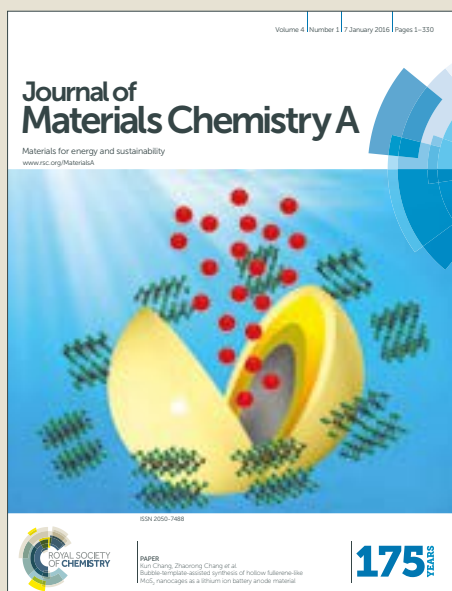


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# Solar-Assisted Fast Cleanup of Heavy Oil Spill by a Photothermal Sponge

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**KEYWORDS:** Photothermal material, solar energy, heavy oil, fast oil cleanup, carbon nanotube, oil viscosity

**ABSTRACT:** Rapid cleanup of heavy oil spill is always considered as a great challenge because the conventional porous oil sorbents cannot efficiently remove them due to the high viscosity of the oil ( $>10^3$  mPa·s). In this work, we take advantage of the photothermal effect to heating the heavy oil by using sunlight as energy source to significantly reduce the viscosity of the heavy oil and thus to achieve a fast heavy oil cleanup. A carbon nanotube (CNT) modified polyurethane

sponge was fabricated as photothermal sorbent that exhibited superhydrophobicity, superoleophilicity, as well as outstanding absorption capacity of heavy oil. Thanks to the excellent photothermal effect of CNTs, the modified sponge achieved nearly full sunlight absorption (99%). The resulting solar heating effectively reduced the viscosity of the heavy oil, which enabled the modified sponge to quickly absorb heavy oil of 20 times its own weight under sun illumination. This solar-assisted heavy oil sorbent design is promising for future remediation of viscous oil-spills.

## 1. INTRODUCTION

Heavy crude oils are widely found and mined in over 70 different countries, with an estimated volume of heavy oil resources being 5.6 trillion barrels worldwide.<sup>1</sup> Moreover, declining production of medium and light crude oil is forcing oil industry to increase the extraction of heavy oils.<sup>2</sup> Heavy oil is also massively produced in petrochemical industry as heavy fuel oil and bitumen for transport industry and construction industry, respectively.<sup>3</sup> Nowadays, the incidents of heavy oil spill from offshore oil field, bunker fuels used by ships and cargos carried on tankers are on the rise.<sup>4</sup> Spills of heavy oils pose severe environmental and ecological impacts, such as causing death of sea bird and marine mammals and leading to long-term contamination of sediments.<sup>5-6</sup> Compared to light oils, heavy oils are more viscous ( $10^3$  to  $10^5$  mPa·s at room temperature) and are thus more difficult to cleaned up.

Conventional wettability based sorbents for spilled oil capture often fail with heavy oils.<sup>7-15</sup> The high viscosity of heavy oils prevents them to diffuse into the inner pores of sorbents, leading to an ineffective oil capture. An effective way to reduce the viscosity of heavy oils is by increasing their temperature.<sup>16-17</sup> Recently, Yu et al. reported a Joule-heated sponge for fast

cleanup of viscous oil spill by using electricity to generate heat in situ.<sup>18</sup> Inspired by Yu's work, we are prompted to use photothermal materials to capture solar heating to drive the cleanup of heavy oil spill. Effective solar energy harvesting and heat generation can be achieved by various photothermal materials, especially low cost and widely available carbon based materials such as graphene oxide, graphene, carbon nanotube (CNT), carbon dots, carbon black, and graphite.<sup>19-24</sup>

In this paper, the photothermal effect is utilized for fast heavy oil cleanup by using sunlight as the energy source. A common polyurethane (PU) sponge was modified by coating CNTs onto the PU skeletons using polydimethylsiloxane (PDMS) as binder. The modified sponge was superhydrophobic and superoleophilic,<sup>25-30</sup> and it effectively heated up the heavy oil under solar radiation and reduced its viscosity by two orders of magnitude. The photothermal sponge was able to rapidly capture heavy oil 20 times of its own weight under simulated solar light illumination, and can be reused repeatedly with more than 85% of oil recovery capability. This solar-assisted photothermal oil sorbent design is believed to inspire more research efforts towards heavy oil spill cleanups.

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** PU sponges were purchased from ITW Texwipe (USA). Ethyl acetate, hexadecane, paraffin oil, mineral oil, silicone oil, hexane, ethanol and multi-walled CNTs ( $\geq 98\%$  carbon basis, O.D.  $\times$  I.D.  $\times$  L  $10 \text{ nm} \pm 1 \text{ nm} \times 4.5 \text{ nm} \pm 0.5 \text{ nm} \times 3\text{-}6 \text{ }\mu\text{m}$ ) were purchased from Sigma-Aldrich. PDMS prepolymer (Sylgard 184) and silicone elastomer curing agent (weight ratio: 10:1) were supplied by Dow Corning. Gasoline, light crude oil and heavy oil were obtained from local stores at Thuwal, Saudi Arabia. Seawater was collected from Red Sea close to the campus of King Abdullah University of Science and Technology (KAUST) in Saudi

Arabia. All chemicals were used as received. Deionized water purified in a Milli-Q system was used in all experiments.

**2.2. Fabrication of CNT modified PU sponge.** The original PU sponge was first cleaned by hexane and ethanol successively assisted by ultrasonication and was then dried in an oven at 60 °C. The modified sponge was prepared by a dip-coating method. Briefly, 200 mg of CNT was added into 200 ml of PDMS prepolymer solution, which was prepared by dissolving PDMS in ethyl acetate with a concentration of 1 mg/ml. After ultrasonication for 20 min, silicone elastomer curing agent (20 mg) was added to the CNT/PDMS mixture suspension. Afterwards, the cleaned sponge was dipped into the CNT/PDMS mixture for 5 min, followed by drying under 80 °C for 4 h. The dipping and drying cycle can be repeated for multiple times. Finally, the CNT modified sponge was obtained by curing the sponge at 80 °C for 4 h.

**2.3. Characterization.** Scanning electron microscopy (SEM) images were taken with an FEI Quanta 600 s. The UV-Vis-NIR spectrum for diffusive reflection and transmission measurement was measured on an Agilent Cary 5000 UV-Vis-NIR spectrophotometer. Contact angles (CAs) were measured on a commercial contact angle system (OCA 35 of DataPhysics) at ambient temperature. The viscosity of heavy oil was measured by a rotatory viscometer (HAAKE Viscotester 6 plus & 7 plus, Thermo Scientific). The temperature and thermal images of the samples under the simulated sunlight illumination were recorded by an FLIR A655 infrared camera. Interfacial temperatures between sponge and the contacting liquid surface were recorded by an Oakton thermocouple thermometer with a 0.5 mm K-type thermocouple sensor. The simulated solar radiation was provided by a 150 W Oriel Solar Simulator with AM1.5 filter. Weight measurement was tested by laboratory balance (Mettler Toledo).

**2.4. Photothermal property.** (a) Photothermal property in air: A solar simulator with an intensity of  $1000 \text{ W m}^{-2}$  (one sun) was used and an infrared (IR) camera was used to collect thermal images and to record the surface temperature change of the samples in air. The unmodified PU sponge and CNT/PDMS-PU-4 sponges (diameter: 3.5 cm, thickness: 3 mm) were placed on a thermally insulating expanded polystyrene (EPS) foam plate and the measurements were conducted at constant ambient temperature ( $\sim 22 \text{ }^\circ\text{C}$ ). The surface temperature change curves of the sponges when the simulated sunlight was turn on and off were recorded. (b) Photothermal property on top of a heavy oil: The unmodified PU sponge and CNT/PDMS-PU-4 sponges were placed on the surface of a heavy oil layer, which floated on top of water body. The sponge was exposed under one sun illumination. The top surface temperatures of the original and modified sponges were recorded by IR camera and the bottom temperatures of the interfaces between the sponges and heavy oil were measured by a thermocouple.

**2.5. Oil absorption performance measurement.** To quantitatively evaluate sponge absorption capability of heavy oil, a customized testing system was assembled. The CNT modified sponge (diameter: 35 mm, thickness: 3 mm) was hung on a holder, which was connected to an electrical balance. A vertically moveable stage was placed into a polystyrene (PS) box, which could tune its height to make contact or break contact with the hung sponge right above it. The heavy oil was put on the vertically moveable stage and a solar simulator was placed on top of the sponge to provide light illumination. The stage was adjusted to make contact with the overhead sponge and the weight changes of the sponge were real time monitored and recorded by a computer.

The oil absorption rate (V) was calculated as:

$$V = \Delta m / T \quad (\text{Equation 1})$$

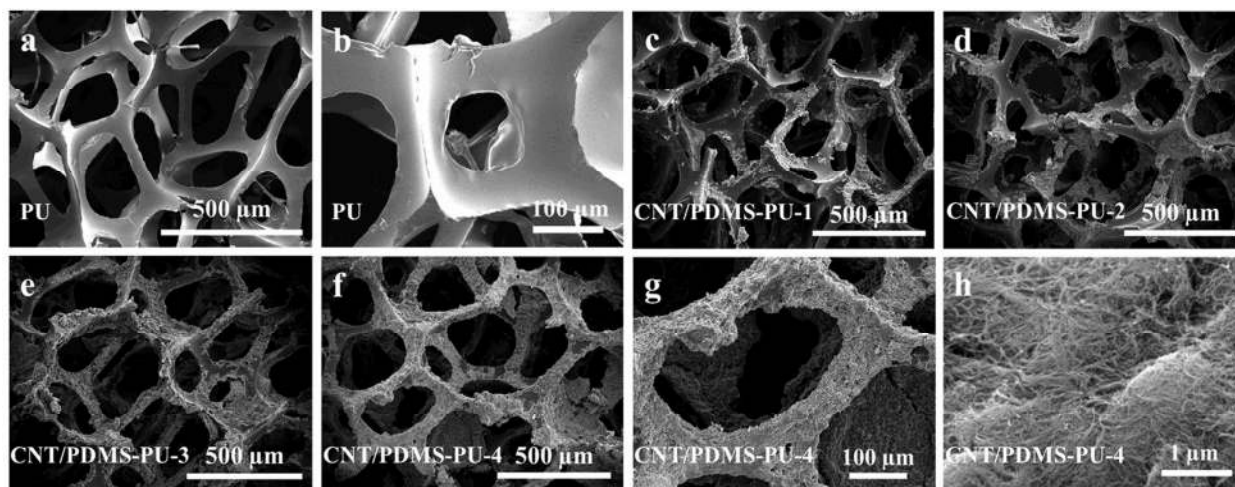
Where  $\Delta m$  is the weight of oil absorbed into the sponges per unit contact area ( $\text{g} \cdot \text{m}^{-2}$ ),  $T$  is the time of oil absorption (min).

### 3. RESULTS AND DISCUSSION

**3.1. The preparation of the CNT modified PU sponge.** Briefly, a PU sponge was modified by CNT with the PDMS acting as a binder to ensure a strong interaction between the CNTs and the PU sponge. The choice of PU sponge as the oil sorbent substrate is because of its thermal stability, elasticity, mechanical robustness, low cost and lightweight.<sup>31-32</sup> The CNT/PDMS was coated onto the sponge skeleton by dipping it into a CNT/PDMS mixture followed by curing at 80 °C to crosslink PDMS. The content of CNT/PDMS in the modified sponge can be tuned by repeating the dipping and curing processes for multiple cycles. For the convenience of discussion, the CNT/PDMS modified sponge is denoted as CNT/PDMS-PU- $x$ , with  $x$  being the number of modification cycles.

Figure 1 compares the SEM images of the sponge before (Figure 1a-b) and after (Figure 1c-h) CNT/PDMS modification. Clearly, the content of CNT/PDMS coatings increases with increasing modification cycles. The loading amount of CNT on CNT/PDMS-PU-1, CNT/PDMS-PU-2, CNT/PDMS-PU-3, and CNT/PDMS-PU-4 was estimated to be 5.1%, 9.2%, 15.2%, and 20.6%, respectively. A homogeneous and compact CNT/PDMS surface coating with micro-nano structure uniformly wraps on the skeleton of the PU sponge after 4 cycles of modification (CNT/PDMS-PU-4) (Figure 1g-h). Neither CNT/PDMS aggregates nor PU pore blockage are observed, implying the robustness of the modification method. As the CNT content increases, the modified sponge appears darker (Figure S1) due to the light absorption by CNTs.<sup>33-36</sup> As a

control, in the absence of the PDMS, the CNTs tend to aggregate and the CNT aggregates can be easily washed off the PU sponge (Figure S2), highlighting an essential role of the PDMS in the method.



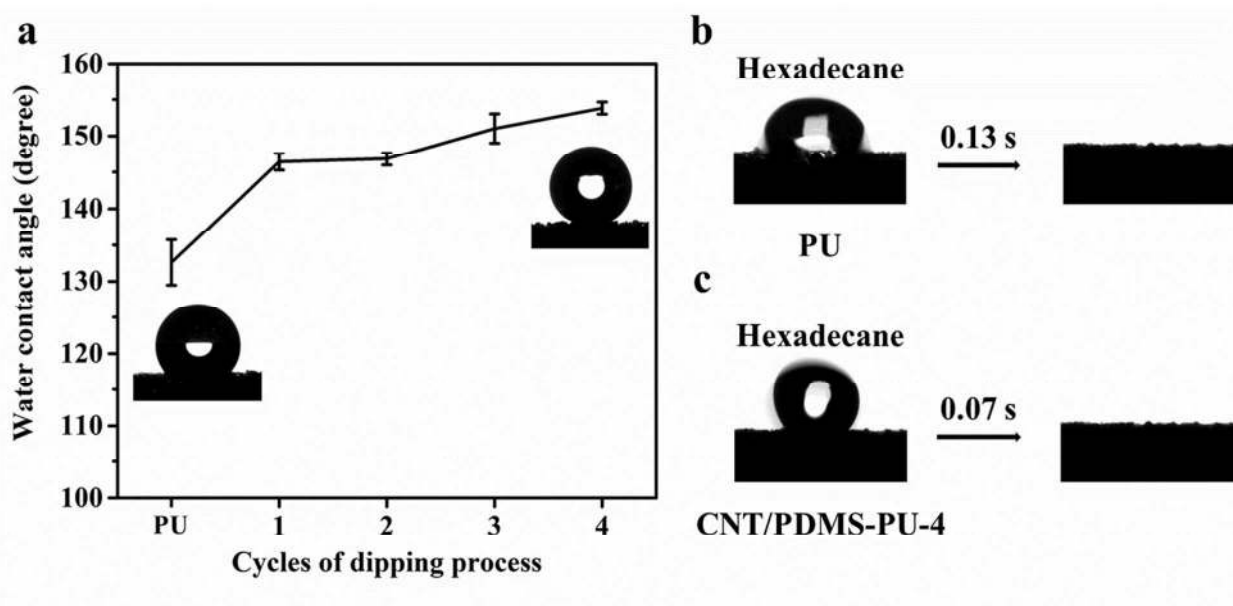
**Figure 1.** SEM images of (a) the unmodified PU sponge and its enlarged view (b), and the CNT modified PU sponges with 1 through 4 modification cycles (c-f). (g-h) Enlarged view of the micro-nano structure in (f).

The CNT/PDMS modification increases surface roughness of the sponge, which leads to enhanced hydrophobicity. The water contact angles on the surface of the modified sponges increase with increasing number of modification cycles (Figure 2a), with the CNT/PDMS-PU-4 sponge having a water contact angle of  $154 \pm 0.8^\circ$  vs.  $133 \pm 3^\circ$  on the unmodified sponge. As a result, hexadecane spreads out on the surface of CNT/PDMS-PU-4 sponge faster than on that of the unmodified sponge (spreading time: 0.07 vs. 0.13 s) (Figure 2b-c), exhibiting its superoleophilicity. The sliding angle of water droplet on the CNT/PDMS-PU-4 sponge was  $10^\circ$ , indicating a low water adhesive force (Figure S3a-d). When the sponge was entirely immersed into water, water couldn't permeate into the pore space of the sponge (Figure S3e-f) while a high-density silicon oil under water was quickly sucked into the sponge upon contact with the



sponge (Figure S3g-h). These results demonstrate the selective oil absorption of CNT/PDMS-PU-4 sponge owing to its superhydrophobic and underwater superoleophilic properties.

The oil absorption capacities ( $k$ ) of various light to medium oils (hexadecane, gasoline, hexane, light crude oil, paraffin oil, mineral oil, silicone oil) of CNT/PDMS-PU-4 sponge were measured by measuring the weight of the oil-soaked CNT/PDMS-PU-4 sponge after the weighed sponge was immersed into the oil liquid for 5 minutes at room temperature (Equation S1, Figure S4). The results show that CNT/PDMS-PU-4 sponge is capable of absorbing oil 12-24 times its own weight, depending on the oil density and swelling extent of the sponge in different oils. The high oil absorption capacity of the modified sponge is attributed to its high porosity (96%, estimated by Equation S2 in Supporting Information (SI)).

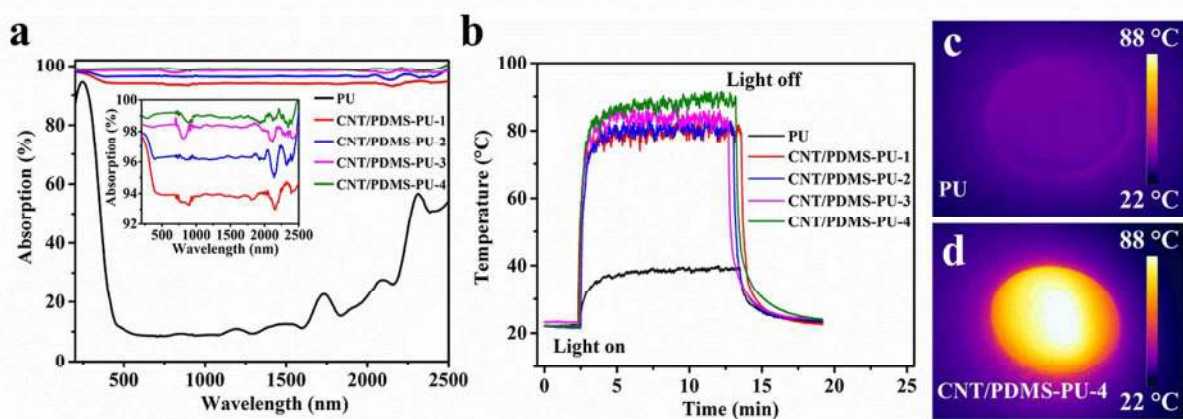


**Figure 2.** (a) Water contact angles of the sponges with modification cycles from 0 to 4. Hexadecane spreading out on the surface of the unmodified PU sponge (b) and CNT/PDMS-PU-4 sponge (c).

**3.2 Photothermal property.** To demonstrate the superior light absorption capability, the diffusive reflection and transmission of the unmodified and modified PU sponges were measured (Figure S5). Clearly, the CNT modified PU sponges have average light diffuse reflection of < 4 % and transmission of <3% in the range of 200 to 2500 nm, compared with 37% and 39% of the unmodified PU sponge respectively. The light diffuse reflection and transmission of the modified sponges decrease with the increasing number of modification cycles, with the CNT/PDMS-PU-4 sponge showing only 1% light diffuse reflection and almost zero transmission. The light absorption is calculated by deducting the light diffuse reflection and transmission from total incident light and is presented in Figure 3a. Consequently, the average light absorption of the CNT modified sponges is >94%, compared to ~24% for the unmodified PU sponge (Figure 3a). In particular, the CNT/PDMS-PU-4 sponge shows 99% sunlight harvesting performance. The greatly enhanced light absorption capability of the modified sponges is attributed to the outstanding photothermal property of CNT, which is known to have a strong light absorbing capability in the entire solar spectrum range.<sup>33-36</sup>

We further investigated the solar-thermal conversion performances of the sponges. To this end, all samples were placed on a thermally insulating EPS foam plate to minimize the heat loss (Figure S6), and an IR camera was used to collect thermal images and to record the temperature change of the samples in air. As shown in Figure 3b-d, under solar irradiation the unmodified PU sponge achieves an equilibrium surface temperature of 38 °C while the equilibrium surface temperature of CNT/PDMS-PU-4 sponge reaches 88 °C. The temperatures of the CNT modified samples increase rapidly when the light is on (Figure 3b), indicating their strong solar light absorbance and effective light-to-heat conversion performance.

Thermal conductivity of the sponge is an important parameter in this project as it affects the heat transfer from the top surface to the bottom of the sponge. The top part of the sponge captures and converts sunlight into heat and transfers the generated heat to the bottom part which is directly contacted with the targeted heavy oil. The equilibrium temperature difference ( $\Delta T$ ) of the top and bottom surfaces of CNT/PDMS-PU-4 sponge under one sun illumination is 12 °C, and the thermal conductivity is thus estimated to be 0.17 W m<sup>-1</sup> K<sup>-1</sup> while that of the PU sponge without CNT modification on the skeleton of the sponge is 0.12 W m<sup>-1</sup> K<sup>-1</sup> (the measurement details can be found in SI). The enhanced thermal conductivity of the CNT/PDMS-PU-4 sponge is supposedly due to the interconnected CNTs in the sponge, which provides additional heat transfer pathways.<sup>37</sup>



**Figure 3.** (a) UV-vis-NIR absorption spectra of the original and modified PU sponges with modification cycles from 1 to 4. Inset in (a) shows the details of the modified sponges. (b) Time course of the surface temperature of the original and modified sponges and IR thermal images of (c) the original and (d) CNT/PDMS-PU-4 sponges under one sun illumination in air.

**3.3 Temperature-dependent viscosity and absorption of heavy oil.** Oil viscosity is a critical parameter that determines the oil absorption rate by macroporous sponges. We investigated the

dependence of viscosity of heavy oil used in this work on its temperature (Figure 4a). The pristine heavy oil was highly viscous (110873 mPa·s) at 22 °C. The inset image in Figure 4a shows that the oil is very thick and sticky at 22 °C and when poured, it is resistant to flow and behave like semi-solid. The viscosity of the heavy oil decreases sharply with increasing the temperature of heavy oil. The oil viscosity decreases to 21801 mPa·s at 30 °C, 4106 mPa·s at 40 °C, and 1639 mPa·s at 50 °C, which is almost two orders of magnitude lower than the one at 22 °C. As shown in Figure 4a, at 70°C, when poured, the heavy oil flows freely the same way light oil does. This dramatic decrease of the oil viscosity improved the kinetics of oil absorption (Figure 4b). When a heavy oil droplet (~10 µl) is dropped on top of CNT/PDMS-PU-4 sponge at 22 °C, it takes as long as 24 h for the sponge to absorb the oil. In contrast, when CNT/PDMS-PU-4 sponge is heated by a hot plate, the heavy oil permeates entirely into the same sponge within 60 min at 30 °C, 8 min at 40 °C, and merely 45 s at 50 °C. This result clearly demonstrates that the oil absorption can be greatly accelerated by only slightly heating the oil to a higher temperature.

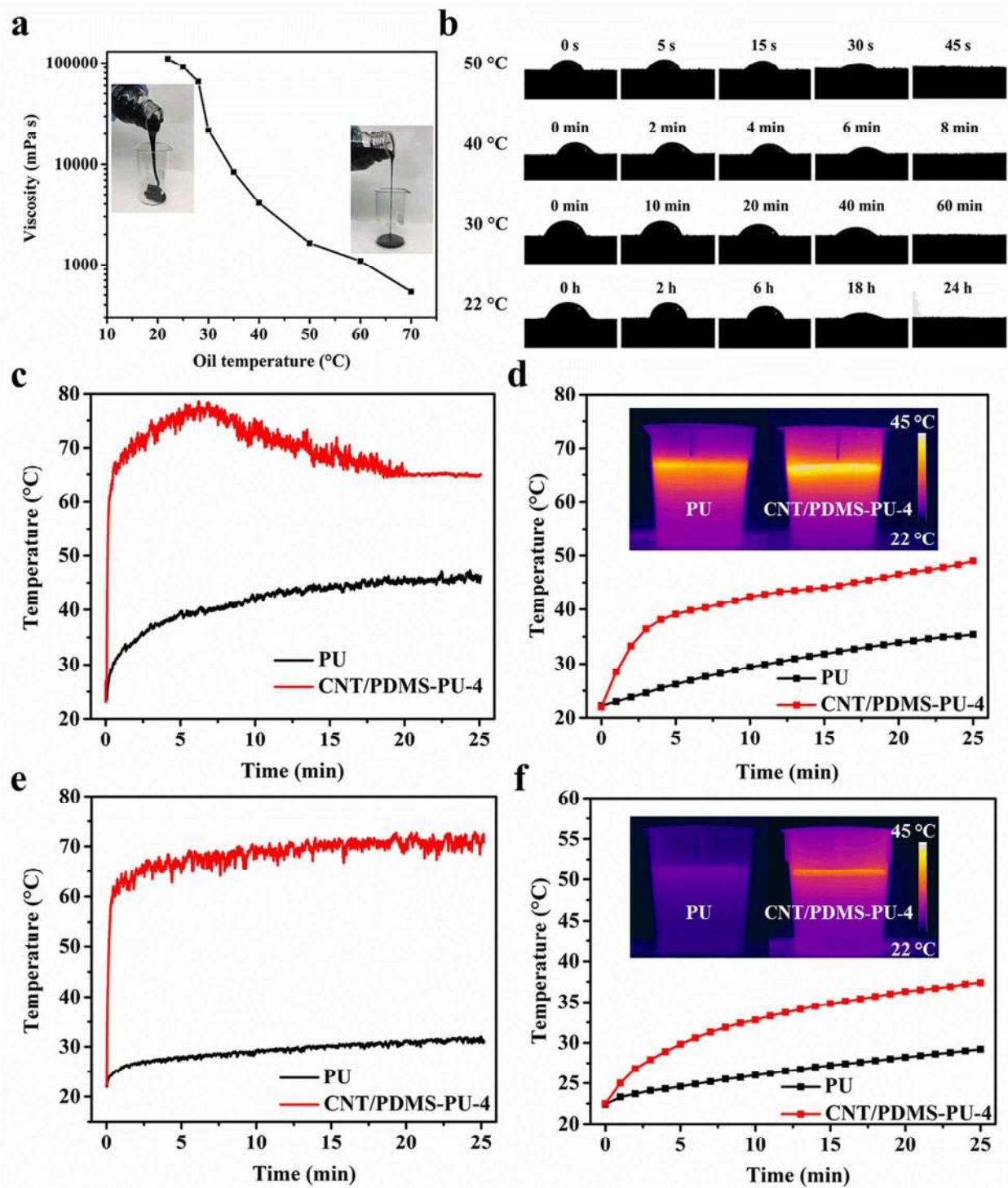
**3.4 Solar-assisted absorption of heavy oil.** In conducting oil absorbability test, the unmodified PU sponge and CNT/PDMS-PU-4 sponges were placed on the surface of a heavy oil layer, which floated on top of water body, as shown in Figure S8a. Figure 4c compares the time course of the top surface temperature of the original and CNT/PDMS-PU-4 sponge when placed on top of the heavy oil layer, which shows an obviously greater temperature rise with the modified sponge than the original one when the light is turned on. After being exposed under one sun illumination for 6 min, the surface temperature of CNT/PDMS-PU-4 sponge reaches its highest temperature of 78 °C, which is slightly lower than that of the same sponge placed on the polystyrene foam plate (88 °C) (Figure 3b) due to the heat transfer to the underlying oil. There is

an immediate surface temperature decline right after the highest temperature point. It can be attributed to the cooling of the sponge by the rapid entrance of the heavy oil after reaching a critical temperature with sufficiently low viscosity. In addition, as oil occupies the pores of the sponge, it greatly increases the thermal conductivity of the entire sponge, which leads to a slightly lower surface temperature comparing to surface temperature recorded from the sponge that was put on top of a thermal insulator EPS foam.

After 20 min solar irradiation, the temperature of CNT/PDMS-PU-4 sponge is significantly higher than that of the original PU sponge (Figure 4d) due to the outstanding light capture capability of CNT/PDMS-PU-4 sponge. Naturally, a higher interfacial temperature between CNT/PDMS-PU-4 sponge and the contacting oil is recorded than the case with the original sponge (Figure 4d).

Similarly, when placed on top of water under identical conditions (Figure S8b), CNT/PDMS-PU-4 sponge exhibits higher top surface and bottom sponge-water interfacial temperatures than the unmodified PU sponge (Figure 4e,f). However, when placed on top of the water, the decline in the surface temperature of CNT/PDMS-PU-4 sponge does not occur. This difference confirms our hypothesis that the sudden top surface temperature decrease of CNT/PDMS-PU-4 in Figure 4c was caused by the absorption of oil. In contrast, water cannot permeate into the pore of the superhydrophobic sponge, which prevents such temperature drop. Compared with the situation of the modified sponge on top of the oil layer, a slightly lower water-sponge interfacial temperature (i.e., 36 °C under 20 min light irradiation) is obtained (Figure 4f). This can be explained by the fact that water possesses higher thermal conductivity than heavy oil,<sup>18</sup> leading to a faster heat loss in that case. From Figure 4a, the temperature of 36 °C at the photothermal sponge and water interface can still lead to significantly reduced oil viscosity and thus much fast

oil penetration rate into porous sorbents (Figure 4b), implying the utility of the photothermal sponges in picking up non-continuous, isolated, and thin heavy oil films floating on water surfaces.



**Figure 4.** (a) The change of the heavy oil viscosity as a function of oil temperature. Inset shows the images of pouring oil at the temperature of 22 °C (left) and 70 °C (right). (b) The permeating

behavior of one heavy oil droplet (10  $\mu\text{l}$ ) on the surface of CNT/PDMS-PU-4 sponge with increasing the surface temperature of the sponge from 22 to 50  $^{\circ}\text{C}$ . (c-f) Time course of the surface temperatures of the original and CNT/PDMS-PU-4 sponges placed on top of oil (c) and water (e). Oil-sponge (d) and water-sponge (f) interfacial temperature comparison of the unmodified versus CNT/PDMS-PU-4 sponges (3 mm thickness) under  $1000 \text{ W m}^{-2}$  one sun irradiation. The inset figures in (d) and (f) are corresponding the IR images of the original and CNT/PDMS-PU-4 sponges placed on top of oil and water after 20 min solar irradiation.

The oil absorption kinetics of the sponge under simulated sunlight were then measured in a lab-made set-up as shown in Figure 5a and Figure S9. The CNT/PDMS-PU-4 sponge was fixed by a framework connected to an analytical balance for testing weight changes. The heavy oil inside a cup was gradually lifted up till the oil surface contacted with the bottom surface of the sponge.

Upon contact, the measured sponge weight jumps immediately and sharply (Figure 5b). This is because the oil adheres onto the bottom of the sponge and the adhesion force between the oil and sponge in this case contributes to this weight change. The sponge is let sit on the oil surface for 17 min in the absence of light illumination during which no weight change of the sponge is observed, showing that the oil is unable to permeate into the sponge at room temperature without light illumination during this period of time.

As light is turned on, the sponge will be heated up under solar radiation, the heavy oil underlying the sponge will then be gradually heated by the sponge, resulting in decreased oil viscosity there. Once the oil viscosity reached certain point, the oil got absorbed into the pore of the sponge, and the absorbed oil mass was real time monitored. The weight of the CNT/PDMS-



PU-4 sponge remains stable for around 6 min after the light is turned on, followed by a sharp rise due to the infiltration of the oil into the sponge. This result agrees well with the time course of the interfacial temperature between CNT/PDMS-PU-4 sponge and oil and temperature-dependent viscosity of heavy oil. During the first 6 min of light illumination, the oil-sponge interfacial temperature shows a sharp rise to nearly 40 °C (Figure 4d), corresponding to a reduction of its viscosity to 4106 mPa·s (Figure 4a). In this process, the solar-generated heat is conducted through the modified sponge from its top surface to the underlying heavy oil, decreases the oil viscosity, and thus allows a rapid oil absorption into the sponge.

It is observed that, during this process, CNT/PDMS-PU-4 sponge gradually sinks into the oil slick as it gradually adsorbs oil from the bottom. As oil continues to spread into and occupy its pores, the sponge becomes entirely immersed into the oil in the end. As shown in Figure 5b, the weight of the sponge reaches a plateau at 9 min, indicating the sponge reaches its oil saturation. As the stage is moved downward to separate the sponge from the residual oil, the sponge weight initially increases, followed by a return to a constant value after the residual oil breaks off from the sponge. As a result, the weight difference ( $\Delta m_{\text{CNT/PDMS-PU}}$  of 2.7 g) in Figure 5b represents the oil absorption mass of CNT/PDMS-PU-4 sponge during the whole oil absorption process (15 min), which is more than 20 times the weight of the CNT/PDMS-PU-4 sponge (0.13 g). As a comparison, the oil absorption mass of the unmodified sponge reaches only 1.3 g after 40 min light illumination and at that time the oil adsorption has not reached its saturation yet (Figure S10) due to the relatively higher oil viscosity here than in the case with the modified sponge. The oil absorption rates of CNT/PDMS-PU-4 sponge and the original PU sponge are thus calculated to be 188 and 34  $\text{g}\cdot\text{m}^{-2}\cdot\text{min}^{-1}$ , respectively. The nearly 5.5 times faster oil adsorption rate by the

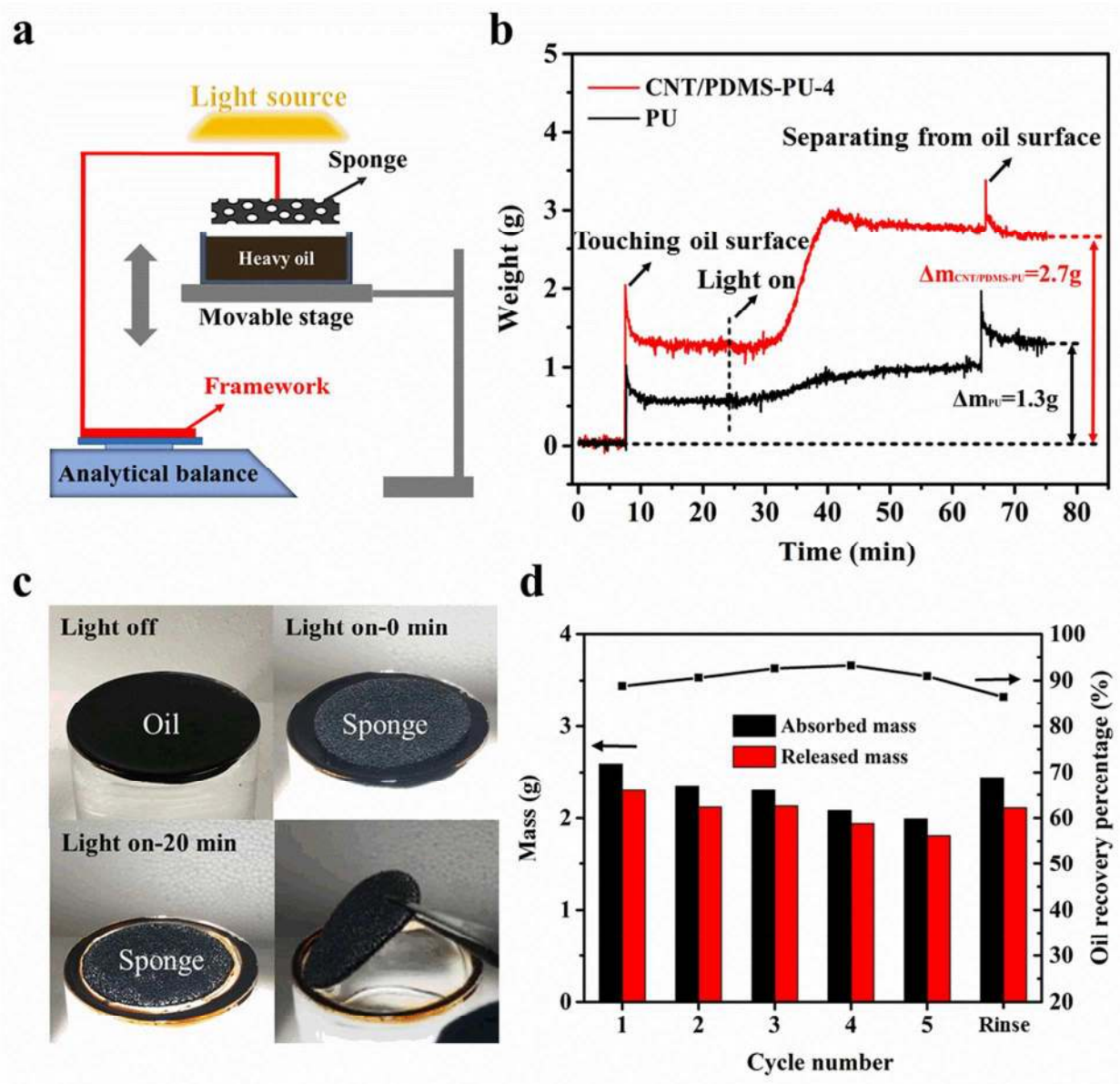
CNT/PDMS-PU-4 sponge clearly demonstrates the advantages of our solar-photothermal sponge design to deliver a faster and more cost-effective heavy oil cleanup.

In addition, to simulate a practical scenario of the heavy oil spill cleanup, 2.7 g of the heavy oil was placed and covered on the surface of seawater collected from Red Sea in a quartz cup with diameter of 45 mm. As shown in Figure 5c, CNT/PDMS-PU-4 sponge (diameter: 35 mm, thickness: 3 mm) was then placed on top of the heavy oil followed by light illumination for 20 min. The result shows that the sponge adsorbed almost of all the heavy oil (2.5 g) at the end of the treatment, except the residual oil adhered on the cup wall. The seawater originally underlying the oil could be clearly seen after the oil slick is adsorbed and removed. In contrast, the original PU sponge cannot realize the cleanup process of heavy oil during 20 min light illumination (Supporting Movie 1).

By tuning the light intensity from 600 to 800, 1000 and 1200 W m<sup>-2</sup>, the surface temperature of CNT/PDMS-PU-4 increased from 52.2 to 65.0 °C (Figure S11a) while the temperature of the oil-sponge interfacial zone increased from 37.8 °C (600 W m<sup>-2</sup>, 20 min) to 50.1 °C (1200 W m<sup>-2</sup>, 20 min). When the light intensity was 600 W m<sup>-2</sup>, CNT/PDMS-PU-4 absorbed 1.22 g oil owing to its low oil-sponge interfacial temperature (37.8 °C). However, when the light intensity was greater than 600 W m<sup>-2</sup>, namely 800, 1000 and 1200 W m<sup>-2</sup>, the amount of heavy oil absorbed by the sponge was 2.67, 2.71, and 2.74 g respectively, after 20 min light exposure (Figure S11b).

The recoverability of the absorbed oils and the reusability of the oil sorbent are very important in practical oil cleanup. Here in this work, the sponge was first oil-saturated by 20 min simulated light illumination and then manual squeezing was applied to force out the heavy oil from the oil-saturated sponge. The same sponge was then reused for the oil adsorption and release again for

multiple times. As shown in Figure 5d, the CNT/PDMS-PU-4 sponge shows a high percentage of oil recovery (over 85%) during 5 cycles of oil adsorption and release. The slight decrease in both oil absorption and release mass is due to the residual oil adhesion on the sponge surface. By rinsing in organic solvent (hexane), the residual oil in the sponge can be removed and the oil absorption capability can be recovered to 94% of the pristine CNT/PDMS-PU-4 sponge. According to the SEM observation (Figure S12), the morphology of the sponge surface did not show an obvious change after 5 cycles of oil absorption and extrusion and rinsing in hexane. These results demonstrate the reusability and recyclability of both the photothermal sponge and its capture heavy oil.



**Figure 5.** (a) Schematic illustration of the lab setup of the solar-assisted oil spill cleanup measurement system. (b) Weight of the oil absorbed into the original (black curve) and CNT/PDMS-PU-4 sponge (red curve) as a function of time at 22 °C. (c) The practical scenario of the oil spill cleanup process. (d) The mass of heavy oil absorption and release of the CNT/PDMS-PU-4 sponge (diameter: 35 mm, thickness: 3 mm) at each oil absorption-recovery cycle under  $1000\text{ W m}^{-2}$  light illumination.

## 4. CONCLUSIONS

In conclusion, we demonstrate for the first time a photothermal oil sorbent to realize a solar-assisted rapid cleanup of heavy oil spill. The CNT modified photothermal sponge fabricated in this work exhibits an efficient heavy oil absorption capability. With the photothermal sponge, the viscosity of the heavy oil dramatically decreases by two orders of magnitude under solar irradiation, which leads to a much faster and effective heavy oil capture compared with the unmodified sponge. This novel photothermal-assisted heavy oil adsorption approach has a great potential to be used in highly efficient remediation of viscous oil-spills.

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