

Solar-assisted efficient cleanup of high-viscosity oil spills using magnetic porous biochar

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1	Sol	ar-assisted efficient cleanup of high-viscosity oil spills using magnetic porous		
2	bio	char		
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14 Abstract: Efficient cleanup of oil spills is still a global challenge due to the high 15 viscosity of crude oil and complicated topographic features. Herein, magnetic porous 16 carbon powders (MPCs) with photothermal effect prepared at a Fe(NO₃)₃: bamboo mass ratio was 1/1 carbonized at 700 °C. After modifying with the n-octadecylamine, 17 the oleophilic MPCs exhibited rapid and selective absorption of different oils from 18 19 polluted water, with an optimal absorption capacity of 3.2–8.1 g/g. Since oil's viscosity 20 is highly temperature-sensitive, MPCs with photothermal characteristics offer apparent 21 advantages in absorbing high viscosity oil. Moreover, due to the incorporation of 22 magnetic components, powder-like MPCs can be conveyed to a specified oil pollution 23 spot (including gaps or cracks) conveniently and collected through a remote magnetic 24 field. This work demonstrates a simple and low-cost way of designing and producing 25 oil/water separation materials, particularly floating high-viscosity oil recovery. 26 Keywords: High viscosity; Oil spill; Photothermal effect; Magnetic biochar; Oil/water

27 separation

29 Introduction

30 The oil spill caused by offshore oil extraction or transportation causes enormous 31 ecological disasters for the marine biosphere and the entire ecosphere of the earth [1-32 5]. The spilt oils will cover the water, block light and oxygen from reaching the deep 33 ocean, and destroy marine life. Therefore, several cleanup solutions, including 34 automated collection, biological breakdown, controlled burning, and chemical dispersants, have been proposed for oil spills [6-10]. Nonetheless, the implementation 35 36 of these solutions has been hampered by a number of problems, including hazardous 37 production, slow degradation, secondary pollution, etc. Consequently, it is essential to 38 utilize more environmentally friendly methods for cleaning up the oil spill.

39 Using sorbent to recover oil from water is the most practical and effective method due 40 to its minimal impact on the natural environment [11-13]. Porous materials have been 41 regarded as effective absorbents, particularly oleophilic porous absorbents that can 42 extract oil from water efficiently. Numerous materials, such as carbon-based aerogels, 43 polymer sponges, and silica aerogels, have been produced based on this concept [14-16]. Upon application of these materials, several variables that influence their sorption 44 45 ability must be considered. One parameter that impacts the separation speed and 46 efficiency is the absorbent's shape. In the ocean, oil typically exists as emulsified 47 droplets. Inadequate contact with the porous absorbent will significantly reduce 48 separation efficiency [17, 18]. Therefore, a block-shaped absorbent is less effective due 49 to its vast size, which results in inadequate interaction with the oil in the complicated 50 topography[19, 20]. Alternatively, powder-like substances with a high specific surface 51 area can produce successful oil-water separation in certain circumstances due to their 52 sufficient interaction with tiny oil droplets [21-23]. In addition, by incorporating 53 magnetic components into the powder absorbents, it is possible to achieve quick oil 54 recycling by applying an external magnetic field and easily entering cracks or gaps.

55 Besides the influence of the absorbent's shape, the viscosity of the oil is also an essential 56 component that influences the adsorption efficiency. The viscosity of crude oil is

usually as high as $10^3 \sim 10^5$ mPa·s, which makes it difficult to be absorbed into porous 57 58 absorbents[24]. Numerous studies have been conducted to reduce the viscosity of crude 59 oil and boost the absorbent's adsorption efficiency. Yu et al. demonstrated a graphene-60 coated sponge, which could clean viscous crude oil as the Joule heating effect was 61 stimulated [25]. Their following work also reported a ferrimagnetic sponge with a 62 magnetocaloric effect [26]. When the sponge was exposed to an alternating current 63 magnetic field, the viscosity of the crude oil around the sponge decreased due to 64 magnetic heating. However, the electric-consumption activation method for the Joule 65 heat effect is uneconomical in the maritime environment.

66 Solar energy is more environmentally benign and adaptable to the ocean than electrical 67 energy. In this field, developing photothermal absorbents that can rapidly convert solar 68 energy to thermal energy will be advantageous [27-29]. Due to its broad-spectrum solar light absorption, ultralow density, high porosity, high lipophilicity, environmental safety, 69 70 and physical/chemical stability, carbon-based materials, such as graphene, carbon 71 nanotubes, and carbon fiber, have been widely studied [30-33]. However, these carbon 72 nanoparticles are too costly for widespread use. Considering that the carbon source 73 from biomass is abundant, renewable, biodegradable, and low-cost, there has been an 74 increased focus on developing carbon-based materials from renewable resources, such 75 as agricultural wastes and natural products [34-36]. However, few investigations have 76 been conducted to creat magnetic and photothermal powder absorbents generated from 77 sustainable natural resources for viscous oil treatment.

In this work, the agricultural waste bamboo powders and ferric nitrate were employed as a carbon source to manufacture magnetic porous carbon powders (MPCs) with desirable photothermal performance for viscous oil cleanup. We utilized a method inspired by mussel to graft nonpolar n-octadecylamine (ODA) onto MPCs using polydopamine (PDA). The hydrophobic product ODA-MPCs developed displayed a high capacity for oil absorption and a high tolerance for acidic, alkaline, and hypersaline conditions. Meanwhile, the MPCs successfully generated heat effects under solar radiation, significantly increasing the oil's fluidity. When the oil's viscosity reaches
5000 mPa·s, its absorption capacity reaches its maximum of 8.1 g/g.

87 Experiments

88 Materials

Bamboo powders were obtained from a local wood factory (Changsha, China). 3-89 90 hydroxytryptamine hydrochloride (dopamine), methylbenzene, n-hexane and tris-91 (hydroxymethyl) aminomethane (TRIS, 99%, a buffer agent) were purchased from 92 Sigma-Aldrich Co., Ltd (Shanghai, China). n-octadecylamine (ODA) and ethanol were purchased from Aladdin Reagent Co., Ltd (Shanghai, China). The peanut oil was 93 94 purchased from the local grocery store. Dow Chemical Company supplied silicon oil 95 (Michigan, America). We purchased tetrahydrofuran and ethyl acetate from Sinopharm 96 Chemical Reagent Co., Ltd. (Shanghai, China). The procurement of conduction oil 97 from MOJIEZUO Co., Ltd. (Shanghai, China). Liaohe Oilfield was the source of 98 petroleum (Panjin, China). All chemical reagents and solvents were used as received 99 without further purification.

100 **Preparation of magnetic porous carbons**

101 The bamboo powders were firstly immersed in ferric nitrate solution at 90 °C under 102 constant stirring until the complete evaporation of visible water. After being dried at 103 100 °C for 6 h, the red powders were transferred to a tube furnace and carbonized at 104 high temperatures for 2 h with 100 mL min⁻¹ of Ar flow protection. The pyrolyzed black 105 powders are washed with *n*-hexane three times and dried at 60 °C for 2 h. The obtained 106 MPCs were labeled as C-1, C-2, C-3, C-4 and C-5, respectively, according to different 107 fabricated preparation conditions. (**Table 1**).

Table 1. Formulas and preparation conditions for MPCs

MPCs	Mass ratio (Fe(NO ₃) ₃ :bamboo)	sintering temperature		
C-1	1:2	600		
C-2	1:1	600		
C-3	2:1	600		
C-4	1:1	700		

C-5	1:1	800
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109 Oleophilic modification of porous carbon

As-prepared MPCs were dispersed in 100 mL buffer solution (10 mM, pH=8.5) 110 111 followed by adding 270 mg dopamine. After a bath sonication of 10 min, the suspension 112 was stirred at room temperature for 24 h. The PDA-coated MPCs were then collected 113 via solid-liquid separation and a water-washing treatment before being dried in a 114 vacuum oven at 50 °C for 24 h. Subsequently, PDA-coated MPCs were redispersed in 115 100 mL ethanol containing 2 mmol ODA for oleophilic modification. After stirring for 116 24 hours, the collected solids were filtrated and rinsed with ethanol to remove unreacted 117 ODA. Finally, the modification product MPCs-ODA was dried at 50 °C under a vacuum 118 for 24 h.

119 Material characterizations

120 The morphologies of all samples were observed by scanning electron microscope 121 (SEM). X-ray diffraction (XRD) measurements were carried out on an X-ray powder 122 diffractometer (Bruker D8 Advance, Germany). N2 adsorption/desorption isotherms 123 were measured using a surface area and porosimetry analyzer (Micromeritics ASAP 124 2460, America) at 77 K in the relative pressure range of P/P_0 . The specific surface area 125 was determined by the Brunauer-Emmett-Teller (BET) method. The magnetic 126 properties of the powders were measured by JDAW-2000C&D vibrating sample 127 magnetometer (VSM). The morphologies of the powders were characterized by JEOL 128 JSM-6490LV scanning electron microscope (SEM). Fourier Transform Infrared spectra 129 (FTIR) were recorded using a Fourier transform infrared spectrometer (Thermo Scientific Nicolet iS50, America) over 4000-400 cm⁻¹. The samples were pressed into 130 131 compact wafers using a stainless steel die under the pressure of 5 MPa for several 132 minutes, a SL20QB contact angle meter was used to detect the contact angle using water 133 as the droplet. Thermal images of the pellets were taken by an infrared thermal imaging 134 camera (Fluke, apparatus model).

135 Sorption capacity test towards oil and organic solvents

136 Typically, 0.5 g dry carbon powders were added into a beaker filled with 20 g organic 137 liquid without stirring. After 30 min, the soaked powders were magnetically collected, 138 and the remaining oil in the beaker was weighed. The maximum oil sorption capacity 139 of the powders was calculated by

 $20 - C_{f}$

. . .

140
$$q = \frac{1}{0.5}$$

141 where q is the maximum sorption capacity ($g_{oil}/g_{sorbent}$), and C_f is the final weight of the

142 oil.

143 **Recycling test**

After the oil-absorption test, the oil-containing superhydrophobic particles were 144 magnetically removed from the mixtures and reused after three tetrahydrofuran rinses. 145 Then, the clean powders were dried at 50 °C for the next oil-absorption cycle. The 146 147 recyclability was evaluated by calculating the oil-absorption capacity of powders that 148 experienced 20-cycles absorption. Also, the CA measurement was operated to evaluate 149 the superhydrophobicity of reused powders.

150 **Chemical stability tests**

151 The chemical stability of magnetic powders was carried out in a series of solutions with 152 pH in the range of 3-13 at room temperature. Firstly, 1 g powders were sprinkled into a 153 beaker and mixed with 100 mL pre-made solution with a stable pH value. After 24 hours, 154 the powders were recollected and dried. And then, the CA and adsorption capacity of 155 powders were measured to determine pH stability. With the same method, a NaCl 156 solution was prepared to imitate the seawater to investigate the stability of powders in 157 a marine environment.

158 **Results and discussion**



159

Fig. 1 Schematic diagram for the fabrication of hydrophobic magnetic carbon powder. As illustrated in Fig. 1, the bamboo powder was used as a carbon precursor and was then mixed with Fe(NO₃)₃ solution. Magnetic particles were formed during the pyrolysis of the biomass-derived carbon. Additional bio-inspired surface modification conferred optimal hydrophobicity on the powders via grafting of long-chain alkane[37, 38].

The crystalline structure of the produced magnetic carbon powders was determined by 166 XRD analysis. As shown In Fig. 2a, the XRD patterns of composite powders are 167 manufactured with different ratios of basic materials. All three types of powders had 168 169 distinctive face-centered cubic Fe₃O₄ (JCPDS NO.19-0629) peak shapes. When the 170 Fe(NO₃)₃ ratio in raw materials increases, the peaks become sharper and more intense, 171 indicating a higher Fe₃O₄ crystalline content. The presence of graphitized carbon also 172 causes a significant peak near about 26.5°. XRD patterns were also employed to 173 examine the impact of sintering temperatures on powder phase transitions. As shown in 174 Fig. 2b, iron-containing crystalline phases, including Fe₃O₄ (JCPDS NO.19-0629), 175 Fe₃C (JCPDS NO.35-0772), and Fe (JCPDS NO.06-0696), appeared. Specifically, for 176 the C-2 fabricated at 600 °C, recognizable Fe₃O₄ peaks together with graphite carbon 177 could be seen. As the temperature rose to 700°C, the Fe peak became apparent, and the 178 Fe₃O₄ peaks faded in the curve of C-4. When the temperature reaches 800 °C, sharp Fe 179 peaks, several Fe₃C peaks, and amorphous carbon peaks can be seen. Therefore, it can 180 be inferred that the Fe-containing compounds were gradually reduced to elemental Fe 181 with the increased sintering temperature. The BET test was subsequently used to 182 determine the precise surface areas of the objects. In Fig. 2c, the nitrogen adsorption 183 curves in C-2 and C-3 have attained saturation at low pressure. Due to micropores and 184 mesopores, a characteristic type-IV isotherm was seen in C-1, C-4, and C-5[39]. As shown in Table 2, C-1, C-4, and C-5 had BET surface areas of 201.0, 186.2, and 178.3 185 m^2/g , respectively, which were more significant than the other two samples and 186 187 advantageous for oil absorption. VSM evaluated the magnetic properties of the samples 188 at room temperature due to the presence of Fe-containing components. The magnetic 189 hysteresis curves of C-1, C-2, C-3, C-4, and C-5 revealed saturation magnetizations 190 (Ms) of 3.8, 19.2, 101.1, 60.5, and 76.0 emu/g (Fig. 2d). The MPC magnetic hysteresis 191 loops exhibited paramagnetic behavior between 20000 and -20000 Oe, devoid of 192 remanence or coercivity. Magnetic saturation values of samples were also impacted by Fe(NO₃)₃/bamboo ratios and sintering temperatures. The paramagnetic characteristic 193 194 and the ability to tailor the saturation values of the magnetic field significantly 195 improved the operability of powder-like oil absorbers.



Fig. 2 XRD patterns of samples prepared at different ratios of raw materials (a) and
prepared at different temperatures (b); Nitrogen adsorption-desorption isotherms (c)
and Magnetization hysteresis loops of samples (d).

Sample	C-1	C-2	C-3	C-4	C-5
Specific surface area (m^2/g)	201.0	143.2	22.8	186.2	178.3
Saturation magnetization (emu/g)	3.8	19.2	101.1	60.6	76.0

200 **Table 2.** Specific surface area and saturation magnetization of samples.

201 Fig. 3a1-e1 illustrates the microstructures of MPCs. All MPCs had a honeycomb-like 202 structure with cell diameters of 20-50 um at low magnification. Additionally, the 203 magnified images (Fig. 3a2-e2) revealed the presence of numerous secondary pores in 204 the cell wall, except for C-3, with sizes of roughly 1 um. After pyrolysis, the porous C-205 3 debris converted into uneven spheres due to the excess ferric salts. The photos in Fig. 206 3a3-e3 provided further detail on the pore wall. We discovered that the walls of C-1 and C-2 were relatively smooth. While the walls of C-4 and C-5 were coated with a 207 dense network of nanopores. Additionally, as illustrated in Fig. 3c2, the stratified 208 209 microstructures of nanospheres in C-3 were revealed. C-4 and C-5 reflected hierarchical 210 structures with honeycomb-like morphologies, including submillimeter-, micro-, and 211 nanopores. The multilevel hierarchical structure was more conducive to oil storage and 212 made it easier for oil to penetrate the interiors of MPCs. In comparison, C-1 and C-2 213 allow for the selection of only two types of pores.

The current work's target absorbents required a high absorption capacity and magnetic intensity. Both C-4 and C-5 had a desirable Ms value and a large specific surface area, which translated to a high absorption capacity and ease of use in oil spill remediation. Thus, considering the energy required for preparation and the functional properties, C-4 generated at 700 °C was chosen as the subject of the ensuing inquiry.



220 Fig. 3 SEM images of C-1 (a1-3), C-2 (b1-3), C-3 (c1-3), C-4 (d1-3) and C-5 (e1-3). 221 As mentioned before, MPCs' hydrophobicity and capacity to float are critical for oil 222 spill remediation. However, due to their high density and hydrophilic surface, the MPCs 223 in their prepared state cannot float stably over water. However, this problem could be 224 solved by a bio-inspired surface grafting technique employed to endow the MPCs with 225 hydrophobicity and avoid secondary contamination from absorbents. Through the 226 typical Schiff base reaction and Michael addition caused by dopamine polymerization, 227 ODA with a long alkyl chain was successfully grafted onto PDA-covered MPCs in this study. The detailed synthesis technique, as depicted in Fig. 4: Dopamine polymerization 228

first formed a PDA layer that shielded MPCs from corrosion and supplied functional groups as a site for grafting hydrophobic chemicals. After that, the ODA was covalently grafted onto MPCs-PDA via a standard Michael addition or Schiff base reaction between amino and quinone groups.





234 Fig. 4 Reaction mechanism of dopamine and ODA during the dip-coating process. 235 In order to compare the surface properties between the samples before and after coating, 236 the FTIR spectra of pure MPCs and ODA-MPCs were compared in Fig. 5a to indicate MPCs' surface functionalization. The absorption peaks at approximately 1610 cm⁻¹ 237 (C=C stretching), 1485 cm⁻¹ (N-H scissoring), and 1284 cm⁻¹ (C-O stretching) prove 238 that PDA was coated on the MPCs. The new peaks at 2915 and 2848 cm⁻¹ on the ODA-239 240 MPCs curve were connected with CH stretching vibrations, which were contributed by the abundant methyl and methylene groups in ODA molecules. The peak at 1150 cm⁻¹ 241 242 might be attributable to the secondary amine's -C-N- stretching vibration, which 243 provided the presence of an interaction between ODA and PDA. FTIR analysis 244 confirms that ODA was successfully grafted onto the surface of MPCs.

MPCs were anticipated to be hydrophobic and float in water after the decoration of ODA. As a result, the clean MPCs and ODA-MPCs were dispersed into the sea surface independently. After 24 hours, nearly all pure MPCs sank to the bottom of the vial, whereas ODA-MPCs powders remained afloat on the water surface. The surface wetting test was used to determine the further hydrophilicity-to-hydrophobicity transition. MPCs had a contact angle of approximately 0°, whereas ODA-MPCs had a contact angle of 135.5°. (**Fig. 5b**). Additionally, when an oil droplet was added to the unmodified MPCs, as demonstrated in **Fig. 5c**, the oil droplets were put to the MPCs and entirely repelled. In comparison, oil droplets could easily permeate ODA-MPCs due to their increased hydrophobicity. Based on the preceding, it can be concluded that ODA-coated MPCs exhibit superior water repellency, oil affinity, and floatability that can be used to address maritime oil spills.



257

Fig. 5 FTIR spectra of PDA, MPCs, PDA-MPCs and ODA-MPCs (a); comparison of floatability (b) (inset: water contact angle); comparison of oil wettability (c).

Subsequently, the uptake capacity of ODA-MPCs was established. As shown in Fig. 260 261 6a, ODA-MPCs had a favorable sorption capability for various oils and nonpolar 262 organic solvents, including high viscosity petroleum and silicone oils. Calculations 263 indicate that the modified magnetic powders have absorption capacities ranging from 264 3.2 to 8.1 g/g. Due to the higher viscosity, the absorbed silicone oil (5000 cP \cdot s) and 265 petroleum can be successfully retained in hierarchically porous architectures of 266 powders. We compare our work to many previously published powder-based oil 267 sorbents using a literature search (Table 3) [21, 23, 40-42]. Although ODA-MPCs have 268 a lower sorption capacity than other sorbents, their manufacture is simpler and less 269 expensive. The raw materials are primarily constituted of biodegradable agricultural 270 and forest byproducts.

materials	sorption capacity (g/g)	magnetic response	photothermal effect	references
fly ash composites	1.69	\checkmark	×	[40]
Fe ₃ O ₄ @C/Cu core-shell sub- micron materials	3.38	×	×	[21]
sawdust	3.59 to 7.83	\checkmark	×	[42]
silver nanocomposite	10.95 ± 0.47	×	×	[41]
hollow carbon microsphere	6.5 to 10.8	\checkmark	×	[23]
MPC	3.2 to 8.1			This work

Table 3. Comparison of powder sorbents reported in recent literature

272 Fig. 6b illustrates the absorption capability of ODA-MPCs after they have been 273 subjected to a 20-cycles absorption experiment. In comparison to the data in Fig. 6a, 274 the change in either sorption capacity or the water contact angles was negligible for the 275 high-viscosity silicone oil, n-hexane, and petroleum, indicating improved cycling 276 performances of ODA-MPCs. The absorbent used in practice must be able to survive 277 in acidic, alkaline, and hypersaline environments, which are prevalent in the marine 278 environment. Thus, the absorption capacity and contact angles of ODA-MPCs were measured after 24 hours of immersion in 3 percent salty water with varying pH values. 279 280 As shown in Fig. 6c, the absorption capacity of ODA-MPCs for crude oil remained 281 constant at approximately 6.2 g/g under diverse circumstances. Additionally, the 282 contact angle values vary somewhat between 132° and 134°. These findings suggested 283 that ODA-MPCs can reserve their capacity for surface wetting and oil absorption into 284 the ocean.





290 Fig. 7a presents the processes of removing crude oil from the water by ODA-MPCs 291 under an external magnetic field. When the powers were cast to an oil layer floating on 292 the water surface, the crude oil gradually accumulated around the powders and was 293 absorbed within 60 s. The absorption-saturated particles were drawn out of the water 294 by a magnetic column due to the introduction of magnetic compounds, thereby 295 releasing clean water. The above test supports the applicability of MPCs under practical 296 marine conditions. Concerning the oil/water separation process, the hydrophobicity and 297 lipophilicity of ODA-MPCs were related to the grafted long-chain alkane and rough 298 surface on substrates, in accordance with the theory of wettability on the solid surface. 299 [43]. The introduced alkane chains decreased the surface tension, limiting the wetting 300 of water droplets. Generally, the influence of surface roughness on wettability could be 301 explained by Wenzel and Cassie's model. For ODA-MPCs, the air bubbles trapped on 302 the rough surface also drastically reduced the contact area of water with the substrates

1

303 and led to the hydrophobic performance described by the traditional Cassie model:

$$\cos \theta r = \varphi \cos \theta e + \varphi - \varphi$$

305 where θr is the water CA on the rough surface, θe is the equilibrium water CA on the 306 smooth surface, and φ is the fraction of the drop footprint area in contact with the solid 307 (the solid fraction) ($\varphi < 1$).

308 Unlike water droplets, the wetting performance was dramatically enhanced, and the true 309 contact angle was significantly enlarged when the substrate of ODA-MPCs suffered 310 from the oils. The Wenzel model could explain this phenomenon:

311
$$\cos \theta r = \frac{1}{f} \cos \theta e$$

Where θ r is the oil CA on the rough surface, θ e is the equilibrium oil CA on the smooth surface, and *f* is the roughness factor, defined as the ratio of the actual area of the rough surface to the geometric projected area (*f*>1). It could be predicted that the long chains are aggregated to build a thin layer of hydrophobic film to repulse water while they can be well stretched to form a transitional layer in the oil droplets (**Fig.7b**). Therefore, the modified MPCs exhibit desirable hydrophobicity and lipophilicity.



319 Fig. 7 Removal of petroleum from water surface by ODA-MPCs with a magnetic field

- 320 (a); schematic illustration for wettability of ODA-MPCs (b).
- 321 Compared to common organic solvents, oils with high viscosity diffuse slowly due to

322 their low fluidity. However, the rheology properties of the oil are temperature-323 dependent. Thus, employing a photothermal approach to achieve efficient oil recovery 324 provides several specific advantages in a marine environment. Due to their broad-325 spectrum solar light absorption, carbon-based materials are an excellent photothermal 326 absorbent for the fast adsorption of high-viscosity oil. Fig. 8a showed thermal infrared 327 pictures of ODA-MPCs demonstrating the normal photothermal effect. When exposed 328 to sunlight, powders reach an equilibrium temperature of 62 °C in a matter of seconds, but without sunlight, they reach a temperature of roughly 38 °C (in summer). A 329 330 difference of 24 °C in temperature notably influences the viscosity of high-viscosity oil. 331 To demonstrate the effect, we studied the spreading behavior of oil droplets on ODA-332 MPCs. The evolution of the droplet's diameter with different exposure durations is 333 recorded by the thermal infrared images in Fig.8b. Under sunlight, it took 22 seconds 334 for the diameter of the oil droplet to double and just 63 seconds for it to reach its 335 maximum diameter. However, in the absence of direct sunlight, the diameter of the oil 336 droplet spreads to twice its initial diameter in 41 seconds and achieves its maximum 337 diameter in 105 seconds. The different spread speeds of the oil droplets with and 338 without sunlight exposure indicated that the increased temperature caused by sunlight 339 might promote the fluidity and diffusion of heavy crude oil, which consequently 340 facilitates the adsorption of high-viscosity oil. In Fig.8c, a schematic representation of 341 the photothermal effect being activated in magnetic porous biochar to reduce the 342 viscosity of oils was shown. Due to their low fluidity, the powder-like MPCs are typically difficult to spread into such thick fluids. When exposed to the sun, the 343 344 generated heat significantly reduces the viscosity of the oil, boosting powder dispersion 345 and absorption efficiency.



(b) oil droplet spreading rate on MPCs



Fig 8. Infrared images: comparison of temperature in MPCs without solar radiation and
under solar radiation (a); time-dependent the spreading rate of an oil droplet on surface
MPCs without solar radiation and under solar radiation (b). schematic illustration of
solar-heated ODA-MPCs for the fast adsorption of high viscosity oil (c).

351 Conclusions

In this study, we produced porous carbon powders with hydrophobicity, photothermal conversion capacity, and magnetic responsiveness for use in crude oil spill recovery. The essential components were inexpensive and ecologically sustainable bamboo powder. By altering the powders modified with ODA, the crude oil absorption capacity increased to greater than 6.2 g/g. Meanwhile, the powders produced could be utilized in acidic, alkaline, and hypersaline settings. In addition, by applying the magnetic field, the porous carbon particles could be localized in the oil-water region for sorption and recovery. In addition, by leveraging the photothermal effect, the area surrounding the powders became much hotter when exposed to sunshine, facilitating the efficient absorption of high-viscosity oil. As a result, we expect that this form of carbon powder will be widely utilized in crude oil spills.

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367 **References**

- [1] G.L. Cao, Y.G. Wang, C.Y. Wang, S.H. Ho, A dually prewetted membrane for
 continuous filtration of water-in-light oil, oil-in-water, and water-in-heavy oil
 multiphase emulsion mixtures, J. Mater. Chem. A 7 (2019) 11305-11313.
- [2] W. Chen, P.C. Zhang, R.H. Zang, J.B. Fan, S.T. Wang, B.L. Wang, J.X. Meng,
 Nacre-Inspired Mineralized Films with High Transparency and Mechanically Robust
 Underwater Superoleophobicity, Adv. Mater. 32 (2020) 1907413.
- 374 [3] X.Q. Cheng, Z.K. Sun, X.B. Yang, Z.X. Li, Y.J. Zhang, P. Wang, H. Liang, J. Ma,
 375 L. Shao, Construction of superhydrophilic hierarchical polyacrylonitrile nanofiber
 376 membranes by in situ asymmetry engineering for unprecedently ultrafast oil-water
 377 emulsion separation, J. Mater. Chem. A 8 (2020) 16933-16942.
- 378 [4] X. Ge, W.X. Qin, H.M. Zhang, G.Z. Wang, Y.X. Zhang, C.Z. Yu, A three379 dimensional porous Co@C/carbon foam hybrid monolith for exceptional oil-water
 380 separation, Nanoscale 11 (2019) 12161-12168.
- 381 [5] M.B. Wu, S. Huang, T.Y. Liu, J. Wu, S. Agarwal, A. Greiner, Z.K. Xu, Compressible
- 382 Carbon Sponges from Delignified Wood for Fast Cleanup and Enhanced Recovery of
- 383 Crude Oil Spills by Joule Heat and Photothermal Effect, Adv. Funct. Mater. 31 (2021)
- 384 2006806.

- 385 [6] A. Farinmade, O.F. Ojo, J. Trout, J.B. He, V. John, D.A. Blake, Y.M. Lvov, D.H.
- 386 Zhang, D. Nguyen, A. Bose, Targeted and Stimulus-Responsive Delivery of Surfactant
- 387 to the Oil-Water Interface for Applications in Oil Spill Remediation, ACS Appl. Mater.
- 388 Inter. 12 (2020) 1840-1849.
- 389 [7] D. Motorin, H. Roozbahani, H. Handroos, Development of a novel method for
- 390 estimating and planning automatic skimmer operation in response to offshore oil spills,
- 391 J. Environ. Manage. (2022) 115451.
- 392 [8] L. G. Faksness, F. Leirvik, I.C. Taban, F. Engen, H.V. Jensen, J.W. Holbu, H. Dolva,
- 393 M. Bratveit, Offshore field experiments with in-situ burning of oil: Emissions and burn
- 394 efficiency, Environ. Res. 205 (2022) 112419.
- 395 [9] M. Omarova, L.T. Swientoniewski, I.K.M. Tsengam, D.A. Blake, V. John, A.
- 396 McCormick, G.D. Bothun, S.R. Raghavan, A. Bose, Biofilm Formation by
- 397 Hydrocarbon-Degrading Marine Bacteria and Its Effects on Oil Dispersion, ACS.
- 398 Sustain. Chem. Eng. 7 (2019) 14490-14499.
- 399 [10] S.H. Wu, H.C. Yang, G.P. Xiong, Y.K. Tian, B.Y. Gong, T.F. Luo, T.S. Fisher, J.H.
- 400 Yan, K.F. Cen, Z. Bo, K.K. Ostrikov, Spill-SOS: Self-Pumping Siphon-Capillary Oil
- 401 Recovery, ACS Nano 13 (2019) 13027-13036.
- 402 [11] L. Oliveira, J. Saleem, A. Bazargan, J.L.D. Duarte, G. McKay, L. Meili, Sorption
- 403 as a rapidly response for oil spill accidents: A material and mechanistic approach, J.
- 404 Hazard. Mater. 407 (2021) 124842.
- 405 [12] J.F. Xu, R. Cao, M.S. Li, G.X. Chen, J.F. Tian, Superhydrophobic and
 406 superoleophilic cuttlebone with an inherent lamellar structure for continuous and
 407 effective oil spill cleanup, Chem. Eng. J. 420 (2021) 127596.
- 408 [13] H.Y. Yu, M. Wu, G.G. Duan, X. Gong, One-step fabrication of eco-friendly
- 409 superhydrophobic fabrics for high-efficiency oil/water separation and oil spill cleanup,
- 410 Nanoscale 14 (2022) 1296-1309.

- 411 [14] Z. Guo, B. Long, S. Gao, J. Luo, L. Wang, X. Huang, D. Wang, H. Xue, J. Gao,
- 412 Carbon nanofiber based superhydrophobic foam composite for high performance413 oil/water separation, J. Hazard. Mater. 402 (2021) 123838.
- 414 [15] P.K. Renjith, C. Sarathchandran, V.S. Achary, N. Chandramohanakumar, V. Sekkar,
- 415 Micro-cellular polymer foam supported silica aerogel: Eco-friendly tool for petroleum
- 416 oil spill cleanup, J. Hazard. Mater. 415 (2021) 125548.
- 417 [16] L. Jin, Y. Gao, Y. Huang, M. Ou, Z. Liu, X. Zhang, C. He, B. Su, W. Zhao, C. Zhao,
- 418 Mussel-Inspired and In Situ Polymerization-Modified Commercial Sponge for
- 419 Efficient Crude Oil and Organic Solvent Adsorption, ACS Appl. Mater. Inter. 14(2)
- 420 (2022) 2663-2673.
- 421 [17] H. Kim, G. Zhang, M. Wu, J.S. Guo, C. Nam, Highly efficient and recyclable
- 422 polyolefin-based magnetic sorbent for oils and organic solvents spill cleanup, J. Hazard.
 423 Mater. 419 (2021) 126485.
- [18] M. Yang, B. Chen, X.Y. Xin, X. Song, J.B. Liu, G.H. Dong, K. Lee, B.Y. Zhang,
 Interactions between microplastics and oil dispersion in the marine environment, J.
 Hazard. Mater. 403 (2021) 123944.
- 427 [19] Z.K. Chen, C.J. An, M. Boufadel, E. Owens, Z. Chen, K. Lee, Y.T. Cao, M.F. Cai,
- 428 Use of surface-washing agents for the treatment of oiled shorelines: Research
- 429 advancements, technical applications and future challenges, Chem. Eng. J. 391 (2020)
- 430 123565.
- 431 [20] Q. Feng, C.J. An, Z. Chen, E. Owens, H.B. Niu, Z. Wang, Assessing the coastal
- 432 sensitivity to oil spills from the perspective of ecosystem services: A case study for
 433 Canada's pacific coast, J Environ. Manage. 296 (2021) 113240.
- 434 [21] T.Q. Liu, Z.J. Li, G.M. Shi, Q. Zhao, X. Chen, X.L. Chen, Y.L. Li, Facile
- 435 preparation of Fe₃O₄@C/Cu core-shell sub-micron materials for oil removal from water
- 436 surface, Appl. Surf. Sci. 466 (2019) 483-489.

- 437 [22] P.M. Reddy, C.J. Chang, J.K. Chen, M.T. Wu, C.F. Wang, Robust polymer grafted
- Fe3O4 nanospheres for benign removal of oil from water, Appl. Surf. Sci. 368 (2016)
 27-35.
- 440 [23] N. Yang, Z.-X. Luo, S.-C. Chen, G. Wu, Y.-Z. Wang, Superhydrophobic magnetic
- 441 hollow carbon microspheres with hierarchical micro/nano- structure for ultrafast and
- 442 highly-efficient multitasking oil-water separation, Carbon 174 (2021) 70-78.
- 443 [24] S. Singh, R. Jelinek, Solar-mediated oil-spill cleanup by a carbon dot-polyurethane
- 444 sponge, Carbon 160 (2020) 196-203.
- 445 [25] J. Ge, L.-A. Shi, Y.-C. Wang, H.-Y. Zhao, H.-B. Yao, Y.-B. Zhu, Y. Zhang, H.-W.
- 446 Zhu, H.-A. Wu, S.-H. Yu, Joule-heated graphene-wrapped sponge enables fast cleanup
- 447 of viscous crude-oil spill, Nat.Nanotechnol. 12 (2017) 434-440.
- 448 [26] Y.H. Song, L.A. Shi, H.Y. Xing, K. Jiang, J. Ge, L. Dong, Y. Lu, S.H. Yu, A
- 449 Magneto-Heated Ferrimagnetic Sponge for Continuous Recovery of Viscous Crude Oil,
- 450 Adv. Mater. 33 (2021) 2100074.
- 451 [27] C. Gong, J.C. Lao, B.Y. Wang, X.Y. Li, G.J. Li, J. Gao, Y.Z. Wan, X.H. Sun, R.S.
- 452 Guo, J.Y. Luo, Fast and all-weather cleanup of viscous crude-oil spills with MXene
- 453 wrapped sponge, J. Mater. Chem. A 8 (2020) 20162-20167.
- 454 [28] Q. Li, Q. Sun, Y. Li, T. Wu, S. Li, H. Zhang, F. Huang, Solar-Heating Crassula
- 455 perforata-Structured Superoleophilic CuO@CuS/PDMS Nanowire Arrays on Copper
- 456 Foam for Fast Remediation of Viscous Crude Oil Spill, ACS Appl. Mater. Inter. 12457 (2020) 19476-19482.
- 458 [29] X.Z. Ma, C. Zhang, P. Gnanasekar, P. Xiao, Q. Luo, S.Q. Li, D.D. Qin, T. Chen, J.
- 459 Chen, J. Zhu, N. Yan, Mechanically robust, solar-driven, and degradable lignin-based
- 460 polyurethane adsorbent for efficient crude oil spill remediation, Chem. Eng. J. 415
- 461 (2021) 128956.
- 462 [30] X.Z. Jin, X.D. Qi, Y. Wang, J.H. Yang, H. Li, Z.W. Zhou, Y. Wang,
- 463 Polypyrrole/Helical Carbon Nanotube Composite with Marvelous Photothermoelectric

- 464 Performance for Longevous and Intelligent Internet of Things Application, ACS Appl.
 465 Mater. Inter. 13(7) (2021) 8808-8822.
- [31] Z. Li, Z. Lin, M. Han, Y. Mu, P. Yu, Y. Zhang, J. Yu, Flexible electrospun carbon
 nanofibers/silicone composite films for electromagnetic interference shielding,
 electrothermal and photothermal applications, Chem. Eng. J. 420 (2021) 129826.
- 469 33[32] Y. Zhao, T. Zhao, Y. Cao, J. Sun, Q. Zhou, H. Chen, S. Guo, Y. Wang, Y. Zhen,
- 470 X.-J. Liang, S. Zhang, Temperature-Sensitive Lipid-Coated Carbon Nanotubes for
- 471 Synergistic Photothermal Therapy and Gene Therapy, ACS Nano 15(4) (2021) 6517-472 6529.
- 473 [33] Y. Wu, H. Huang, W. Zhou, C. You, H. Ye, J. Chen, S. Zang, J. Yun, X. Chen, L.
- 474 Wang, Z. Yuan, High-Porosity Lamellar Films Prepared by a Multistage Assembly
- 475 Strategy for Efficient Photothermal Water Evaporation and Power Generation, ACS
- 476 Appl. Mater. Inter. 14(25) (2022) 29099-29110.
- 477 [34] Z. Liu, M. Chen, C. Lin, F. Li, J.T. Aladejana, J. Hong, G. Zhao, Z. Qin, X. Zhu,
- W. Zhang, D. Chen, X. Peng, T. Chen, Solar-assisted high-efficient cleanup of viscous
 crude oil spill using an ink-modified plant fiber sponge, J. Hazard. Mater. 432 (2022)
 128740.
- [35] S. Wu, D. Chen, G. Zhao, Y. Cheng, B. Sun, X. Yan, W. Han, G. Chen, X. Zhang,
 Controllable synthesis of a robust sucrose-derived bio-carbon foam with 3D
- 483 hierarchical porous structure for thermal insulation, flame retardancy and oil absorption,
- 484 Chem. Eng. J. 434 (2022) 134514.
- 485 [36] Y. Yue, Y. Wang, J. Li, W. Cheng, G. Han, T. Lu, C. Huang, Q. Wu, J. Jiang, High
- 486 strength and ultralight lignin-mediated fire-resistant aerogel for repeated oil/water
- 487 separation, Carbon 193 (2022) 285-297.
- 488 [37] S. Chen, Y. Cao, J. Feng, Polydopamine As an Efficient and Robust Platform to
- 489 Functionalize Carbon Fiber for High-Performance Polymer Composites, ACS Appl.
- 490 Mater. Inter. 6 (2014) 349-356.

- 491 [38] L. Luo, X. Chen, Y. Wang, J. Yue, Z. Du, X. Huang, X.-Z. Tang, Bio-inspired
- 492 modification of silicon carbide foams for oil/water separation and rapid power-free
- 493 absorption towards highly viscous oils, Ceram. Int. 44 (2018) 12021-12029.
- 494 [39] G. Zeng, X. Li, Y. Wei, T. Guo, X. Huang, X. Chen, X.-Z. Tang, Significantly
- 495 toughened SiC foams with enhanced microwave absorption via in situ growth of Si₃N₄
- 496 nanowires, Chem. Eng. J. 426 (2021) 131745.
- 497 [40] L. Bandura, R. Panek, J. Madej, W. Franus, Synthesis of zeolite-carbon composites
- 498 using high-carbon fly ash and their adsorption abilities towards petroleum substances,
- 499 Fuel 283 (2021) 119173.
- 500 [41] M.A. Ali, S.A. Shaaban-Dessuuki, N.A. El-Wassefy, S.I. Mostafa, M.H. Hussein,
- 501 Adsorption of crude and waste diesel oil onto agar-carboxymethylcellulose-silver
- nanocomposite in aqueous media, Inorg. Chem. Commun. 133 (2021) 108915.
- 503 [42] Z. Yin, Y. Li, T. Song, M. Bao, Y. Li, J. Lu, Y. Li, Preparation of superhydrophobic
- 504 magnetic sawdust for effective oil/water separation, J. Clean. Prod. 253 (2020) 120058.
- 505 [43] B. Wang, W. Liang, Z. Guo, W. Liu, Biomimetic super-lyophobic and super-
- 506 lyophilic materials applied for oil/water separation: a new strategy beyond nature,
- 507 Chem. Soc. Rev. 44 (2015) 336-361.