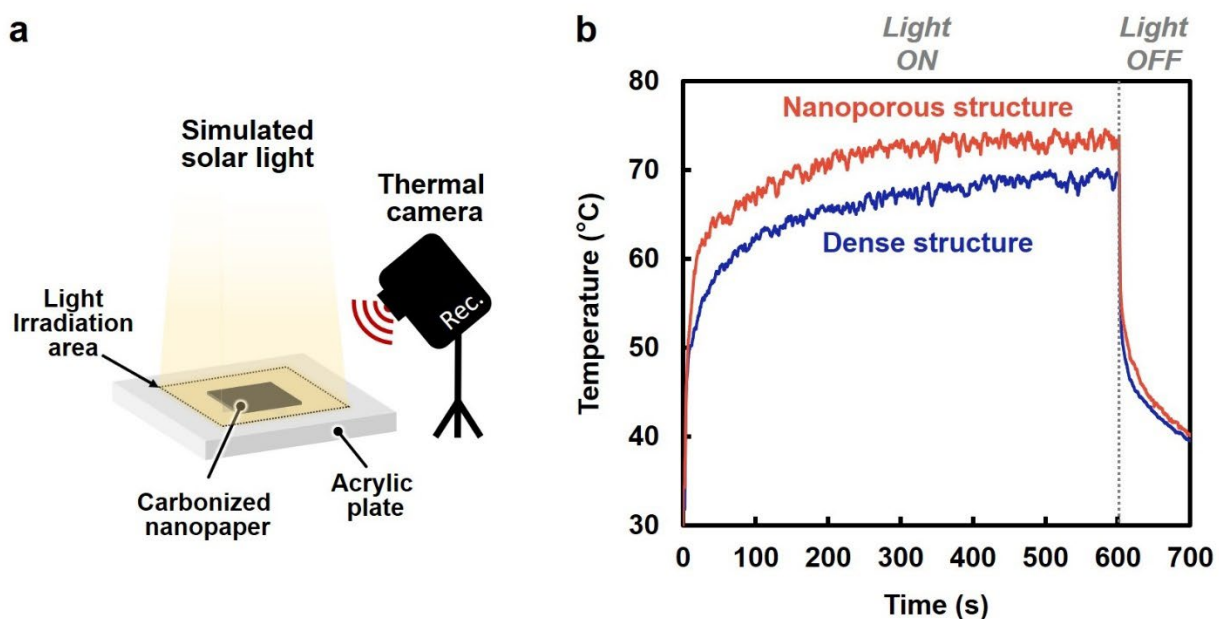
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116 **Figure 2.** Preparation, porous structures, and light absorption properties of nanopapers
 117 carbonized at 500 °C. (a) Preparation schematic and optical images, (b, c) cross-section (inset)
 118 and surface field-emission scanning electron microscopy (FE-SEM) images, respectively, (d)
 119 pore size distribution of carbonized nanopaper exhibiting dense or nanoporous structures, (e)
 120 solar spectral irradiance (AM1.5G) and ultraviolet-visible-near infrared (UV-vis-NIR)
 121 absorption, and (f) reflection of carbonized nanopaper exhibiting dense or nanoporous structures.

122 The carbonized nanopaper exhibiting the nanoporous structures showed greater light
123 absorption (up to 97.2%) than that exhibiting the dense structures in the entire examined
124 wavelength range (300–2500 nm), indicating that the nanoporous structures are beneficial for
125 absorbing solar light (**Figure 2e**). As shown in **Figures 2a and f**, the dense structures gave the
126 nanopaper a glossy appearance because of light reflecting off the structure surfaces. The
127 nanoporous structures, on the other hand, gave the nanopaper a dark appearance by suppressing
128 the light reflection (**Figures 2a and f**), albeit some light was transmitted at wavelengths above
129 1500 nm. Raman, X-ray diffraction (XRD), and Fourier-transform infrared (FT-IR) analyses
130 suggested that the difference between the nanopaper molecular structures was negligible,
131 regardless of whether the nanopaper exhibited dense or nanoporous structures (**Figure S1**). This
132 result was possibly because the nanopapers had been carbonized at the same temperature. Thus,
133 the nanoporous structures enhanced the carbonized nanopaper light absorption by suppressing
134 the light reflection. These results indicated that the tailored carbonized nanopaper subwavelength
135 nanoporous structures deserved the light confinement effect,³¹ wherein the incident light is
136 effectively captured owing to multiple light reflections and scattering in the nanopaper matrix.

137 Subsequently, the solar thermal heating performances of the carbonized nanopaper were
138 evaluated under simulated solar light irradiation [AM1.5G, light intensity: 1.0 kW m^{-2} (1 sun)].
139 The change in surface temperature of the carbonized nanopaper irradiated under 1 sun was
140 measured using a thermal camera (**Figure 3a**). The carbonized nanopaper temperature
141 immediately increased upon 1 sun irradiation and saturated within 600 s (**Figure 3b**). Then, the
142 equilibrium surface temperature of the carbonized nanopaper exhibiting the nanoporous
143 structures reached $73.9 \pm 0.80 \text{ }^\circ\text{C}$, which was higher than that of the carbonized nanopaper
144 exhibiting the dense structures ($69.2 \pm 0.65 \text{ }^\circ\text{C}$). These results indicated that the nanoporous

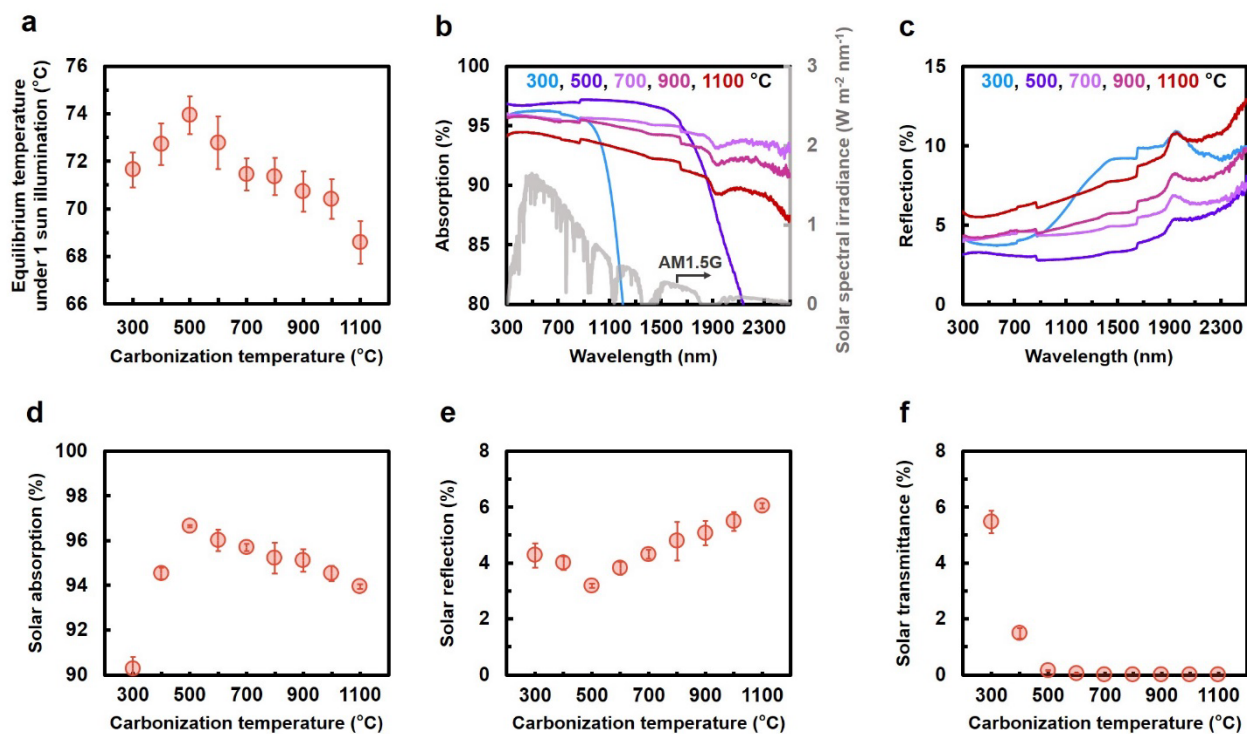
145 structures gave the nanopaper superior solar thermal heating compared to the dense structures.
146 Notably, the carbonized nanopaper exhibiting the tailored nanoporous structures also afforded
147 higher light absorption and solar thermal heating performances than the carbonized cellulose
148 pulp paper exhibiting porous microstructure derived from pulp-fiber-network-derived microscale
149 pores (equilibrium surface temperature: 68.2 ± 0.96 °C) (**Figure S2**). Thus, designing
150 subwavelength nanoporous structures in the carbonized nanopaper resulted in effective solar
151 thermal heating by enhancing the solar absorption.



152
153 **Figure 3.** Photothermal heating performances of nanopapers (approximately 1 cm × 1 cm)
154 carbonized at 500 °C and exhibiting different porous structures. (a) Schematic illustration of
155 experimental setup used to measure surface temperature during simulated solar light irradiation,
156 and (b) surface temperature evolutions measured under 1 sun irradiation for carbonized
157 nanopapers exhibiting dense or nanoporous structures.

158 **Solar thermal heating performances of nanopapers carbonized at different temperatures**

159 Because the original nanopaper exhibiting nanoporous structures showed poor solar
160 absorption and solar thermal heating (*e.g.*, the equilibrium surface temperature was only 37.9 °C
161 for the nanopaper irradiated under 1 sun) (**Figure S3**), not only designing the subwavelength
162 nanoporous structures but also carbonizing the nanopaper are the key to optimizing solar thermal
163 heating. To elucidate the relationship between the nanopaper carbonization degree and the solar
164 thermal heating performances, the nanopaper exhibiting nanoporous structures was carbonized in
165 the temperature range of 300–1100 °C. The weight retention of the nanopaper was decreased
166 from approximately 39.4 to 20.4% with increasing carbonization temperatures from 300 to
167 1100 °C, respectively (**Figure S4**). Then, the photothermal heating properties of the carbonized
168 nanopapers were evaluated. As shown in **Figure 4a**, the photothermal heating performance of
169 the carbonized nanopaper (1 cm × 1 cm, thickness = 160–200 μm) was dependent on
170 carbonization temperature. Although the equilibrium surface temperature measured under 1 sun
171 irradiation increased from 71.6 to 73.9 °C upon increasing carbonization temperature from 300
172 to 500 °C, respectively, it gradually decreased from 73.9 to 68.6 °C upon increasing
173 carbonization temperature from 500 to 1100 °C, respectively. Thus, the nanopaper carbonized at
174 500 °C exhibited the best photothermal heating. According to the statistical analysis, the
175 equilibrium surface temperature under 1 sun irradiation of the nanopaper carbonized at 500 °C
176 was significantly different from those of the nanopapers carbonized at 300, 400, 600–1100 °C
177 (*p*-value: ≤ 0.028).



178

179 **Figure 4.** Photothermal heating and light absorption of nanopaper exhibiting nanoporous
 180 structures carbonized at different temperatures. (a) Equilibrium surface temperature; (b) solar
 181 spectral irradiance (AM1.5G) and UV-vis-NIR absorption; (c) reflection spectra; solar light (d)
 182 absorption, (e) reflection, and (f) transmittance of nanopapers carbonized at different
 183 temperatures.

184 To elucidate why the nanopaper carbonized at 500 °C exhibited the best photothermal
 185 heating, the light absorption of the nanopapers carbonized at different temperatures were
 186 compared (**Figure 4b**). With increasing carbonization temperature, the light absorption range of
 187 the carbonized nanopaper extended toward the long-wavelength region. For instance, the
 188 nanopapers carbonized above 700 °C exhibited over 90% light absorption across a broad
 189 wavelength range. However, the nanopaper carbonized at 500 °C exhibited the highest light
 190 absorption (up to 97.2%) in the wavelength range 300–1700 nm, which accounts for most solar

191 light energy. **Figure 4c** shows the light reflection of the nanopapers carbonized at different
192 temperatures. The nanopaper carbonized at 300 °C exhibited relatively strong light reflection in
193 the long-wavelength region (>1300 nm), where it also exhibited low light absorption. Notably,
194 the nanopaper carbonized at 500 °C exhibited the lowest light reflection in the entire examined
195 wavelength range (300–2500 nm), while the nanopapers carbonized above 500 °C exhibited
196 increased light reflection.

197 To compare the solar absorptions of the nanopapers carbonized at different temperatures
198 more clearly, the solar absorption was calculated according the following equation:³²

$$199 \quad \bar{\alpha} = \frac{\int_{\lambda_{min}}^{\lambda_{max}} I_{solar}(\lambda) \cdot \alpha_{solar}(\lambda) d\lambda}{\int_{\lambda_{min}}^{\lambda_{max}} I_{solar}(\lambda) d\lambda}, \quad (1)$$

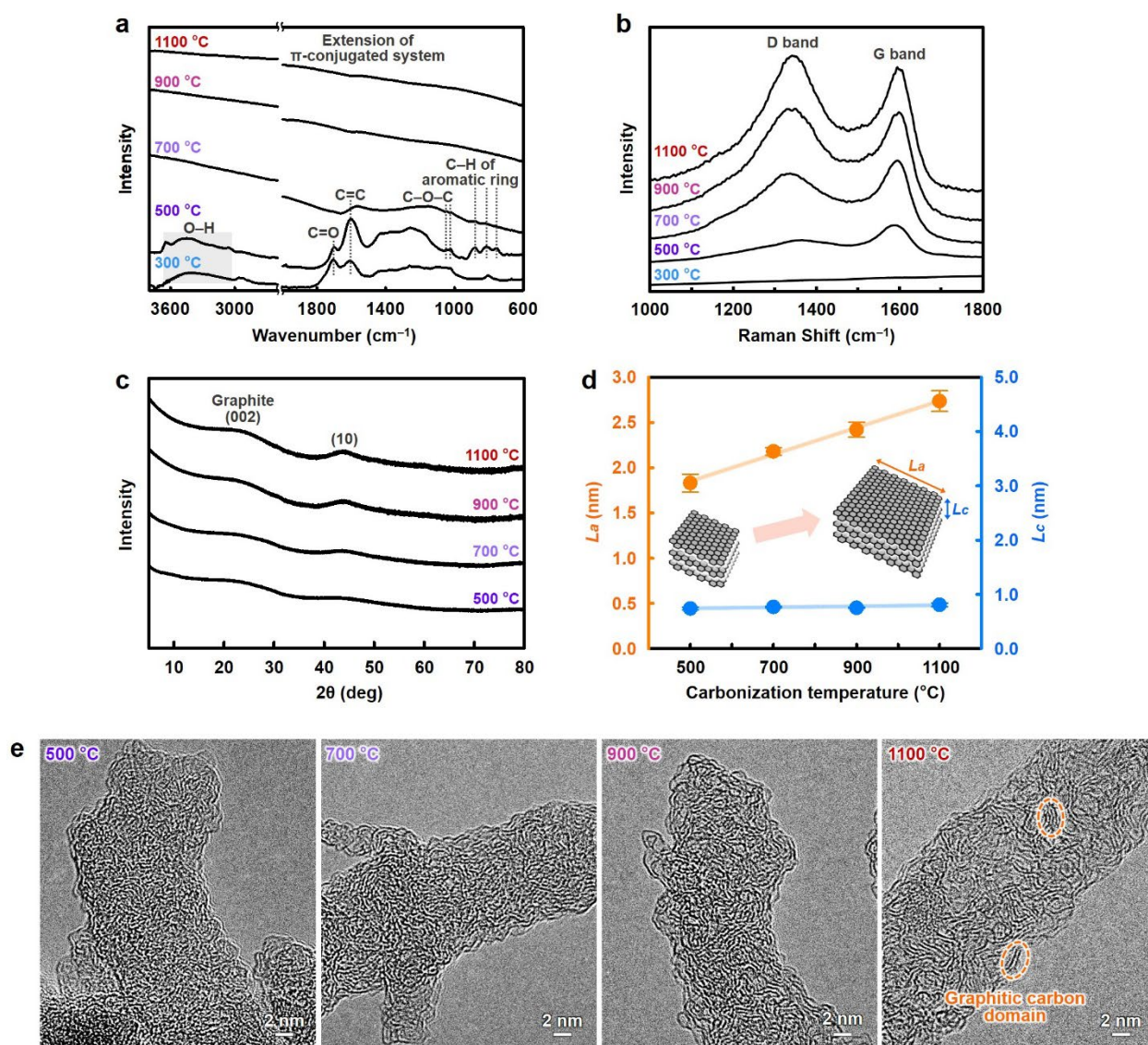
200 where $\bar{\alpha}$ is the solar absorption (%), λ is the wavelength (nm), λ_{min} and λ_{max} are 300 and 2500 nm,
201 respectively, $I_{solar}(\lambda)$ is the AM1.5G solar spectral irradiance at λ , and $\alpha_{solar}(\lambda)$ is the light
202 absorption (%) at λ . Additionally, the solar reflection and transmittance were similarly
203 calculated. **Figures 4d–f** show the as-calculated solar absorption, reflectance, and transmittance
204 of the nanopapers carbonized at different temperatures. The nanopaper carbonized at 500 °C
205 exhibited the highest solar absorption (96.7%) because it also exhibited the lowest solar
206 reflectance (3.14%) and only a slight solar transmittance (0.16%). According to the statistical
207 analysis, the solar absorption of the nanopaper carbonized at 500 °C was significantly different
208 from those of the nanopapers carbonized at 300, 400, 600–1100 °C (p-value: ≤ 0.038). The solar
209 absorption of nanopaper carbonized at 500 °C (96.7%) was superior to those of various
210 carbonized biomass materials, such as carbonized mushroom (96%)¹², carbonized corncob
211 (95.7%)³³, and arched bamboo charcoal (94.1%)³⁴. Regardless of the carbonization temperature,
212 the carbonized nanopapers exhibited almost no photoluminescence, indicating that most of the

213 solar light absorbed by the carbonized nanopaper had been converted to heat (**Figure S5**). These
214 results suggested that the nanopaper carbonized at 500 °C exhibited the best photothermal
215 heating (*i.e.*, the equilibrium surface temperature was 73.9 °C for the nanopaper irradiated under
216 1 sun; **Figure 4a**) because it exhibited excellent solar absorption by suppressing solar reflection.
217 The high surface temperature of the nanopaper carbonized at 500 °C and then irradiated under 1
218 sun was also attributed to the relatively low through-plane thermal conductivity (0.07 W m^{-1}
219 K^{-1}) (see **Figure S6** for more details). Thus, the nanopaper carbonized at 500 °C exhibited
220 excellent solar thermal heating and was also applied to solar-driven thermoelectric power
221 generation (**Figure S7**).

222 **Impact of carbonized nanopaper molecular structures on solar thermal heating**

223 Because the carbonized nanopaper nanoporous structures changed negligibly with the
224 carbonization temperature (**Figure S8**), the carbonization-temperature-dependent solar
225 absorption and thermal heating properties of the carbonized nanopaper were attributed to the
226 different cellulose nanofiber molecular structures formed at different carbonization temperatures.
227 To elucidate this point, during carbonization, the carbonized cellulose nanofiber molecular
228 structures were analyzed using FT-IR spectroscopy, Raman spectroscopy, XRD analysis, and
229 high-resolution transmission electron microscopy (HR-TEM). Although the original cellulose
230 molecule consists of sp^3 -hybridized carbon structures, the FT-IR spectra indicated that sp^2 -
231 hybridized carbon (C=C) and oxygen-containing functional groups such as C=O, C–O–C, and
232 C–OH had formed in the samples carbonized up to 500 °C (**Figure 5a**). The C=O, C–O–C, and
233 C–OH peaks weakened with increasing carbonization temperature. The C=C peak disappeared
234 from the spectra for the samples carbonized at or above 900 °C, suggesting that the π -conjugated
235 system had been extended because the sp^2 -hybridized carbon domains had grown.³⁵ A G band

236 appeared in the Raman spectra of the samples carbonized at or above 500 °C, indicating that sp^2 -
 237 hybridized graphitic carbon domains had formed (**Figure 5b**).³⁶ A D band also appeared,
 238 suggesting that the disordered graphitic carbon structures (*e.g.*, at the edge of the graphitic
 239 domains and in-plane imperfections)³⁶ remained even in the sample carbonized at 1100 °C.



240
 241 **Figure 5.** Molecular structural evolution of cellulose nanofibers during carbonization. (a) FT-IR,
 242 (b) Raman, and (c) XRD spectra; (d) graphitic carbon fragment crystallite sizes in in-plane (L_a)

243 and stacking (L_c) directions; and (e) HR-TEM images of cellulose nanofiber carbonized at
244 different temperatures.

245 XRD was used to further analyze the sp^2 -hybridized graphitic carbon domain growth
246 during carbonization. As shown in **Figure 5c**, two broad peaks associated with the crystalline
247 reflections (002) and the two-dimensional reflections (10) of graphite appeared at approximately
248 22° and 44° , corresponding to interplanar distances (d_c and d_a) of ~ 0.4 and ~ 0.2 nm,
249 respectively³⁷. These peaks intensified with increasing carbonization temperature. The graphite
250 crystallite sizes in the stacking and in-plane directions (L_c and L_a , respectively) were estimated
251 using these peaks and Scherrer's formula (**Figure 5d**).³⁷ Although L_c remained constant at ~ 1.0
252 nm, L_a gradually increased from ~ 1.8 to 2.7 nm upon increasing carbonization temperature from
253 500 to 1100 $^\circ\text{C}$, suggesting that the graphitic carbon domains gradually grew in the in-plane
254 rather than the stacking direction. These trends were consistently observed in the corresponding
255 HR-TEM images (**Figure 5e**). Notably, numerous randomly oriented graphitic carbon domains
256 exhibiting layer structures with the width and thickness of a few nanometers more prominently
257 appeared at higher carbonization temperatures, which confirmed that graphitic carbon domains
258 had progressively grown in the carbonized cellulose nanofiber with increasing carbonization
259 temperature.

260 Such progressive graphitic carbon domain growth governed the carbonization-
261 temperature-dependent solar absorption and thermal heating of the nanopaper as follows. The
262 original nanopaper exhibited poor solar absorption (**Figure S3**) owing to the wide $\sigma-\sigma^*$ energy
263 gap of the sp^3 -hybridized carbons in the cellulose molecule. The nanopaper carbonized at 300 $^\circ\text{C}$
264 exhibited sp^2 -hybridized carbon domains (*i.e.*, π -orbitals), wherein the $\pi-\pi^*$ energy gap is within

265 the σ - σ^* one³⁸ and promotes light absorption at lower energies (*i.e.*, longer wavelengths) than
266 the original nanopaper. In the nanopapers carbonized at temperatures of 500 °C or above, the
267 light-absorption wavelength range can be further extended to longer wavelengths by growing
268 graphitic sp^2 -hybridized carbon domains (**Figure 4b**) because the π - π^* energy gap decreases
269 with the growth of these domains³⁸. However, excess sp^2 -hybridized graphitic carbon domain
270 growth increases light reflection across a broad wavelength range (**Figure 4c**). Such light
271 reflection would be associated with graphitic-carbon-domain-induced metallic luster, as
272 previously reported for graphite films,³⁹ graphene nanosheets,⁴⁰ and graphene papers.⁴¹ To
273 effectively absorb solar irradiation, therefore, the graphitic carbon domain growth should be
274 tailored to extend the light-absorption wavelength range while suppressing the light reflection. In
275 this study, the nanopaper carbonized at 500 °C exhibited this optimal balance; the graphitic
276 carbon domains therein exhibited an L_c and L_a of ~ 0.74 and 1.83 nm, respectively (**Figure 5d**).
277 Such semicarbonized cellulose molecular structures provided the highest solar absorption
278 (96.7%) and the lowest solar reflectance (3.14%) (**Figures 4d** and **e**, respectively); therefore, the
279 nanopaper carbonized at 500 °C exhibited the best solar thermal heating (**Figure 4a**).
280 Furthermore, the low through-plane thermal conductivity of the semicarbonized nanopaper (0.07
281 $\text{W m}^{-1} \text{K}^{-1}$) (**Figure S6**) can be beneficial for localized heating⁴², providing a higher surface
282 temperature for the nanopaper irradiated under 1 sun than even state-of-the-art nanocarbon
283 materials, such as a carbon nanotube black body, graphene paper, and graphene oxide film
284 (**Table 1**). Such higher surface temperature can contribute to the effective use of renewable solar
285 energy such as solar-driven thermoelectric power generation. For example, Komatsu et al. has
286 recently reported the macroscopic weavable fibers of carbon nanotubes with giant thermoelectric
287 power factor ($14 \text{ mW m}^{-1} \text{K}^{-2}$)⁴³, indicating that even a 1 K temperature difference can produce

288 mW levels of energy. Thus, the excellent solar thermal heating performance of the
289 semicarbonized nanopaper exhibiting nanoporous structures can be significant toward the
290 effective use of renewable solar energy.

291 **Table 1.** Photothermal heating performances of nanopaper semicarbonized at 500 °C and various
292 conventional carbon materials irradiated under 1 sun.

Carbon material	Surface temperature (°C)
CNT [†] black body	55.0 ± 0.28
Graphite sheet	64.5 ± 1.98
Graphene paper	65.2 ± 1.46
Graphene oxide film	69.4 ± 1.53
Semicarbonized nanopaper exhibiting nanoporous structures	73.9 ± 0.80

293 [†]CNT, carbon nanotube.

294

295 CONCLUSION

296 In summary, a semicarbonized cellulose nanofiber paper was tailored with
297 subwavelength nanoporous structures and adequately grown graphitic carbon domains for
298 application to solar thermal heating. The tailored subwavelength nanoporous structures enhanced

299 the solar absorption by suppressing the light reflection. The graphitic carbon domains grown by
300 semicarbonization at 500 °C balanced the tradeoff between extending the light-absorption
301 wavelength range and suppressing the light reflection. Thus, the semicarbonized subwavelength-
302 nanopore-structured nanopaper exhibited high solar absorption, and therefore, effective solar
303 thermal heating, which enabled the nanopaper to be applied to thermoelectric power generation.
304 While a further challenge remains to make the tailoring process of the nanoporous structures
305 greener, the study findings can provide a guideline for structurally designing biomass-derived
306 carbon materials for application to solar absorption and thermal heating. Furthermore, the
307 concept for tailoring the carbonized cellulose nanofiber nanoporous and molecular structures can
308 be applied to various carbonized bionanomaterials, opening a pathway to develop structurally
309 and functionally designable carbonized bionanomaterials for diverse applications.

310 EXPERIMENTAL SECTION

311 **Materials**

312 According to the method detailed in our previous report,²⁵ never-dried softwood bleached
313 kraft pulp and a high-pressure water-jet system equipped with a counter-collision chamber (Star
314 Burst, HJP-25005E, Sugino Machine Co., Ltd., Uozu, Japan) were used to prepare a cellulose
315 nanofiber/water dispersion. Briefly, the pulp suspension was ejected from a \varnothing 0.12-mm nozzle at
316 245 MPa for 100 passes. Iodine (>99.8% purity) and *tert*-butyl alcohol (*t*-BuOH, >99.0% purity)
317 were purchased from Nacalai Tesque, Inc., Kyoto, Japan. A CNT black body was obtained from
318 MICROPHASE Co., Ltd., Tsukuba, Japan. A graphite sheet (EYGS121810) was purchased from
319 Panasonic Corp., Osaka, Japan. A graphene paper (900451-1EA) and a graphene oxide film
320 (798991-1EA) were obtained from Merck KGaA, Darmstadt, Germany.

321 **Nanopaper preparation and carbonization**

322 The nanopaper was prepared and carbonized according to the method detailed in our
323 previous report.²⁵ Briefly, a cellulose nanofiber/water dispersion (0.2 wt.%, 200 mL) was suction
324 filtered through a hydrophilic polytetrafluoroethylene (PTFE) filter (H020A090C, pore diameter
325 of 0.2 μm , Toyo Roshi Kaisha, Ltd., Tokyo, Japan), rinsed with *t*-BuOH (200 mL), and suction
326 filtered again. The wet sheet was peeled off the PTFE filter, immersed in liquid nitrogen for 1
327 min, and freeze-dried (EYELA, FDU-2200, Tokyo Rikakikai Co., Ltd., Tokyo, Japan) overnight
328 to prepare a nanopaper exhibiting a nanoporous structure. A nanopaper exhibiting a dense
329 structure was prepared without using any *t*-BuOH by hot pressing at 110 °C and 1.1 MPa for 30
330 min (AYSR-5, Shinto Metal Industries, Ltd., Osaka, Japan). Porous-microstructured cellulose
331 pulp paper was similarly prepared using *t*-BuOH by hot pressing. Prior to carbonization, the
332 nanopaper and pulp paper were treated with I₂ gas (the same weight as the paper) at 100 °C for
333 24 h in a sealed flask to retain the original morphology during carbonization.²⁵ The I₂-treated
334 papers were then carbonized in a furnace (KDF-75, DENKEN-HIGHDENTAL Co., Ltd., Kyoto,
335 Japan) in three stages under nitrogen flowing at 500 mL min⁻¹, while removing the generated
336 corrosive HI gas in the furnace. First, the temperature was increased at 2 °C min⁻¹ from room
337 temperature to 240 °C and was maintained there for 17 h. This treatment is also effective to
338 avoid destruction of the original fibrous morphology during carbonization.⁴⁴ Then, the
339 temperature was increased at 2 °C min⁻¹ to peak carbonization temperatures in the range 300–
340 1100 °C and was maintained there for 1 h. Finally, the nanopaper was cooled at 2 °C min⁻¹ to
341 room temperature. Regardless of the peak carbonization temperature, the dimensions of the
342 carbonized papers were set at approximately 1 cm × 1 cm by adjusting the original paper size.

343 **Nanopaper thermal heating performance evaluated under solar light irradiation**

344 The solar thermal heating performances of the carbonized nanopaper were evaluated by
345 measuring the nanopaper surface temperatures under solar light irradiation, according to a
346 method detailed in our previous report.⁴⁵ Prior to the temperature measurements, the emissivity
347 of each nanopaper was evaluated using black body tape exhibiting an emissivity of 0.95 (HB-
348 250, OPTEX Co., Ltd., Shiga, Japan) as a reference. The nanopaper and black tape were heated
349 using a temperature controller (SBX-303, Sakaguchi E.H. VOC Corp., Tokyo, Japan) to 75 °C.
350 The nanopaper emissivity was estimated by adjusting the nanopaper temperature measured using
351 an infrared thermal camera (FLIR ETS320, FLIR Systems, Inc., Wilsonville, USA) according to
352 the black tape reference temperature. For the surface temperature measurements, a solar
353 simulator (AM1.5G, HAL-320W, Asahi Spectra Co., Ltd., Tokyo, Japan) was used as the light
354 source. The samples (1 cm × 1 cm) were put on an acrylic plate (3 cm × 3 cm) exhibiting a
355 central hole (0.7 cm × 0.7 cm), and the surface temperature changes of the samples illuminated
356 using the solar simulator (light intensity: 1 sun) were recorded using the infrared thermal camera
357 according to the nanopaper-calibrated emissivity. The equilibrium surface temperature of the
358 samples was calculated as the average surface temperature during 1 sun-irradiation time of 500–
359 600 s (approximately 850 plots). For data reproducibility and statistical analyses, more than 6
360 samples were prepared for each condition; a p value less than 0.05 was considered statistically
361 significant. The solar thermal heating performance was measured at 25 °C and 65% relative
362 humidity. The CNT black body, graphite sheet, graphene paper, and graphene oxide film solar
363 thermal heating performances were similarly evaluated for comparison.

364 **Nanopaper application to solar-driven thermoelectric power generation**

365 The nanopaper (3.5 cm × 3.5 cm) carbonized at 500 °C was attached to a commercial
366 thermoelectric power generator (4.0 cm × 4.0 cm, 66900, Artec Co., Ltd., Osaka, Japan) using a

367 heat-dissipation adhesive (COM-G52, COM Institute, Inc., Osaka, Japan) to fabricate a
368 thermoelectric power generation module, three of which were integrated into one solar-driven
369 thermoelectric power generation device. A propeller motor (P70-3935, working voltage and
370 current ranges of 0.4–1.5 V and 16–20 mA, respectively, Narika Corp., Tokyo, Japan) was used
371 to generate electrical energy. On a sunny day (October 21, 2020; 24.5 °C, 34°49'30" N,
372 135°31'28" E), natural sunlight was irradiated on one side of the nanopaper carbonized at 500 °C
373 while the other side was cooled using an ice pack.

374 **Characterization**

375 The nanopaper surface morphology was observed using FE-SEM (SU-8020, Hitachi
376 High-Tech Science Corp., Tokyo, Japan) at an accelerate voltage of 2 kV to avoid damage to the
377 nanofibers. The pore size distribution was evaluated at 77 K based on nitrogen adsorption
378 analysis using the BET theory and the DFT method (NOVA 4200e, Quantachrome Instruments,
379 Kanagawa, Japan). The light transmittance, reflectance, and absorption were measured using
380 UV–vis–NIR spectroscopy (UV-3600i Plus, Shimadzu Corporation, Kyoto, Japan) with an
381 integrating sphere attachment (ISR-603, Shimadzu Corp., Kyoto, Japan). Absorption spectra
382 were calculated from total transmittance and total reflectance spectra. For data reproducibility
383 and statistical analyses, more than 6 samples were prepared for each condition; a p value less
384 than 0.05 was considered statistically significant. The FT-IR (KJP-05120S, PerkinElmer Japan
385 Co., Ltd., Kanagawa, Japan) spectra were recorded in attenuated total reflection (ATR) mode.
386 The Raman spectra were recorded using a RAMAN-touch apparatus (Nanophoton Corp., Osaka,
387 Japan) and a 532-nm incident laser. To analyze the carbon fragment crystal structures, the XRD
388 (Ultima IV, Rigaku Corporation, Tokyo, Japan) spectra were recorded using Ni-filtered Cu-K α
389 radiation (1.5418 Å), and the nanopapers were scanned in the range $2\theta = 5\text{--}80^\circ$ at 30-kV

390 acceleration and 40 mA. The graphitic carbon fragment crystallite sizes in the stacking (L_c) and
391 in-plane (L_a) directions were estimated using the XRD spectra and the Scherrer formula $L =$
392 $k\lambda/\beta\cos\theta$, where λ , β , and θ are the X-ray wavelength, full width at half maximum, and Bragg
393 angle, respectively. L_c and L_a were estimated using the crystalline reflections (002) and the two-
394 dimensional reflections (10) with $k = 0.89$ and 1.84 , respectively, according to the method
395 described in a previous report.³⁷ HR-TEM (JEM-ARM 200F, JEOL Ltd., Tokyo, Japan)
396 observation was operated at 200 kV. The photoluminescence spectra were recorded using a
397 Quantaaurus-QY instrument (C11347-01, HAMAMATSU PHOTONICS K. K., Shizuoka, Japan).
398 The nanopaper thermal conductivity was calculated based on the following equation:

$$K = \alpha \cdot \rho \cdot C_p, \quad (2)$$

399 where K , α , ρ , and C_p indicate the nanopaper thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$), thermal
400 diffusivity ($\text{mm}^2 \text{s}^{-1}$), density (g cm^{-3}), and specific heat capacity ($\text{J g}^{-1} \text{K}^{-1}$), respectively. The
401 through-plane thermal diffusivity (α) was measured using a light flash apparatus (LFA447
402 HyperFlash, NETZSCH, Selb, Germany). The specific heat capacity (C_p) was measured using
403 differential scanning calorimetry (Thermo Plus EVO II, Rigaku Corp., Tokyo, Japan). Al_2O_3 was
404 used as a reference, and the thermograms were generated by heating the nanopapers at $10 \text{ }^\circ\text{C}$
405 min^{-1} in the temperature range $0\text{--}110 \text{ }^\circ\text{C}$ in a N_2 atmosphere.⁴⁶

407 ASSOCIATED CONTENT

408 **Supporting Information**

409 The following files are available free of charge upon reasonable request from the corresponding
410 author or on the Internet at <http://pubs.acs.org>.

411 Molecular structures of carbonized nanopapers exhibiting nanoporous and dense structures

- 412 (PDF)
- 413 Porous structures, light absorption and reflection measurements, and solar thermal heating
- 414 performances of cellulose pulp paper carbonized at 500 °C exhibiting porous microstructures
- 415 (PDF)
- 416 UV–vis–NIR absorption spectrum of original nanopaper (PDF)
- 417 Weight retention of nanopaper carbonized at different temperatures (PDF)
- 418 Carbonized nanopaper photoluminescence spectra (PDF)
- 419 Carbonized nanopaper thermal property measurements (PDF)
- 420 Solar-driven thermoelectric power generation using carbonized nanopaper (PDF)
- 421 Nanoporous structures of nanopapers carbonized at different temperatures (PDF)

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433 **Author Contributions**

434 The manuscript was written through contributions of all the authors, who have approved the final
435 manuscript version.

436 H. Koga designed the study. T. Yeamsuksawat and H. Koga wrote the manuscript. T.
437 Yeamsuksawat and Y. Morishita prepared the samples. T. Yeamsuksawat, Y. Morishita, J.
438 Shirahama, and Y. Huang performed the experiments. T. Yeamsuksawat, Y. Morishita, J.
439 Shirahama, Y. Huang, T. Kasuga, M. Nogi, and H. Koga analyzed the results, discussed the results
440 and implications, and commented on the manuscript at all the preparation stages.

441 **Notes**

442 The authors declare no competing financial interests.

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455 **ABBREVIATIONS**

456 ATR, attenuated total reflection; CNT, carbon nanotube; FE-SEM, field-emission scanning
457 electron microscopy; FT-IR, Fourier-transform infrared; HR-TEM, high-resolution transmission
458 electron microscopy; NIR, near infrared; PL, photoluminescence; PTFE, polytetrafluoroethylene;
459 TEM, transmission electron microscopy; *t*-BuOH, *tert*-butyl alcohol; UV, ultraviolet; vis, visible;
460 XRD, X-ray diffraction.

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