Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
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Electronic Supplementary Information (ESI)

Photothermal Induced In-situ Double Emulsion Separation by a Carbon Nanotube/Poly(N-isopropylacrylamide) Modified Membrane with Superwetting Property

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I. Calculation

The specific simplify process of the Cassie-Baxter equation:

The Cassie-Baxter equation:

$$cos\theta = f_1 cos\theta_1 + f_2 cos\theta_2 \quad \text{……………………………..…(S1)}$$

Substituting $f_1 + f_2 = 1$ into Equation S1, we obtained Equation S2 as follows

$$cos\theta = f_1 cos\theta_1 + (1 - f_1) cos\theta_2 \quad \text{………..………………(S2)}$$

f_1: the apparent area fraction of IAHB

f_2: the apparent area fraction of IEHB

$cos\theta_1$: the cosine of the WCA on IAHB

$cos\theta_2$: the cosine of the WCA on IEHB

$cos\theta$: the cosine of the WCA on the material

The WCA on IEHB was 0°, so the Equation S2 can be written as:

$$cos\theta = f_1 cos\theta_1 + 1 - f_1 \quad \text{………………………….……(S3)}$$

As a result,

$$f_1 = \frac{1 - cos\theta}{1 - cos\theta_1} \quad \text{………………….……………...………(S4)}$$

In this work, the WCA of IAHB part is between 150°-180°.

Substituting θ_1=150° into Equation S4, we obtained:

$$f_1 = \frac{1 - cos\theta}{1.866} \quad \text{……………………………...…………(S5)}$$

Substituting θ_1=180° into Equation S4, we obtained:

$$f_1 = \frac{1 - cos\theta}{2} \quad \text{……………………………………......(S6)}$$

Combing Equation S5 and Equation S6 together, the final interval was obtained

$$[f_1 \in (0,1): \frac{1 - cos\theta}{2} < f_1 < \frac{1 - cos\theta}{1.866}] \quad \text{……………………...…(S7)}$$

II. Supporting Figures and Table

Table S1: The comparison of previous excellent works with our work. The PNIPAAm/CNT@PVDF provided a novel responsive way as well as an approach to treat double emulsion, while the separation efficiency was as good as the previous works.

	Response approach	Separation object	Separation efficiency	Ref
Aminoazobenzene@Ag modified mesh	Photo response	Immiscible oil/water separation	>99.9%	20
PMMA-b-PNIPAAm fibrous membrane	Thermal response	Immiscible oil/water separation	>98.5%	38
TiO_2/ODP based mesh	Photo response	Dye polluted oil/water separation	unmentioned	39
PFOA modified kaolin material	PH response	Surfactant stablized emulsion separation	>99%	40
Au@PDA/PEPA@nylon	PH response	Surfactant stablized emulsion separation	>96%	35
3D hollow porous rape pollens	Calcination and steam modification	Surfactant stablized emulsion separation	>98.5%	36
$Co(OH)_2$@CMF	Liquid responsive	Surfactant stablized emulsion separation	>97.5%	37
Copolymer/SiO_2-coated cotton fabric	PH response	Surfactant stablized Emulsion separation	>98%	41
PNIPAAm/CNT@PVDF	Photothermal response	Double emulsion separation	>97.5%	This work

Table S2: The corresponding calculating process of the ratio change of IAHB under different irradiation times.

Irradiation time (s)	WCA (°)	cosθ	(1-cosθ)/2	(1-cosθ)/1.866
0	0	1	0	0
5	105.4	-0.26556	0.63278	0.66608
10	131.8	-0.66653	0.83326	0.87712
15	140.8	-0.77494	0.88747	0.93418
20	137.4	-0.73610	0.86805	0.91374
25	146.3	-0.83195	0.91598	0.96419
30	153.6	-0.89571	0.94786	0.99774
35	152.6	-0.88782	0.94391	0.99359
40	150.4	-0.86949	0.93475	0.98394

Table S3: The summary of the abbreviations used in the manuscript.

Abbreviations	**Full name**
CNT	carbon nanotube
PNIPAAm	Poly(N-isopropylacrylamide)
PVDF	Poly(vinylidene fluoride)
LCST	the lowest critical solution temperature
IEHB	intermolecular hydrogen bond
IAHB	intramolecular hydrogen bond
ST	surface temperature
WCA	water contact angle
OCA	oil contact angle
UOCA	underwater oil contact angle
Abs	heat absorption
For	heat formation
Rel	heat release
Con	heat consume
O/W/O emulsion	oil-in-water-in-oil emulsion
W/O/W emulsion	water-in-oil-in-water emulsion

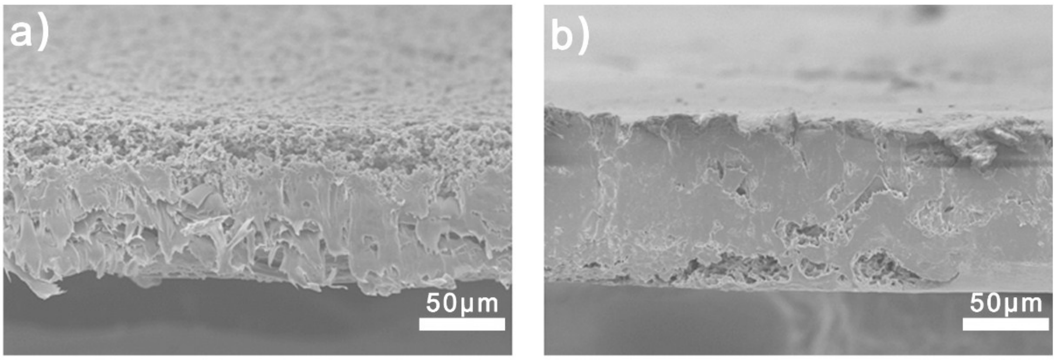

Figure S1: The cross section SEM images of a) original PVDF and b) PNIPAAm/CNT@PVDF, indicating the successfully modification of PNIPAAm and CNT.

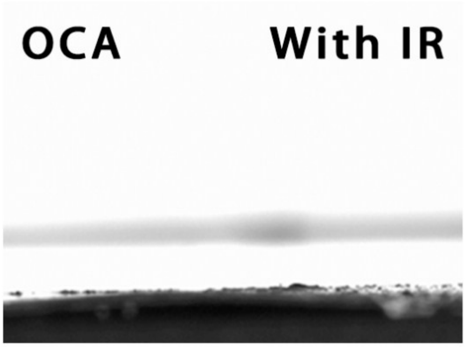

Figure S2: The OCA of the as-prepared membrane under IR was 0°, indicating the superoleophilic property

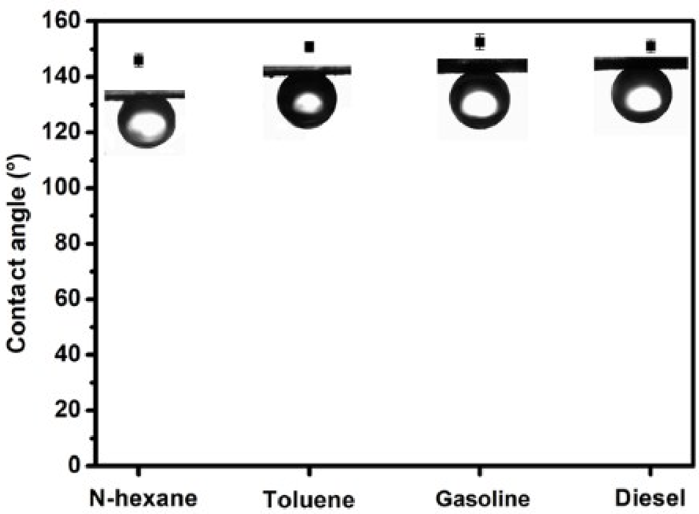

Figure S3: The underwater light oil content angles of four different oils without IR. The PNIPAAm/CNT@PVDF was underwater superoleophobic without IR.

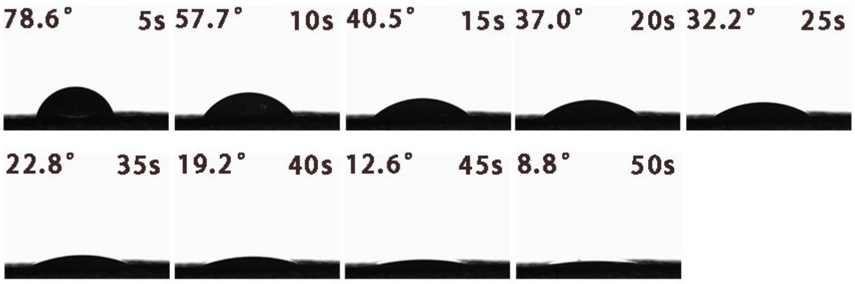

Figure S4: The wetting speed of water droplet on the membrane without IR was slow, which could be ascribed to the inevitable intermolecular hydrogen bonding formation process.

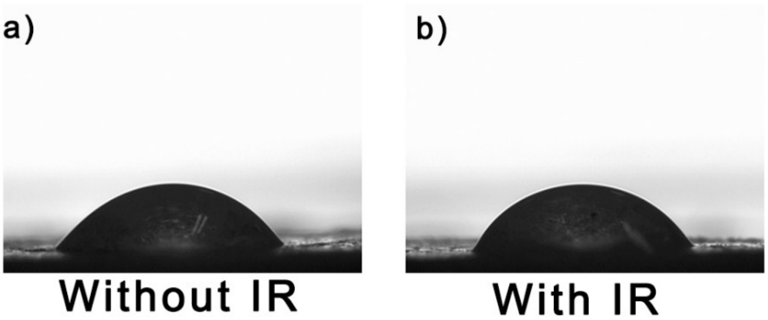

Figure S5: The WCA of the CNT@PVDF. The material didn't show responsive property without PNIPAAm.

Figure S6: The wetting behavior of PNIPAAm@PVDF under IR was uneven, because the absence of CNT limited the photo-thermal conversion property.

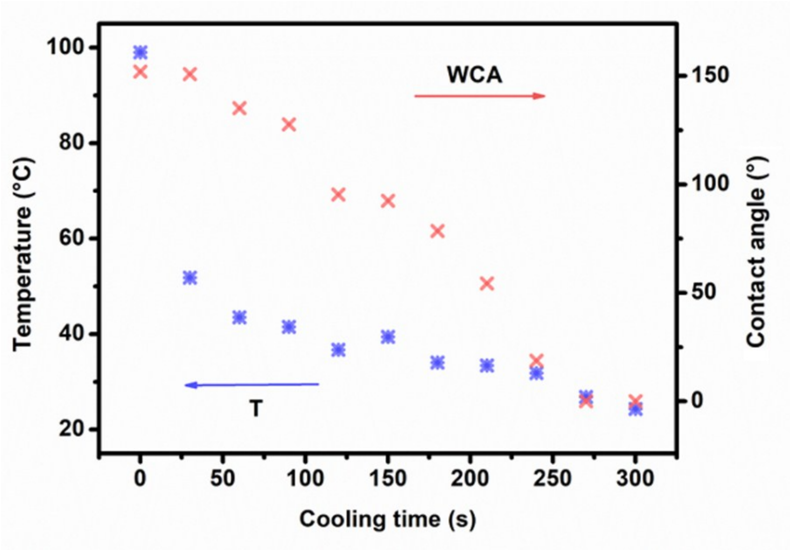

Figure S7: The cooling down process of PNIPAAm/CNT@PVDF after IR illumination. The temperature and contact angle decreased with the cooling time increased.

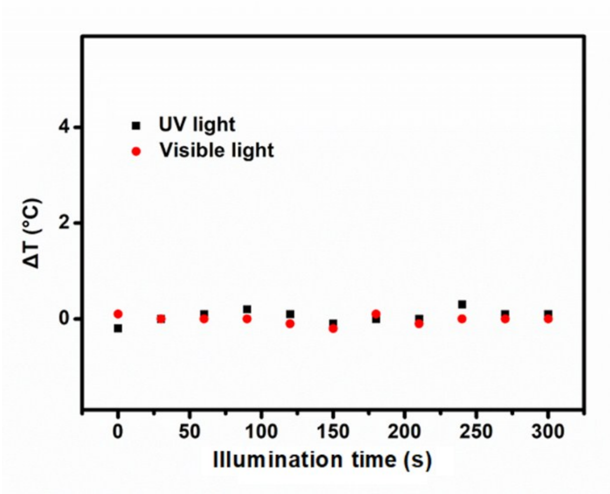

Figure S8: The temperature of PNIPAAm/CNT@PVDF kept unchanged under UV light and visible light.

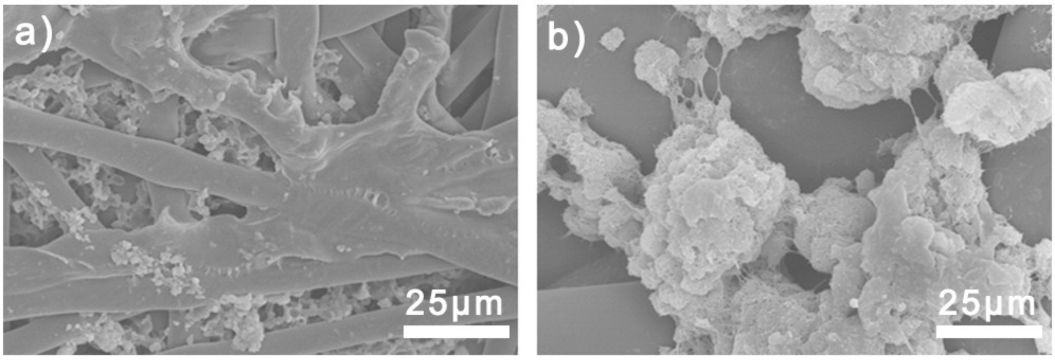

Figure S9: The SEM images of PNIPAAm/CNT@PVDF after 20 times of use.

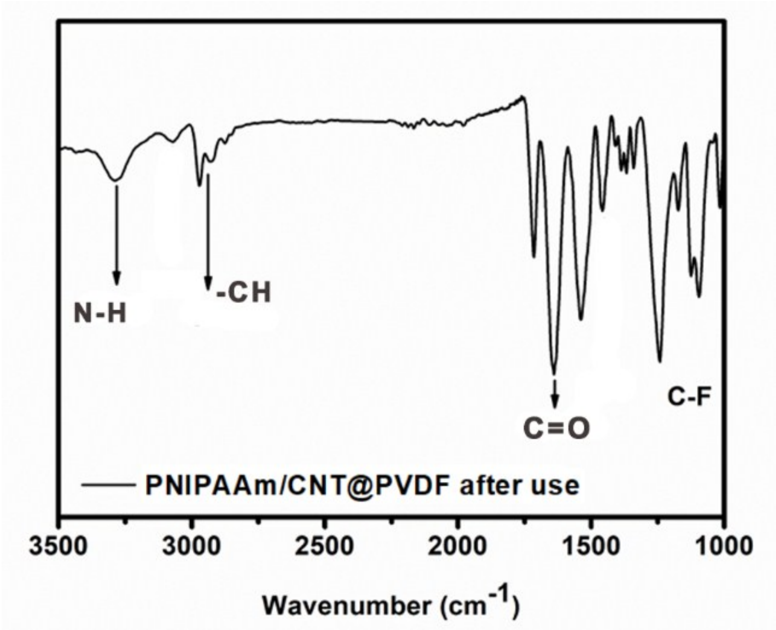

Figure S10: The FT-IR spectrum of PNIPAAm/CNT@PVDF after 20 times of use.

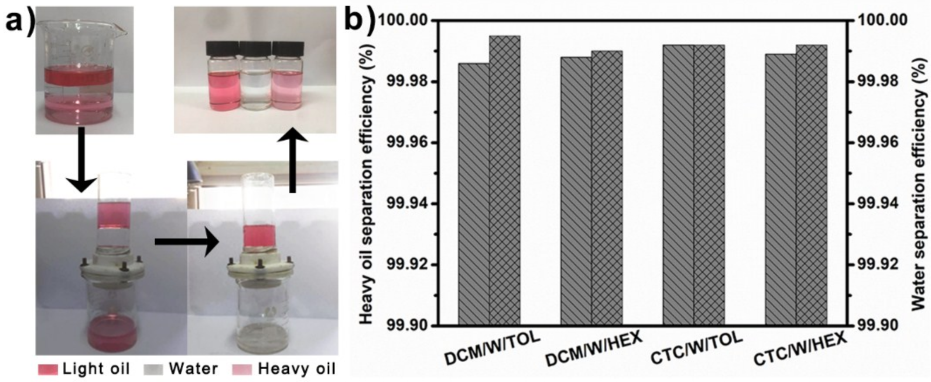

Figure S11: a) The continuous separation of multiphase immiscible liquids upon the IR variation and b) the separation efficiencies of PNIPAAm/CNT@PVDF for four kinds of multiphase immiscible liquids.

The special photothermal responsive property means the feasibility for multiphase immiscible liquids mixture separation. Therefore, the proof-of-concept experiment was conducted as displayed in Figure S11a. A piece of the PNIPAAm/CNT@PVDF was fixed between two tetrafluoroethylene fixtures attached with glass tubes in the dead-end model filtration device. The layered mixture of light oil (dyed with oil red), pure water and heavy oil (also dyed with oil red) was poured into the device. By controlling the irradiation condition, the liquid channel was manually controlled, which allowed the multiphase immiscible liquids with different SSE penetrate the material in sequence. Herein, four different multiphase immiscible systems including DCM/W/TOL, DCM/W/HEX, CTC/W/TOL and CTC/W/HEX were utilized to measure the separation efficiency of the material (DCM: dichloromethane, CTC: carbon tetrachloride, W: water, HEX: n-hexane, TOL: toluene). The volume ratio of the three liquid is 1:1:1. As displayed in Figure S11b, the separation efficiencies for all the heavy oils are above 99.98 %, and the separation efficiencies for water are all above 99.99 %, which indicates the satisfactory multiphase immiscible liquids mixture separation property of PNIPAAm/CNT@PVDF based on the manually controllable liquid channel.