Supplementary Information

Flexible superhydrophobic polysiloxane aerogels for oil-water separation via one-pot synthesis in supercritical CO_2

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General procedure for the synthesis of the methyl hydrogen polysiloxane (A).

For A1 (m=5, n=25), ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm) 0.08 (br s, 20H, -Si(C<u>H</u>$_3$)$_2$), 0.15 (br s, 2H, -SiH(C<u>H</u>$_3$)$_2$), 0.18 (br s, 2H, -SiH(C<u>H</u>$_3$)), 4.46-4.88 (br s, 1H, -Si<u>H</u>(CH_3) and -Si<u>H</u>(CH_3)$_2$); ^{29}Si NMR (300MHz, δ, ppm) -6.64 (-SiH(CH_3)$_2$), -21.57 (-Si(CH_3)$_2$), -37.15 (-SiH(CH_3)); MALDI-TOF MS (m/z) Calcd. for the repeating unit: -Si(CH_3)$_2$-O-, 74 and -SiH(CH_3) -O-, 60; found: 74 and 60, respectively.

For A2 (m=7, n=23), ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm) 0.08 (br s, 13H, -Si(C<u>H</u>$_3$)$_2$), 0.15 (br s, 2H, -SiH(C<u>H</u>$_3$)$_2$), 0.18 (br s, 2H, -SiH(C<u>H</u>$_3$)), 4.46-4.88 (br s, 1H, -Si<u>H</u>(CH_3) and -Si<u>H</u>(CH_3)$_2$); ^{29}Si NMR (300MHz, δ, ppm) -6.09 (-SiH(CH_3)$_2$), -20.19(-Si(CH_3)$_2$), -36.51 (-SiH(CH_3)); MALDI-TOF MS (m/z) Calcd. for the repeating unit: -Si(CH_3)$_2$-O-, 74 and -SiH(CH_3) -O-, 60; found: 74 and 60, respectively.

The synthesis of the vinyl-terminated polydimethylsiloxane (B).

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm) 0.07 (br s, 97H, -Si(C<u>H</u>$_3$)$_2$), 0.16 (br s, 6H, -SiVi(C<u>H</u>$_3$)$_2$), 5.73 (br dd, 1H, -Si(CH_3)CH=C<u>H</u>$_2$, *J* =20.3, 4.0 Hz), 5.93 (br dd, 1H, -Si(CH_3)CH=C<u>H</u>$_2$, *J* =14.8, 4.0 Hz), 6.13 (br dd, 1H, -Si(CH_3)C<u>H</u>=CH_2, *J* =20.2, 14.8 Hz); ^{29}Si NMR (300MHz, δ, ppm) -4.18 (-Si(CH_3)$_2$CH=CH_2), -22.06(-Si(CH_3)$_2$) ; MALDI-TOF MS (m/z) Calcd. for the repeating unit: -Si(CH_3)$_2$-O-, 74; found: 74.

Table S1 Physical properties of polysiloxane aerogels synthesized in $scCO_2$ at 40 ^oC

Aerogels[a]	Reaction concentration[b] [mg ml^{-1}]	Reaction pressure [MPa]	Density [mg cm^{-3}]	Skeletal Density [g cm^{-3}]	Porosity [%]	Specific surface area [m^2 g^{-1}]	T_d[c] [°C]	Water contact angle [^{o}]
A1-B	136	16	-[d]	-	-	-	-	-
	136	22	227	1.10	79.4	58.67	404	154
	95		-	-	-	-	-	-
	68		-	-	-	-	-	-
A2-B	136	22	258	1.10	76.5	33.44	407	150
	95		156	1.12	86.0	45.98	406	153
	68		145	1.10	86.8	34.70	400	156

[a] the chemical structures for A are shown in Figure 1; [b] the reaction concentration was calculated by the following equation, reaction concentration = $(m_A+m_B)/V$, where m_A, m_B are the mass of the methyl hydrogen polysiloxane (A) and vinyl-terminated PDMS (B), respectively. V is the volume of the reaction vessle; [c] the decomposition temperature at the weight loss of 5%; [d] '-' means that aerogel could not form in this condition.

Table S2 Mechanical property comparison of the as-synthesized polysiloxane aerogels with various silica aerogels

Material	Young's modulus (KPa)	Reference[a]
A1-B aerogel	7	our work
silica	[b]	20
silica /polyurethanes composite	40	30
silica	[b]	31
silica /sodium dodecyl sulfate composite	200-900	32
silica	640-4200	33

[a]: cited in the manuscript; [b]: means that toughness monoliths aerogel could not be formed.

Table S3 Thermal stability comparison of the as-synthesized polysiloxane aerogels with various aerogels

Material	T_d [^{o}C]	Reference[a]
A1-B aerogel	400 (5% weight loss)	our work
polyvinyl alcohol/cellulose nanofibrils/graphene oxide	337 (20% weight loss)	34
polyvinyl alcohol/cellulose nanofibril	302.5 (30% weight loss)	17

[a]: cited in the manuscript.

Table S4 Comparison of various absorbent materials

Material	Absorption capacity (g g^{-1})	Reference
A1-B aerogel	5-15	our work
Silica aerogel	5-11	20[a]
Graphene-based aerogel	28-40	1
Polysiloxane sponge	4-11	2

[a]: cited in the manuscript.

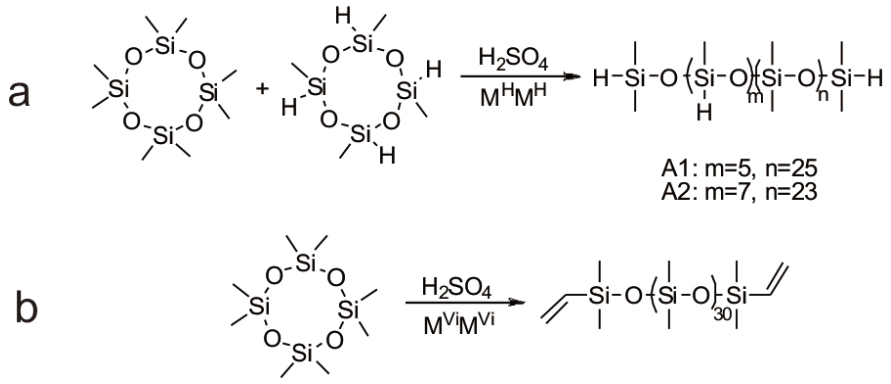

Fig. S1. a) Synthesis route of the methyl hydrogen polysiloxane (A). b) Synthesis route of the vinyl-terminated polydimethylsiloxane (B).

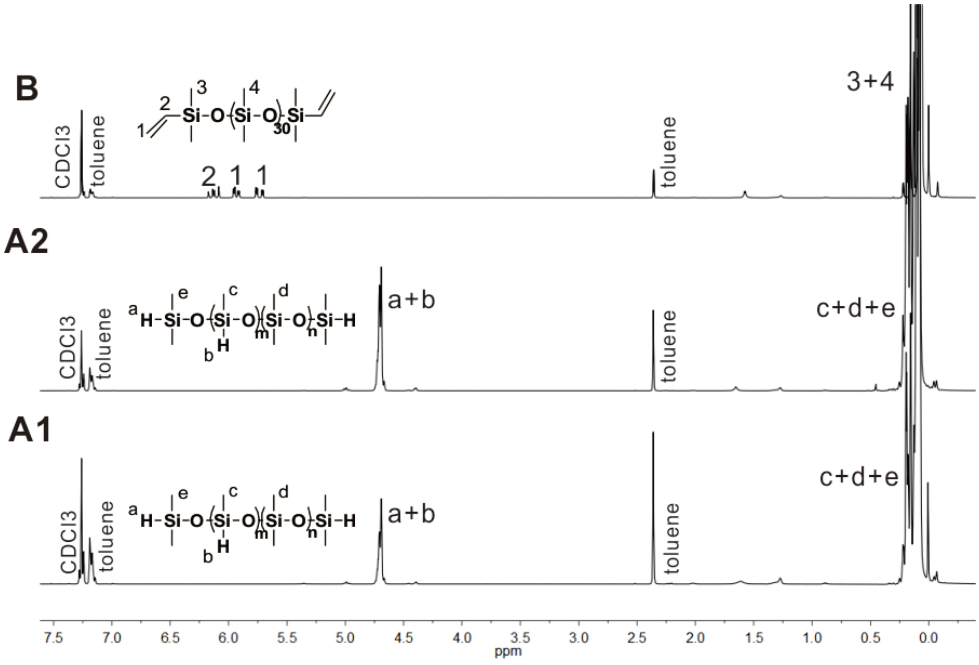

Fig. S2. ^{1}H NMR spectra of A1, A2 and B.

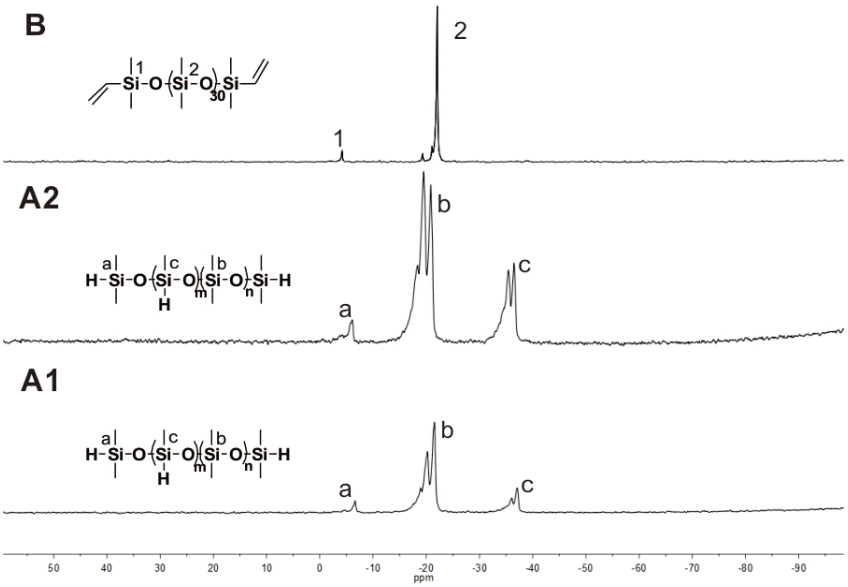

Fig. S3. ^{29}Si NMR spectra of A1, A2 and B.

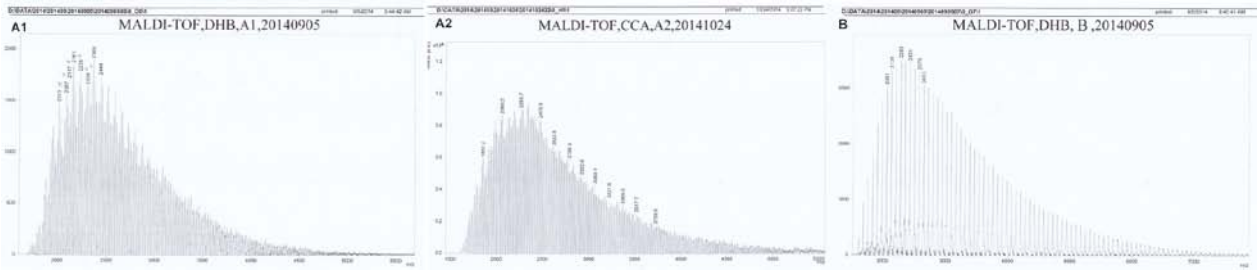

Fig. S4. MALDI-TOF spectra of A1, A2 and B.

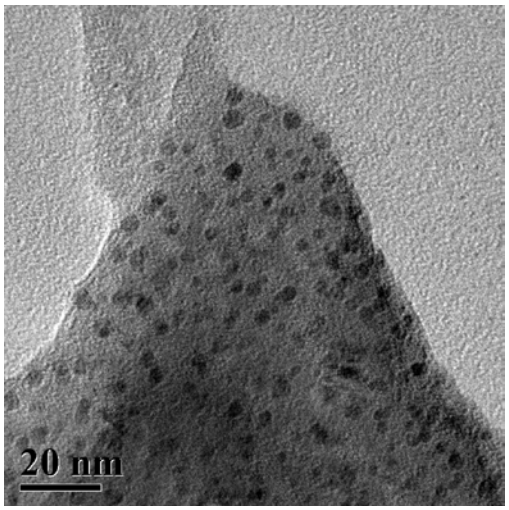

Fig. S5. (a) TEM image for A1-B aerogel from 136 mg/mL.

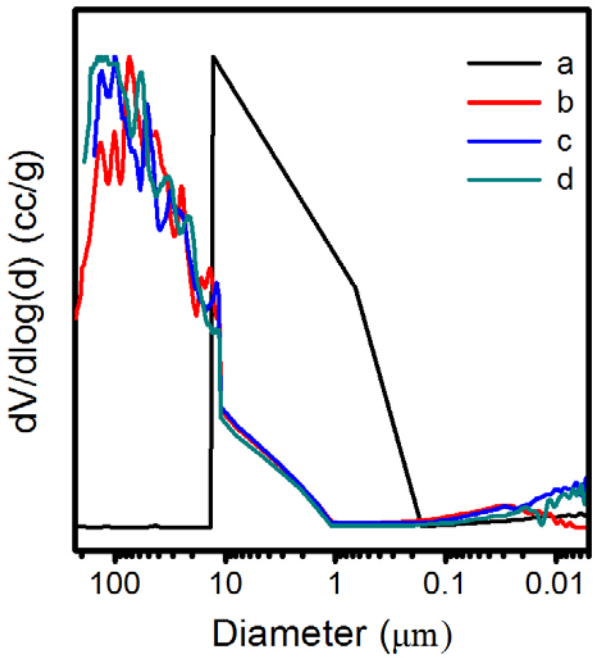

Fig. S6. Pore size distributions of A1-B aerogel from 136 mg/mL (a) and A2-B aerogels from 68mg/mL (b), 95 mg/mL (c), and 136 mg/mL (d) in $scCO_2$ at 22 Mpa

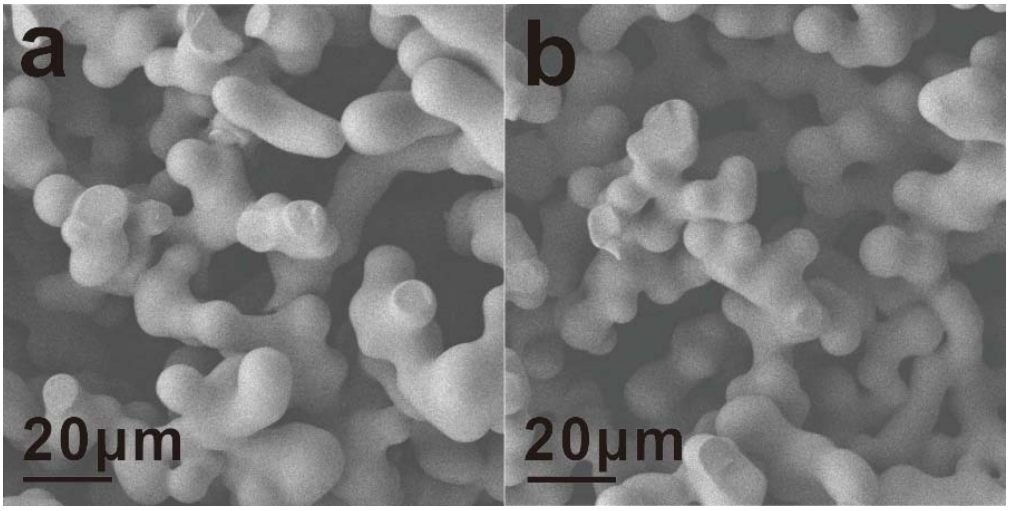

Fig. S7. (a) SEM images for A1-B aerogel after 100 cycles of compression test at room temperature, (b) SEM images for A1-B aerogel after the absorption of hexane.

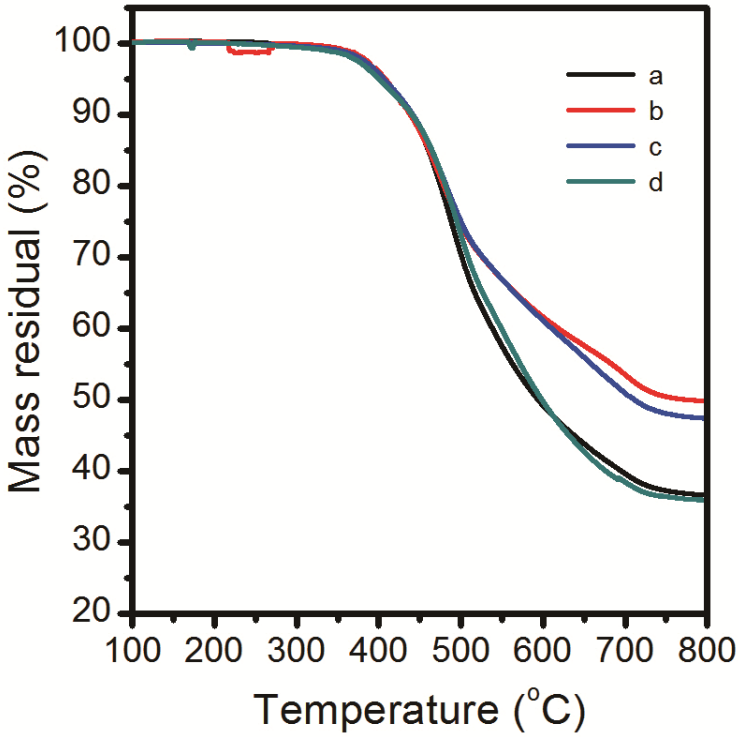

Fig. S8. TGA results of A1-B aerogel from 136 mg/mL (a) and A2-B aerogels from 136 mg/mL (b), 95 mg/mL (c), and 68 mg/mL (d) in $scCO_2$ at 22 MPa.

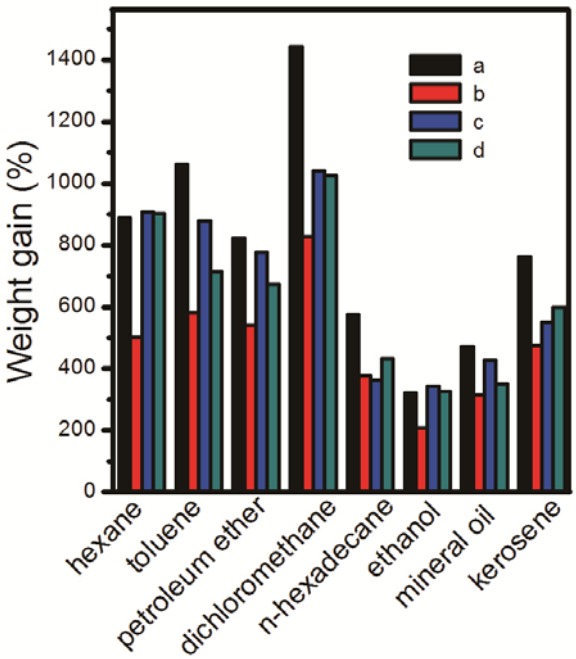

Fig. S9. Absorption capacities of aerogels for various organic solvents, as indicated by weight gain: A1-B aerogel from 136 mg/mL (a), A2-B aerogels from 136 mg/mL (b), 95 mg/mL (c), 68 mg/mL (d) in $scCO_2$ at 22 MPa.

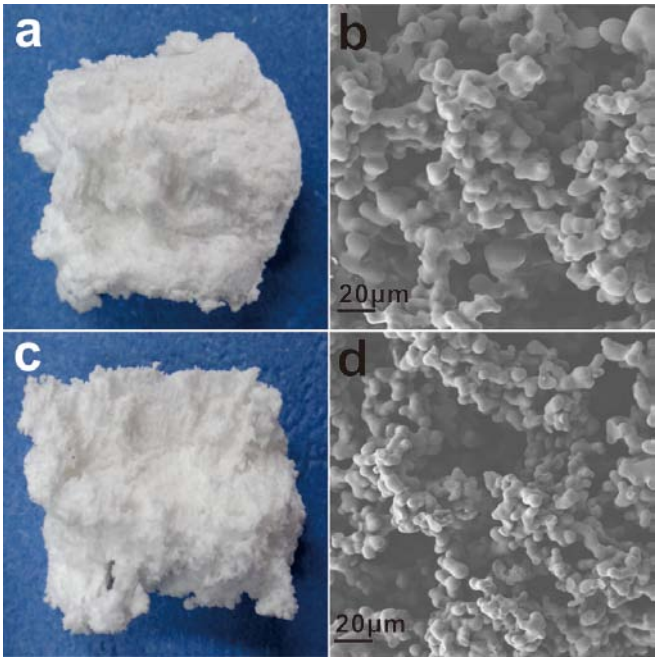

Fig. S10. Photographs and SEM images of A2-B aerogels from 95 mg/mL (a, b) and 68 mg/mL (c, d) in $scCO_2$ at 22 MPa.

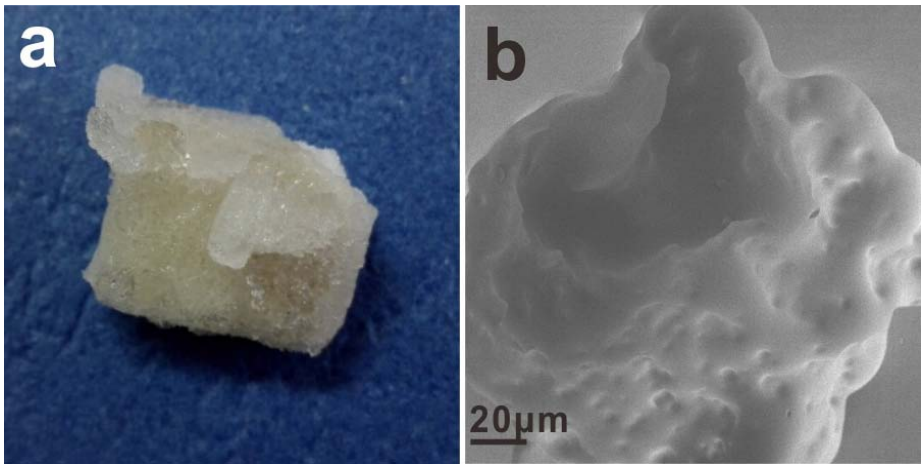

Fig. S11. Photograph (a) and SEM image (b) of A1-B monoliths from 136 mg/mL in $scCO_2$ at 16 MPa.

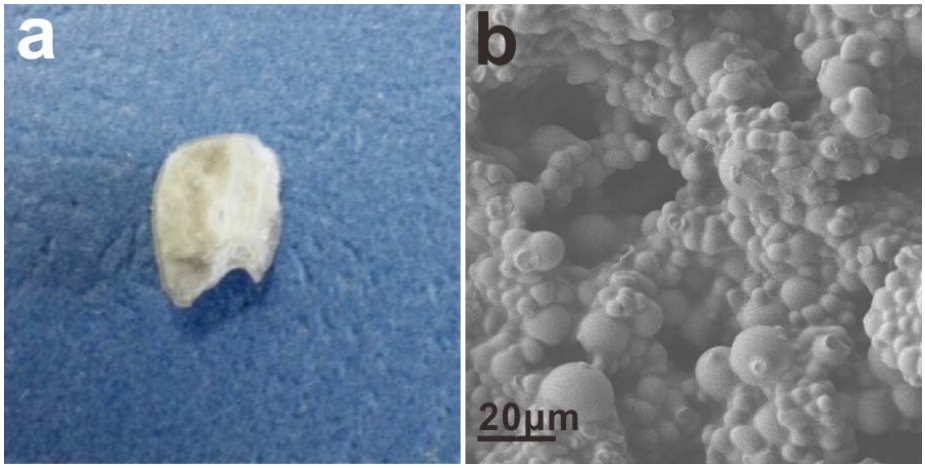

Fig. S12. Photograph (a) and SEM image (b) of A1-B aerogel from 136 mg/mL dioxane at atmospheric pressure.

References:

1 T. Wu, M. Chen, L. Zhang, X. Xu, Y. Liu, J. Yan,W. Wang and J. Gao, *J.Mater. Chem, A*, 2013, **1**, 7612-7621.

2 S. Choi, T. Kwon, H. Im, D. Moon, D. J. Baek, M. Seol, J. P. Duarte and Y. Choi, *ACS Appl. Mater. Interfaces*, 2011, **3**, 4552-4556.