

Supporting Information

Solar-Driven Self-Heating Sponges for High-Efficient Crude Oil Spill Remediation

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Experimental Section

Materials: Dopamine hydrochloride was purchased from Sigma-Aldrich (China). Tetraethyl orthosilicate (TEOS), hexane, ditin butyl dilaurate, CuSO₄, H₂O₂ and tris(hydroxymethyl) aminomethane were obtained from Sinopharm Chemical Reagent Co. Ltd (China). Dihydroxyl-terminated polydimethylsiloxane (PDMS(OH), average molecular weight: 400 g/mol) was purchased from Wuxi Quanli Chemical Co., Ltd. (China). The melamine sponges were bought from Clean Wrap Company (China) (average pore size: 120 μm). The crude oil was kindly provided by PetroChina Co. Ltd (China). All the reagents were used as received without further purification. The water used in all experiments was deionized and ultrafiltered to 18.2 MΩ·cm with an ELGA 136 LabWater system (France).

Preparation of the self-heating hydrophobic/oleophilic sponges: The melamine sponges were firstly washed by ethanol to remove adsorbed impurities and then dried in a vacuum

oven at 60 °C. PDA deposition was conducted according to our previous method.^[13a] Briefly, dopamine hydrochloride (2 mg/mL), CuSO₄ (5×10^{-3} M) and H₂O₂ (19.6×10^{-3} M) were dissolved in Tris-buffer solution (200 mM, pH 8.5), and then the sponges were immersed into the aqueous solution for 40 min, followed by water rinsing and dried in vacuum oven at 60 °C. Multi-deposition of PDA was operated by repeating the above-described process to enhance the photothermal conversion effect. Finally, the as-prepared PDA-coated sponges were put into hexane solution with PDMS (OH) (10 g/L)/TEOS (0.5 g/L)/ditin butyl dilaurate (0.05 g/L) for 30 min and then moved into an oven at 60 °C for 2 h. As a control, blank sponges were modified to hydrophobic only with PDMS (OH)/TEOS/ditin butyl dilaurate mixture.

Characterization: The porous morphologies were observed by the field emission scanning electron microscopy (FESEM, Hitachi, S4800, Japan). The chemical compositions of the sponge surfaces were characterized by an X-ray photoelectron spectrometer (XPS, PerkinElmer, USA) with Al K α excitation radiation (1486.6 eV). The surface wettability was analyzed on the basis of water contact angle measurement using the drop Meter A-200 contact angle system (MAIST Vision Inspection & Measurement Co. Ltd, China). The absorption and reflectance spectra were measured using a ultraviolet spectrophotometer (UV 2450, Shimadzu, Japan). The viscosity of the crude oil was determined by a rotational rheometer (MCR302, Antonpaar, Austria). The surface temperatures of the samples were analyzed by a thermal infrared camera (FLIR E60, Flir System. Inc., USA). The structural stability of the sponges was studied by Instron

3343B11658 system (Instron, USA) and the stress-strain curves were obtained with a strain rate of 50 mm/min.

Static crude oil adsorption measurement: During the static adsorption process, abundant crude oil was contained in a beaker, and then a sponge sample with $2 \times 2 \times 1$ cm shape was placed on the oil surface. The sunlight was provided by a solar simulator (PL-XQ500W, Changzhou Hongming Instrument Technology Co., Ltd, China) and the power density was about 1.5 kW/m^2 . We recorded the mass changes of the different sponges every 1 min under simulated sunlight irradiation. The oil adsorption capacity (A , g/m^3) was calculated according to the following equation:

$$A = \frac{m_1 - m_0}{V}$$

where m_0 and m_1 represent the weight (g) of sponges before and after oil adsorption, respectively. V is the volume (m^3) of sponges.

Continuous crude oil recovery method: Water (100 mL) and crude oil (50 mL) were added into a beaker to simulate real oil spill pollution. A hydrophobic/oleophilic PDMS/PDA-coated sponge ($2 \times 2 \times 1$ cm) was equipped with a homemade device and then placed into the pollutant surface, where the sponges were floated on the crude oil surface. One end of a pipe was connected with the sponge while the other end was linked with a peristaltic pump (300 RPM). The pump's outlet was connected to a collecting beaker. In this process, the sunlight power density was about 1.5 kW/m^2 , and the PDMS-coated sponges were used as the reference to carry out the similar experiments.

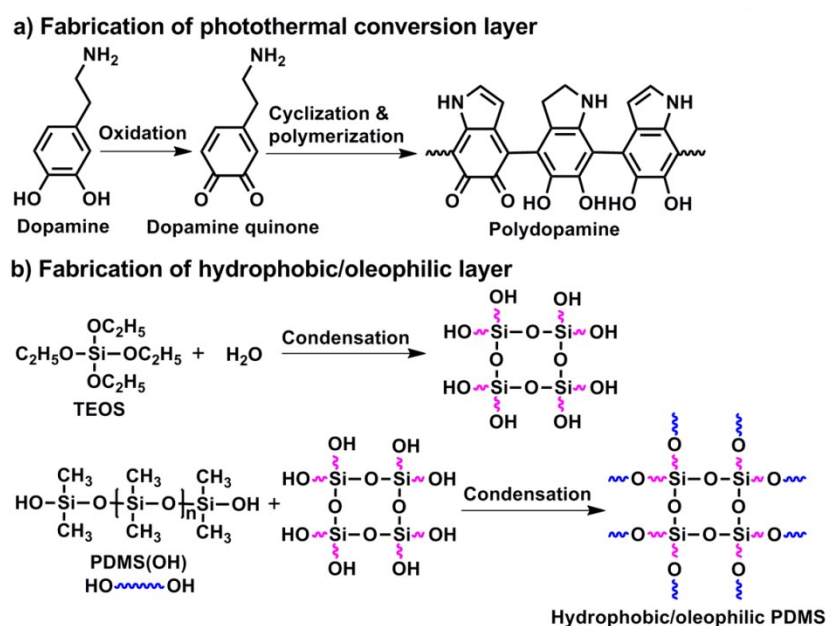


Figure S1. Schematic illustration of the reaction mechanism for fabricating self-heating hydrophobic/oleophilic sponges: (a) Mechanism of photothermal conversion layer formation via a typical mussel-inspired PDA deposition, (b) Mechanism of hydrophobic/oleophilic layer construction. The hydrophobic/oleophilic layer mainly comprises of PDMS, which was fabricated via a condensation reaction between dihydroxyl-terminated polydimethylsiloxane (PDMS(OH)) and tetraethyl orthosilicate (TEOS) using dibutyltin dilaurate as a catalyst.

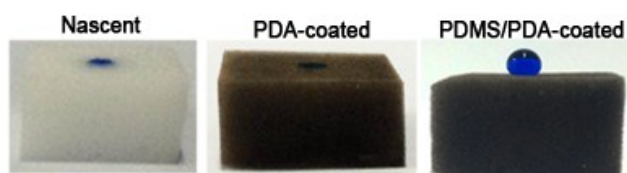


Figure S2. Digital images of a water drop on the surface of nascent, PDA-coated and PDMS/PDA-coated sponges. The water drop was dyed by methyl blue. As we can see, the nascent and PDA-coated sponges are very hydrophilic. However, the surface wettability is instantly transformed from hydrophilicity to hydrophobicity after the participation of PDMS layer. In addition, the color of the PDMS/PDA-coated sponges still remains black.

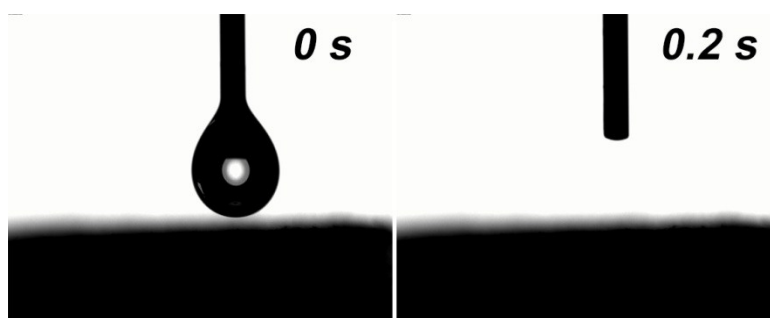


Figure S3. Images of oil contact angle measurement for PDMS/PDA-coated sponges. 1, 2-dichloroethane was selected as the model oil in this experiment.

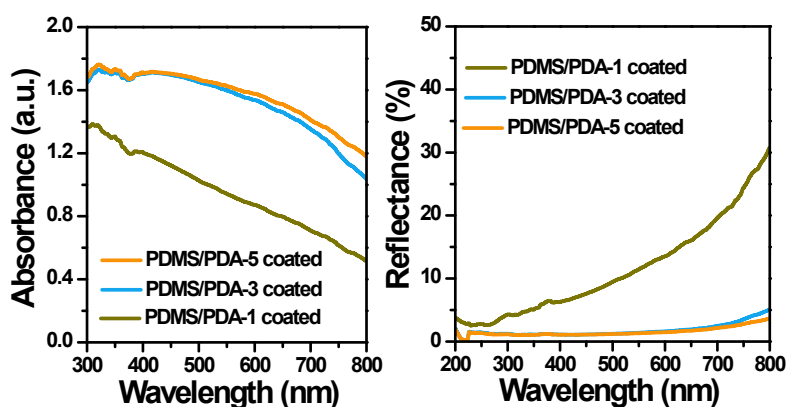


Figure S4. UV-vis absorption spectra and diffusive reflectance spectra of different sponges. PDMS/PDA1, PDMS/PDA3 and PDMS/PDA5 represent the deposition cycles of PDA are 1, 3 and 5, respectively. The deposition time of every cycle is 40 min. The environment humidity is 60%. All the experiments were executed at room temperature. It is obvious that along with the increase of PDA deposition cycle, the light absorbability constantly increases, and PDMS/PDA3-coated and PDMS/PDA5-coated sponges hold a similar light absorption, indicating an equal photothermal conversion efficiency.

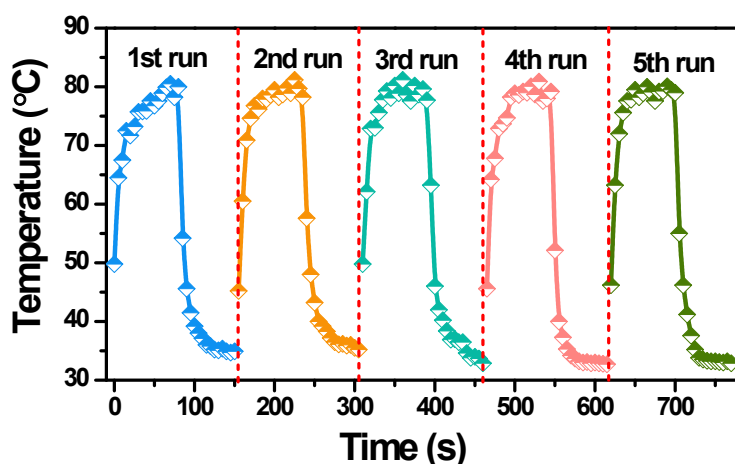


Figure S5. Reusability of the photothermal conversion effect of self-heating sponge under the simulated sunlight irradiation. Every run includes two process: temperature-rise and temperature-fall period. The simulated sunlight power density is about 1.5 kW/m^2 . The sponge size is $2 \times 2 \times 1 \text{ cm}$. The environment humidity is 60%. All the experiments were executed at room temperature. The self-heating sponges still possess excellent photothermal conversion effect under multiple cycles of simulated sunlight on-off cycles, demonstrating that the PDA coating is very stable and robust without any damages after multiple photothermal conversion processes.

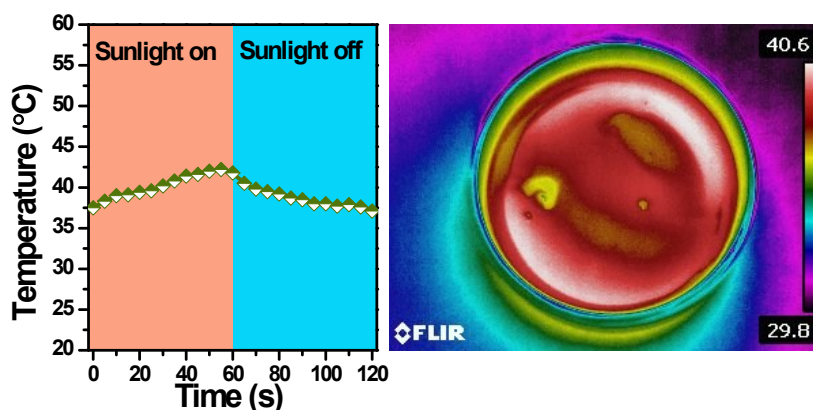


Figure S6. Time-dependent temperature evolution curves and IR images of high viscosity crude oil under sunlight irradiation. The orange and blue region in left image represent temperature-rise and temperature-fall period, respectively. The environment humidity is 60%. All the experiments were executed at room temperature. It clearly shows the crude oil temperature only increases about $4 \text{ }^\circ\text{C}$ after 60 s sunlight irradiation, indicating crude oil has the low photothermal conversion efficiency.

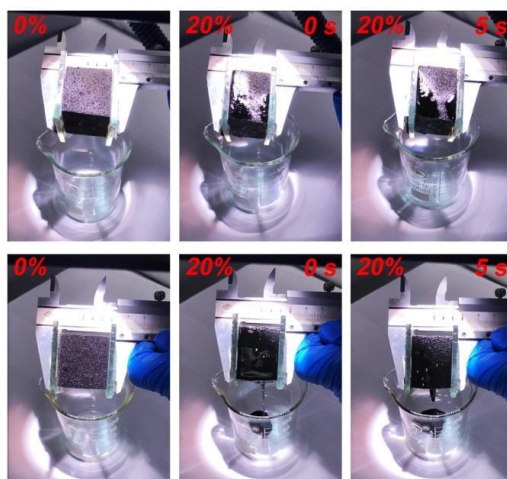


Figure S7. Recovery of high viscosity crude oil from (a) the PDMS-coated and (b) the PDMS/PDA-coated sponges by compressing corresponding sponge strain under the simulated sunlight irradiation. Before the strain experiment, PDMS-coated and the PDMS/PDA-coated sponges first adsorb the equal crude oils. The simulated sunlight power density is about 1.5 kW/m^2 . The sponge size is $2 \times 2 \times 1 \text{ cm}$. The environment humidity is 60%. All the experiments were executed under room temperature. It can be seen that the crude oils can be immediately squeezed from the PDMS/PDA-coated sponges when the sponges are compressed by 20 % of strain. With increasing the compressive time, a growing amount of crude oils are extruded, indicating that the adsorbed crude oils can be high-efficiently recovered. In contrast, there are no crude oils outflowed from the PDMS-coated sponges upon the same compressive force.

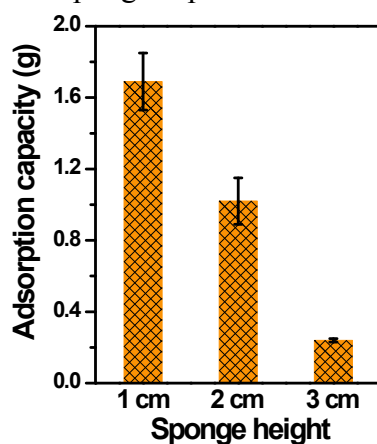


Figure S8 Influence of the sponge height on adsorption capability of the crude oil. The contact area between the crude oil and the sponge is kept the same ($2 \times 2 \text{ cm}^2$). The adsorption time is 3 min. It is obvious that the adsorption capability of the crude oil gradually decreases along with the increase of sponge height due to the increase of the thermal conductive pathway. Therefore, we found a suitable sponge height with the value of 1 cm in our experiments, so as to achieve a relatively high adsorption capability. Inspired by this, increasing thermal conductivity of the material is a good idea to enhance the adsorption capability.

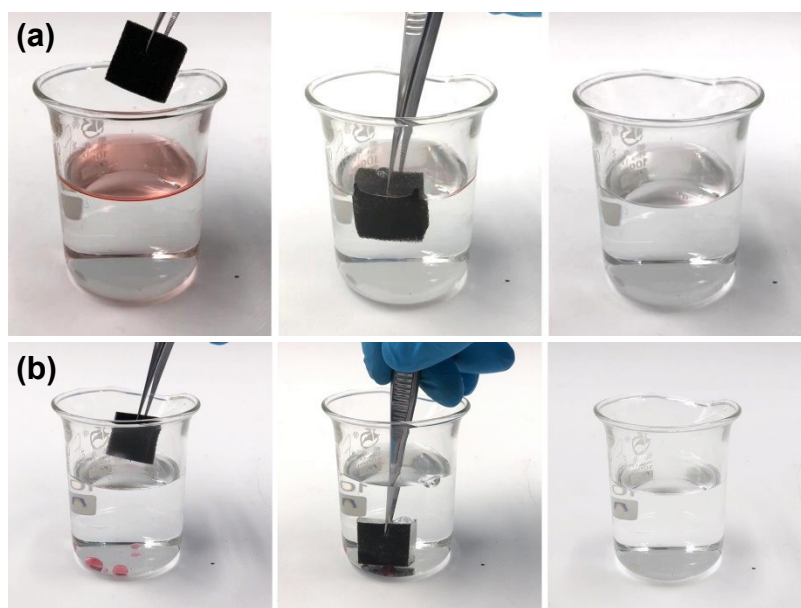


Figure S9. Digital images for the process of absorption and collection of non-polar solvent (dyed with oil red) from the surface of water: (a) n-hexane and (b) 1, 2-dichloroethane.

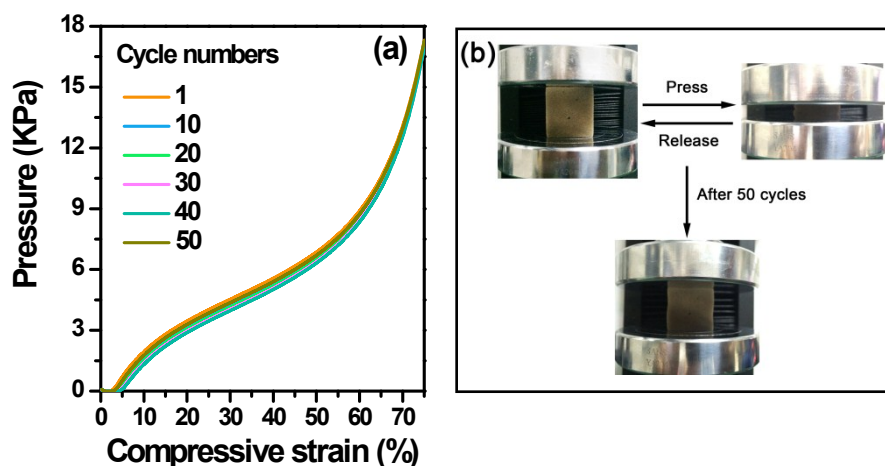


Figure S10. (a) Cyclic compressive stress-strain curves of self-heating sponge. (b) Digital photographs of self-heating sponge during the compression process. The environment humidity is 60%. All the experiments were executed at room temperature. It can be seen that the stress-strain curves almost overlap with the initial state after 50 experimental cycles, and the sponge shape can be well recovered even after multiple compression-recovery cycles. These results suggest that our self-heating sponges possess excellent elastic property and flexibility, which enables the materials with good manipulation processibility for device fabrication and oil recovery.

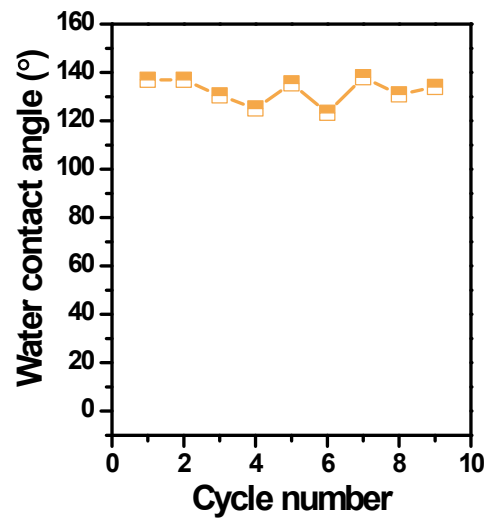


Figure S11. Water contact angle of PDMS/PDA-coated sponges after multiple adsorption-desorption cycles.