Supplementary Information

A bioinspired attachable, self-standing nanofibrous membrane for versatile use in oil-water separation

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Experimental Section

Materials

Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP, $(-CH_2CF_2-)_m[-CF_2CF(CF_3)-]_n$, M_w ~400,000, M_n ~130,000, m:n = 10:1 (molar ratio)) was purchased from Sigma-Aldrich (St. Louis, MO, USA). Ethyl-alpha-cyanoacrylate (Et-CA, Alonalpha 201, $NCCH_2COOEt$, purity > 99 % with 2,2'-methylenebis(6-tert-butyl-4-methylphenol) < 0.2 %) was gifted from Toagosei Co., Ltd. (Tokyo, Japan). Both polymers, which mainly consisted of a nanofibers sheet, were biocompatible, fulfilling the "Food and Drug Administration" standard. Acetone (CH_3COCH_3), toluene ($Ph\text{-}CH_3$), hexadecane ($C_{16}H_{34}$), *n*-dodecane ($C_{12}H_{26}$), decane ($C_{10}H_{22}$), and oleic acid ($CH_3(CH_2)_7CH=CH(CH_2)_7COOH$) were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). Gasoline (grade: 90-91 octane) was purchased from a gas station. Ultrapure water was obtained using an Aquarius GS-500 (CPW, Advantec Co., Saijo, Japan) and dyed with Brilliant Blue (Tokyo Chemical Industry Co., Ltd., Tokyo, Japan). Melamine sponges, poly(vinylchroride) tubes (PVC tubes), and aluminum foil were purchased from a supermarket. Plastic syringes (Volume ~20 mL) and needles (21G ½) were purchased from Terumo Co. (Tokyo, Japan).

Fabrication of a PVDF-HFP/Et-CA nanofibers sheet

A nanofibers sheet (NFs-S) was designed by an electrospinning method. PVDF-HFP (1 g) and Et-CA (0.1 g) were dissolved in acetone (3.9 g) by stirring for 24 h at 60 °C. The solution was loaded into a plastic syringe with needles. The vertical tip-to-collector distance between the tip of the nozzle and the aluminum foil (used as a collector) was 20 cm. The applied voltage was set at 20 kV by a high voltage power unit. The flux of the syringe pump was set at 3 mL/h. The nanofibers collection area was about 450 cm^2. The electrospinning time was 2400 s and the weight change before and just after electrospinning was 3.0 g. The electrospun nanofibers on the aluminum foil were dried for one day. The designed NFs-S was easily peeled from the aluminum foil. The self-standing NFs-S was attached to a melamine sponge, glass container, or PVC tube. Furthermore, we found that the NFs-S was able to be attached to materials firmly and closely by wetting the NFs-S using isopropanol (IPA, $CH_3CH(OH)CH_3$). When wetted with IPA, the NFs-S become sticky, and after drying it was firmly attached to the materials.

Characterization

The morphology of the NFs-S was measured by field emission scanning electron microscopy (FE-SEM, Miniscope® TM3030Plus; Hitachi, Japan) with an applied voltage of 15.0 kV; all samples were coated with osmium before observation. The surface chemical components of the NFs-S were analyzed by energy-dispersive X-ray spectrometry (EDX, QUANTAX 70; Bruker Nano GmbH, Berlin, Germany). Fiber diameter distributions in the NFs-S were obtained by SEM images using the Image J software (U. S. National Institutes of Health, Bethesda, Maryland, USA). The elastic force and extension rate of the NFs-S were evaluated by using TRAPEZIUM LITE (Shimadzu Co., Ltd., Kyoto, Japan). The contact angles of the liquids on the NFs-S were measured by a commercial contact angle system (FACE; Kyowa Interface Science Co., Ltd., Niiza, Japan). Each static contact angle measurement was performed using 10 μL liquid droplets at room temperature (20 °C) (n = 5 for each sample surface). The wetting processes on the NFs-S at room temperature were observed by time-resolved images of the 10 μL casting liquid droplets on the NFs-S monitored by a high-speed camera (HAS-D3, Ditect, Tokyo, Japan). The separation efficiency for the oil-water mixtures was calculated by the following equation:

$$\text{Separation efficiency } /\% = \frac{w_{water}}{w_{water}+w_{oil}} \times 100 \quad (1)$$

where w_{water} and w_{oil} are the weight of water and oil that remained in the PVC tube, respectively (n = 3 for each oil on NFs-S). The flux of the penetrating oil on the NFs-S was calculated by the following equation:

$$\text{Flux / L h}^{-1}\text{ m}^{-2} = \frac{V_{penetration}}{t_{penetration} \times A_{sheet}} \quad (2)$$

where $V_{penetration}$ is the volume of penetrated oil on the NFs-S, $t_{penetration}$ is the time of oil penetration, and A_{sheet} is an area of the NFs-S that was penetrated by the oil. To mitigate the influence of gravity on the flux, the penetrating oil was cast in small volumes that just covered the whole surface of the NFs-S. The mechanical strength of the melamine sponge covered by the NFs-S was evaluated by cycles of compression and release using pressing equipment (AH-2003, AS ONE Co., Osaka, Japan). The intervals between compression and release were within 30 seconds at room temperature. Water in oil emulsion was prepared by mixing water and toluene in 1:10 w: w and sonicated by homogenizer (voltage: 100-120 V, current 4 A, frequency: 50-60 Hz, UP200S, Hielscher-Ultrasound Technology, Germany) for 30 minutes.

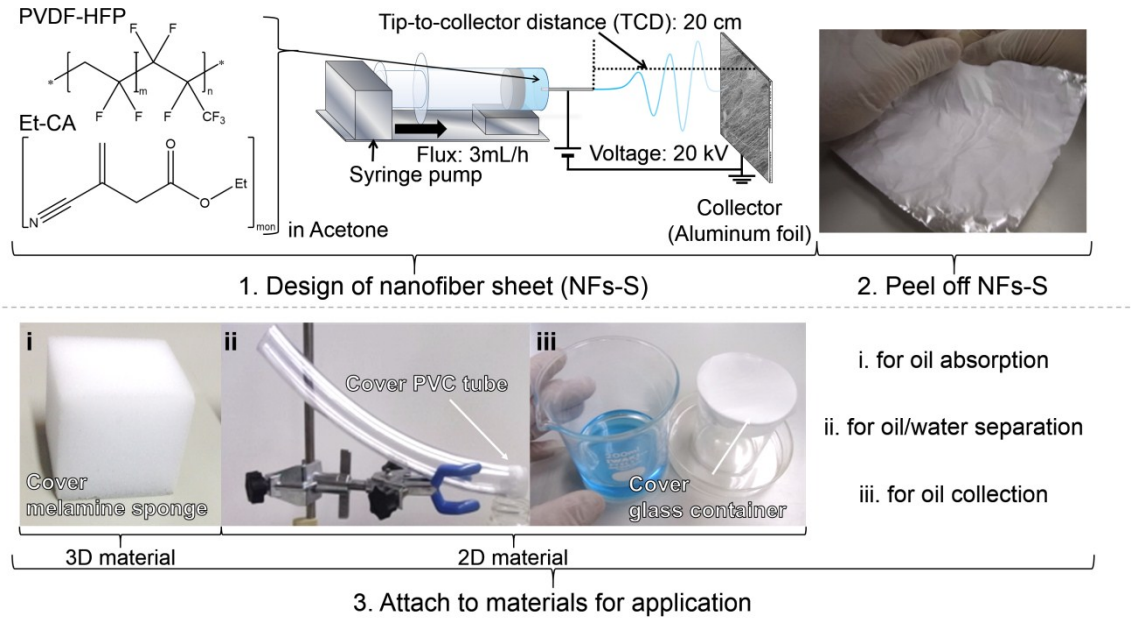

Figure S1. Schematic images of the designing procedure. **1.** The design of the NFs-S using an electrospinning method. **2.** Peeling the NFs-S from the aluminum foil, which allows the NFs-S to become self-standing. **3.** The self-standing NFs-S was attached to a melamine sponge for oil absorption, to the tip of PVC tube for oil-water separation by filtration, and to a container for oil collection.

Table S1. The cost of materials for fabrication of the NFs-S. All costs were taken from Sigma-Aldrich (St. Louis, MO, USA) HP at http://www.sigmaaldrich.com (accessed on 22 January 2016).

	Weight / g m^{-2}	Cost / US$ g^{-1}	Cost / US$ m^{-2}
PVDF-HFP	0.40	0.479	0.19160
Et-CA	0.04	15.450	0.61800
Acetone	1.56	0.049	0.07644
Total	-	-	0.88604

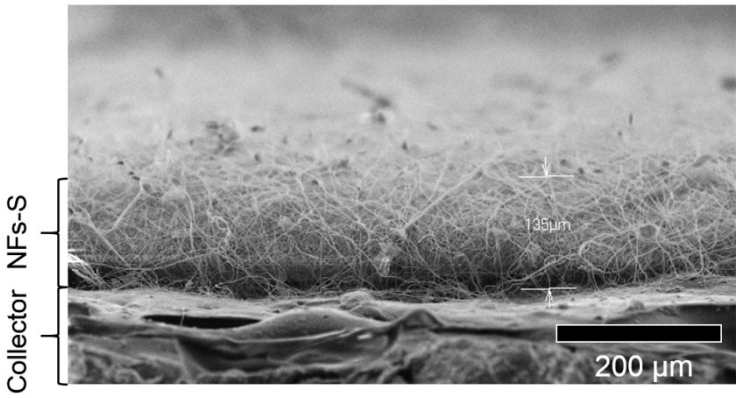

Figure S2. Cross-sectional SEM images of the NFs-S. The thickness of the NFs-S is 135 μm.

Table S2. Normalized atom ratio of fluorine, carbon, oxygen, and nitrogen by changing the ratio of PVDF-HFP to Et-CA.

		PVDF-HFP:Et-CA ratio / w:w		
		1:0.1	0.9:0.2	0.8:0.3
Normalized atom ratio	Fluorine	36.412±4.865	40.989±5.302	42.483±5.454
	Carbon	56.838±4.841	51.510±4.265	50.378±4.145
	Oxygen	4.354±0.564	4.709±0.576	4.181±0.512
	Nitrogen	2.396±0.333	2.791±0.348	2.958±0.360

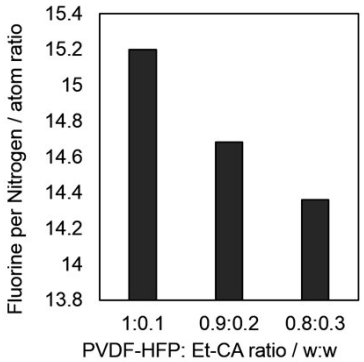

Figure S3. Atomic ratio of fluorine per nitrogen for each ratio of PVDF-HFP with Et-CA.

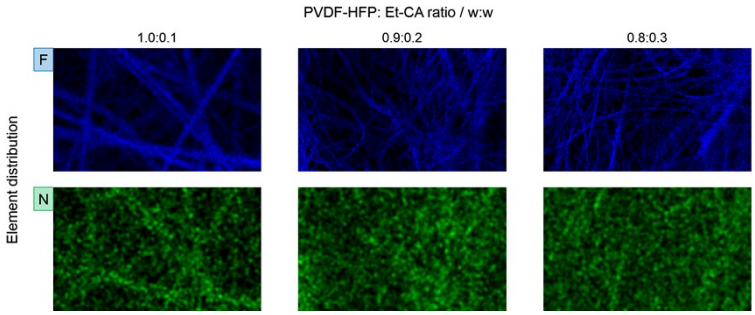

Figure S4. Elemental distribution of fluorine and nitrogen in the fibers with respect to the ratio of PVDF-HFP to Et-CA.

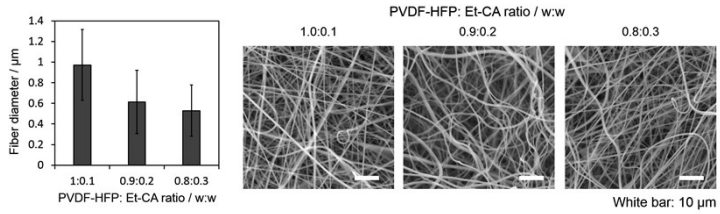

Figure S5. Fiber diameters and SEM images of the fibers for each ratio of PVDF-HFP to Et-CA.

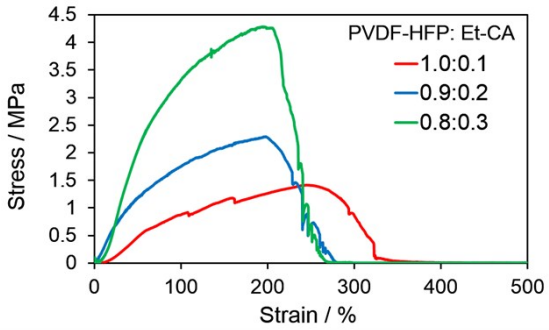

Figure S6. Extension ratio of the NFs-Ss for each ratio of PVDF-HFP to Et-CA.

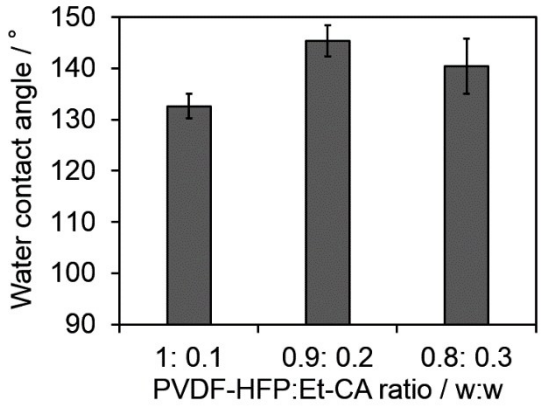

Figure S7. Water contact angle on the NFs-Ss for each ratio of PVDF-HFP to Et-CA.

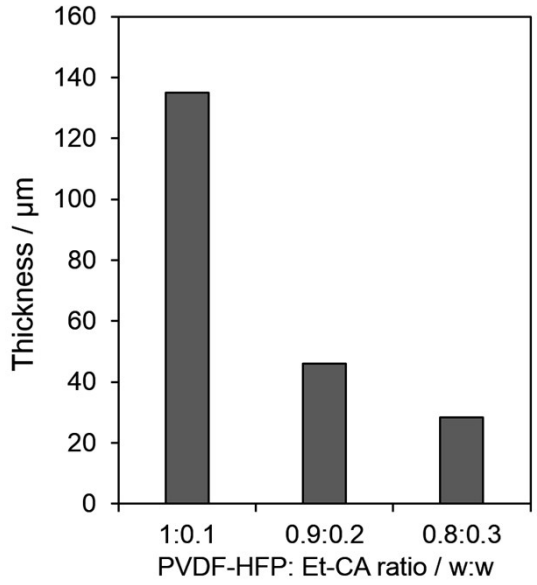

Figure S8. The thickness of the NFs-S for each ratio of PVDF-HFP to Et-CA.

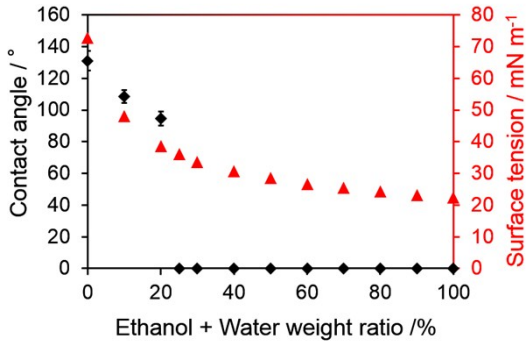

Figure S9. The contact angles and surface tensions[a)] (20 °C) for an ethanol-water mixture. The limit for wetting or repelling is at a surface tension in the range of 36.09-38.56 mN m^{-1}.

a) C. Vazquez, E. Alvarez, J. M. Navaza, *J. Chem. Eng. Data* **1995**, *40*, 611–614.

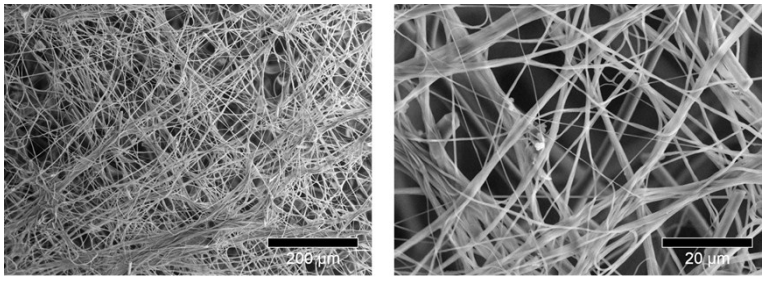

Figure S10. SEM images of the NFs-S covering a sponge at two different scales after extracting oil.

Table S3. Characteristics for each oil.

	Viscosity / mP s	Surface tension / mN m^{-1}	Density / g m^{-3}
Toluene	0.560	28.50	0.865
Hexadecane	3.061	27.47	0.773
n-Dodecane	1.352	25.35	0.745
Decane	0.841	23.83	0.730
Oleic acid	31	32	0.894
Gasoline[a)b)]	0.86	21.56	0.726

a) L. Zhu, J. Chen, Y. Liu, R. Geng, J. Yu, *J. Loss Prev. Process Ind.* **2012**, *25*, 916–922.
b) F. Wang, J. Wu, Z. Liu, *Energy Fuels* **2006**, *20*, 2471-2474.

Table S4. Summary of 2D and 3D materials for oil/water separation properties.

Materials	Preparation methods	Separation efficiency (%)	Flux (L m^{-2} h^{-1})	Cost (US$)	Reference
Polyaniline coated cotton fabric	vapor phase deposition	97.8	n.a.	4.5	c)
polydopamine/n-dodecyl mercaptan mesh	Michael addition reaction	98.12	n.a.	7.6	d)
cellulose hollow fiber	immersion precipitation technique	>97	7.7	<5	e)
cellulose acetate-graft-polyacrylonitrile membranes	phase inversion method	>97	300	16.9	f)
Vertically-aligned carbon nano-tube	thermal chemical vapor deposition	n.a.	85.6	-	g)
poly(2-methacryloyloxylethyl phosphorylcholine)	grafting	>99.9	880	37.2	h)
PMMA- b-P4VP membrane	copolymer synthesis and electro spinning	>98	n.a.	7.8	i)
polybenzoxazine/TiO2	dip coating and thermal curing	>98	2900	23.6	j)
carbon soot caoted steel mesh	combustion by candle	>99	10.2	<1	k)
PTFE coated mesh	spray method	n.a.	n.a.	6.1	l)
PVDF membrane	phase-inversion process	>99.9	3415	51.3	m)
PVDF-HFP/Et-CA nanofibrous membrane	Just attach the NFs-S	99.8	3000	0.88	This work

c) X. Zhou, Z. Zhang, X. Xu, F. Guo, X. Zhu, X. Men, B. Ge, *ACS Appl. Mater. Interfaces* **2013**, *5*, 7208.

d) Y. Cao, X. Zhang, L. Tao, K. Li, Z. Xue, L. Feng, Yen Wei, A*CS Appl. Mater. Interfaces*, **2013**, *5*, 4438.

e) H. Li, Y. Cao, J. Qin, X. Jie, T. Wang, J. Liu, Q. Yuan, *J. Membrane Sci*. **2006**, *279*, 328.

f) W. Chen, Y. Su, L. Zheng, L. Wang, Z. Jiang, *J. Membrane Sci*. **2009**, *337*, 98.

g) C. Lee and S. Baik, *Carbon* **2010**, *48*, 2197.

h) K. He, H. Duan, G. Y. Chen, X. Liu, W. Yang, D. Wang, *ASC Nano* **2015**, *9*, 9188.

i) J. Li, Y. Zhou, Z. Luo, *ACS Appl. Mater. Interfaces* **2015**, *7*, 19643.

j) W. Zhang, X. Lu, Z. Xin, C. Zhou, *Nanoscale* **2015**, *7*, 19476.

k) J. Li, R. Kang, X. Tang, H. She, Y. Yang, F. Zha, *Nanoscale* **2016**, *8*, 7638.

l) L. Feng, Z. Zhang, Z. Mai, Y. Ma, B. Liu, L. Jiang, D. Zhu, *Angew. Chem. Int. Ed.* **2004**, *116*, 2046.

W. Zhang, Z. Shi, F. Zhang, X. Liu, J. Jin, L. Jiang, *Adv. Mater*. **2013**, *25*, 2071.

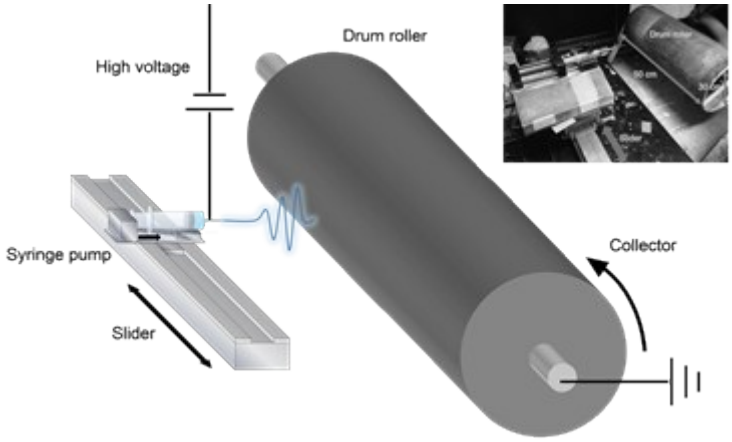

Figure S11. Electrospinning device for large-scale fabrication of NFs-Ss. The slider moves in the direction of the arrow and the drum roller rotates to design uniform and large-scale NFs-Ss.