Supporting Information

Green Synthesis of Ant Nest-Inspired Superelastic Silicone Aerogels

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Number of Figures: 33

Number of Tables: 5

Number of videos: 3

Experimental Section

Materials. Methyltrimethoxysilane (MTMS), dimethyldimethoxysilane (DMDMS), dimethoxymethylvinylsilane, dimethyldiethoxysilane, *1H,1H,2H,2H*-perfluorodecyltriethoxysilane and tetraethoxysilane were purchased from Gelest. Dihexadecyl dimethyl ammonium bromide (DHDAB), acetic acid (HAc), Na_2CO_3, $NaHCO_3$, ammonia, toluene, *n*-hexadecane, methylene blue and oil red O were purchased from China National Medicines Co., Ltd. All chemicals were used as received without further purification. Deionized water was used for all the experiments and tests.

Green synthesis of ANSAs. The ANSAs are synthesized by hydrolytic condensation of MTMS and DMDMS via a one-pot method. Hydrolytic condensation of the precursors was carried out in weak acidic buffer solutions (pH 4.52-5.32). Typically, 1.93 mg (0.0034 mmol) of DHDAB in 1.0 mL of water and 2 mg (0.019 mmol) of Na_2CO_3 in 2.0 mL of water were added into a glass vial containing 4.7 mL of HAc solution (0.0385 mmol). The HAc/Na_2CO_3 molar ratio is 2.03. Then, 1.43 g (10.5 mmol) of MTMS and 0.84 g (7.0 mmol) of DMDMS were sequentially added into the weak acidic buffer solution. There is a clear interface between the buffer solution and the precursors because they are immiscible with each other. Thus, the mixture was vibrated at 200 rpm for 1 h at 30 °C in a thermostatic incubator shaker. Due to hydrolysis of the precursors and the presence of DHDAB, a homogeneous and transparent sol was formed. Then, the sol was transferred into a sealed glass tube, which was placed in an oven at 95 °C for 24 h without any shake to form the silicone hydrogel. The hydrogel was washed in turn with water for 3 times and ethanol for 3 times by squeezing to remove the trace amounts of DHDAB, NaAc, HAc and other residuals, e.g., hydrolyzed precursors and oligomers, and then dried in an oven at 60 °C under ambient pressure. The silicone hydrogels were washed with water and ethanol unless otherwise specified.

It should be noted that the total content of DHDAB, NaAc and HAc in the silicone hydrogels is negligible (0.094 mmol mol^{-1}) as only trace amounts of DHDAB, HAc and Na_2CO_3 were used as shown in Table S1. Besides Na_2CO_3, the ANSAs can also be prepared using $NaHCO_3$ (e.g., 0.036 mmol) or ammonia (e.g., 0.039 mmol) via the same procedure.

Preparation of superamphiphobic ANSAs. A piece of the as-prepared ANSA 28 mm in length and 20 mm in diameter was immersed in a mixture of ethanol (40 mL), ammonia solution (10

mL), tetraethoxysilane (50 μL) and *1H,1H,2H,2H*-perfluorodecyltriethoxysilane (0.6 mL) at 25 °C for 4 h. The sample was repeatedly squeezed to refresh the solution inside the alcogel in order to facilitate the reaction between the residual Si-OH groups and silanes. Subsequently, the superamphiphobic ANSA was washed with ethanol to remove ammonia and the unattached polycondensed silanes, and then dried in an oven at 60 °C.

Preparation of ANSA coatings. The ANSA coatings were prepared via a slightly modified method compared to the preparation of monolithic ANSAs. A piece of glass slide as the substrate was immersed in the sol before placed in an oven at 95 °C for 24 h to form the silicone hydrogel. The monolith was removed and the ANSA coating was washed in turn with water for 3 times and ethanol for 3 times, and then dried in an oven at 60 °C under ambient pressure. Besides glass slides, other materials including Cu plate, Al plate, stainless steel plate, wood plate, polyethylene (PE) plate, polypropylene (PP) plate and polytetrafluoroethylene (PTFE) plate were also used as substrates.

Measurements of mechanical properties. The mechanical properties of the ANSAs were measured using a universal testing machine (CMT4304, Shenzhen SANS Test Machine Co. Ltd., Shenzhen, China) equipped with 50 N and 200 N load cells at room temperature. For uniaxial compression tests, the cylindrical samples 20 mm in length and 12 mm in diameter were quickly compressed with a rate of 10 mm min^{-1} unless otherwise specified. For three-point bending tests, the cylindrical samples 75 mm in length and 12 mm in diameter were bent by an arc-shaped crosshead 10 mm in diameter with a 27 mm span using a 50 N load cell at a rate of 5 mm min^{-1}.

Measurements of contact angles and sliding angles. Measurements of contact angles and sliding angles of various liquids were performed with a Contact Angle System OCA20 (Dataphysics, Germany) equipped with a tilting table. The syringe was positioned in a way that the droplets of water and organic liquids (5 μL) could contact the surface of the sample before leaving the needle. Tilting angle of the table was adjustable (0 ~ 70°) and allowed the subsequent measurement of sliding angles at the same position on the sample. Measurements of the contact angles and sliding angles were carried out on the cross section of the samples. A minimum of six readings was recorded for each sample.

Measurement of oil absorbency. A piece of sample was immersed in oil at room temperature. The sample was taken out from the oil after 1 min, drained for several seconds and wiped with filter paper to remove excess oil. The oil absorbency k of the sample was determined by weighing the sample before and after oil absorption and calculated according to Eq. (S1).

$$k = (M_{eq} - M_0)/M_0 \times 100\% \quad \text{(S1)}$$

where M_{eq} is the weight of the wet sample at absorption equilibrium (g) and M_0 is the weight of dry sample (g).

The influence of repeated absorption-desorption of oils on oil absorbency of the ANSA was investigated to evaluate its reusability. The sample was immersed in toluene to reach equilibrium, and then weighted to calculate the absorbency. The sample was squeezed and washed with ethanol for three times, and then dried in an oven at 60 ℃. This absorption-desorption procedure was repeated for 10 times.

Characterization. The micrographs of the samples were taken using a field emission scanning electron microscope (SEM, JSM-6701F, JEOL). Before SEM observation, all samples were fixed on aluminum stubs and coated with a layer of gold film (~7 nm). The elemental maps of the samples were obtained using an energy dispersive spectrometer of SEM. The infrared spectrum of the sample was recorded by a Thermo Nicolet NEXUS TM spectrophotometer using KBr pellets. The surface chemical composition of the sample was analyzed via X-ray photoelectron spectroscopy (XPS) using a VG ESCALAB 250 Xi spectrometer equipped with a Monochromated AlKa X-ray radiation source and a hemispherical electron analyzer. The spectrum was recorded in the constant pass energy mode with a value of 100 eV, and all binding energies were calibrated using the C 1s peak at 284.6 eV as the reference. The solid-state ^{29}Si MAS NMR experiment was performed on Bruker AVANCE III 600 spectrometer at a resonance frequency of 119.2 MHz. The ^{29}Si MAS NMR spectrum with high-power proton decoupling was recorded on a 4 mm probe with a spinning rate of 10 kHz, a π/4 pulse length of 2.6 μs, and a recycle delay of 80 s. The chemical shifts of ^{29}Si were referenced to TMS. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out using a simultaneous thermal analyzer (NETZSCH STA 449F3, Germany) in the range of 25 to 600 °C at a rate of 10 K min^{-1} under air atmosphere.

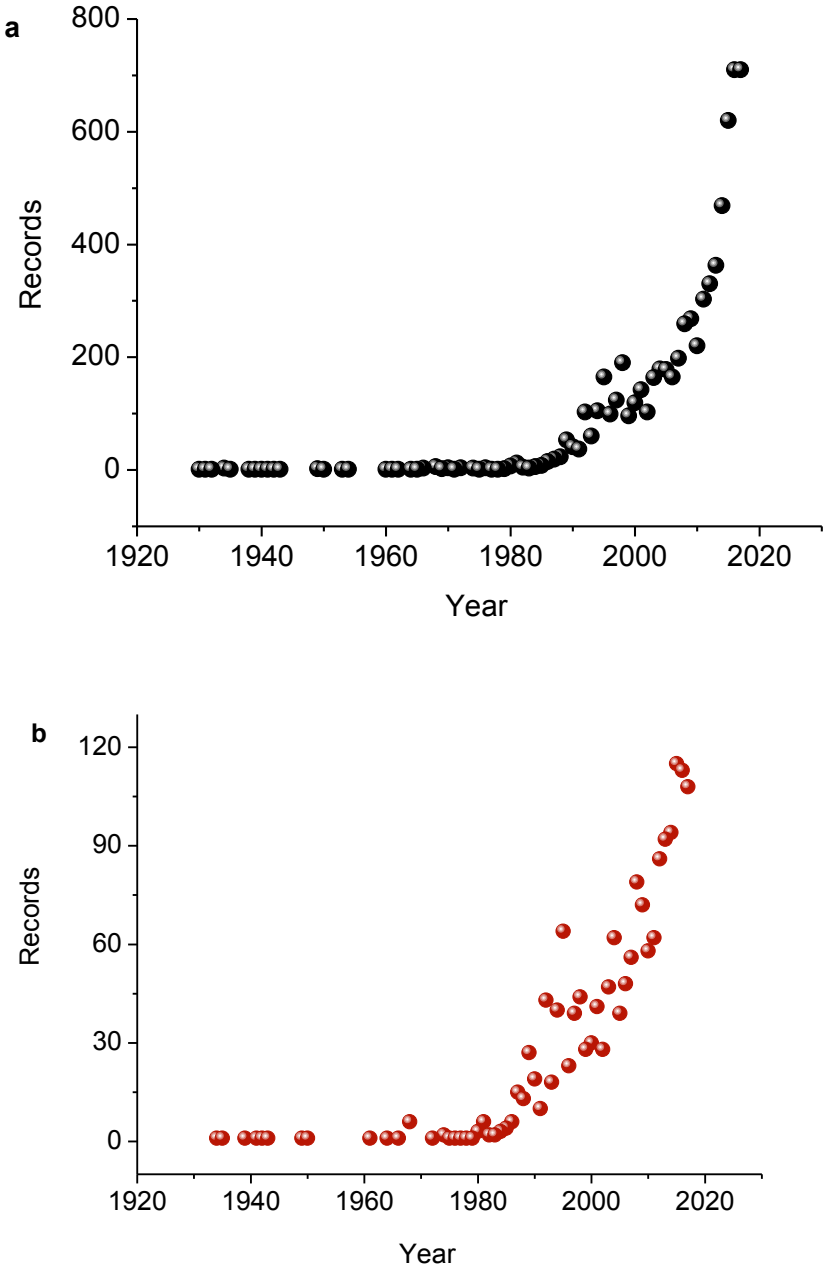

Figure S1. Papers indexed in the Web of Science with the title of a) "aerogel*" and b) "aerogel*" AND "silica".

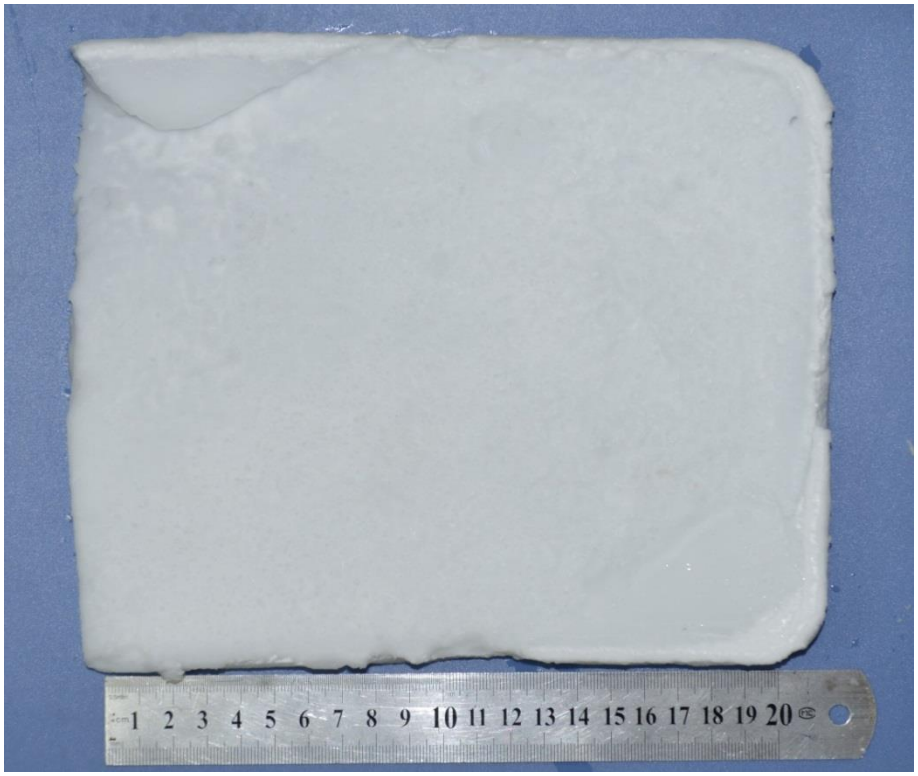

Figure S2. A photograph of the ANSA-3# in large size.

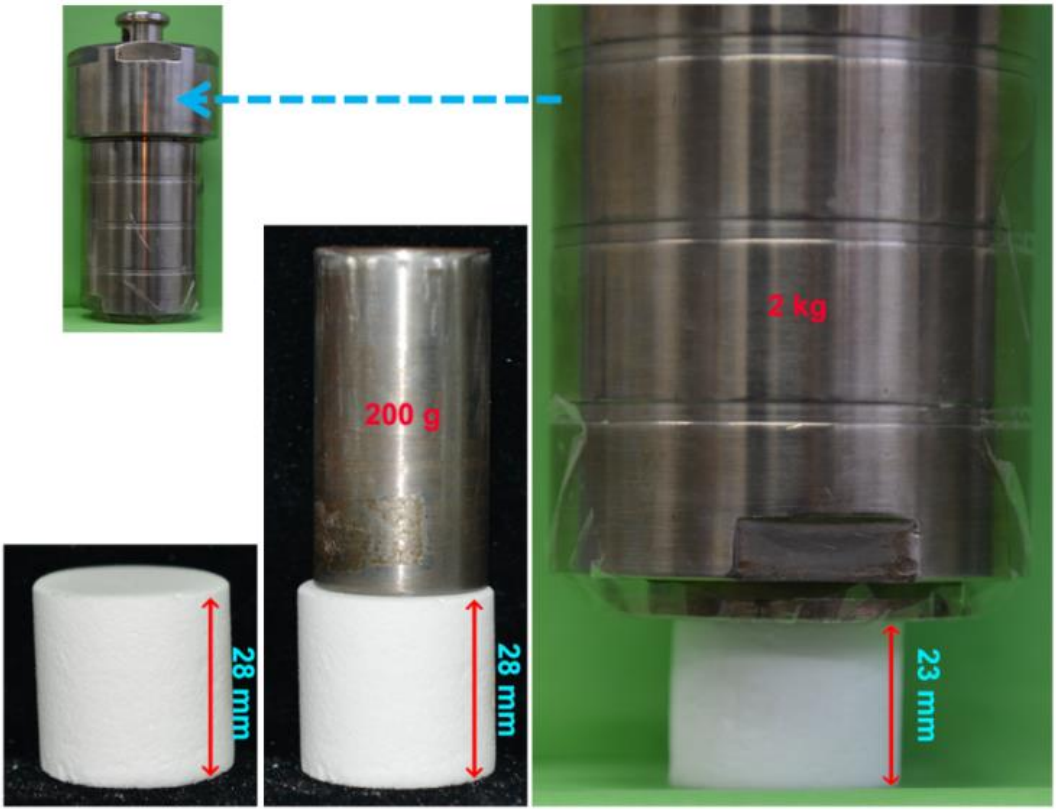

Figure S3. Photographs of the ANSA-3#, the ANSA-3# with a 200 g weight without deformation, and the ANSA-3# with a 2 kg weight with 18% reversible deformation.

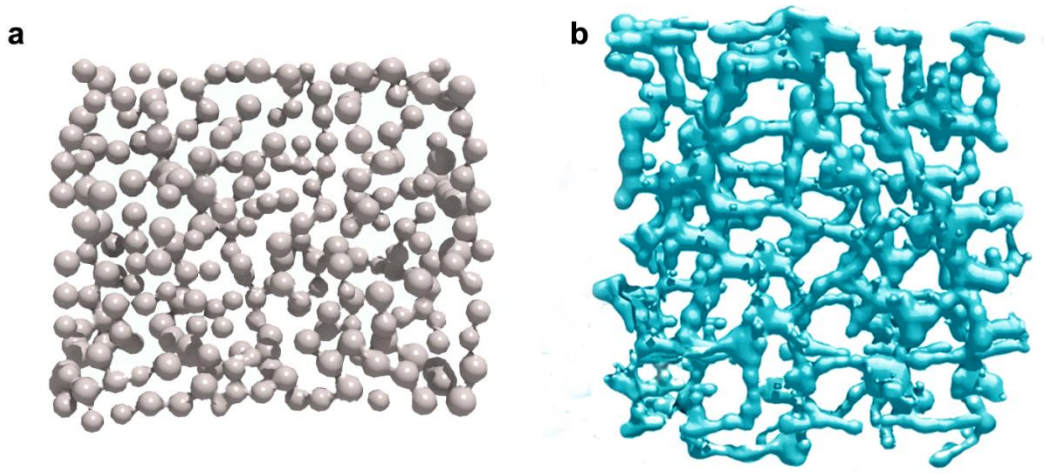

Figure S4. Schematics of a) conventional silica aerogels with weak necklace-like networks and b) the ANSAs with networks resembling a miniature replica of the hollow space of an ant nest.

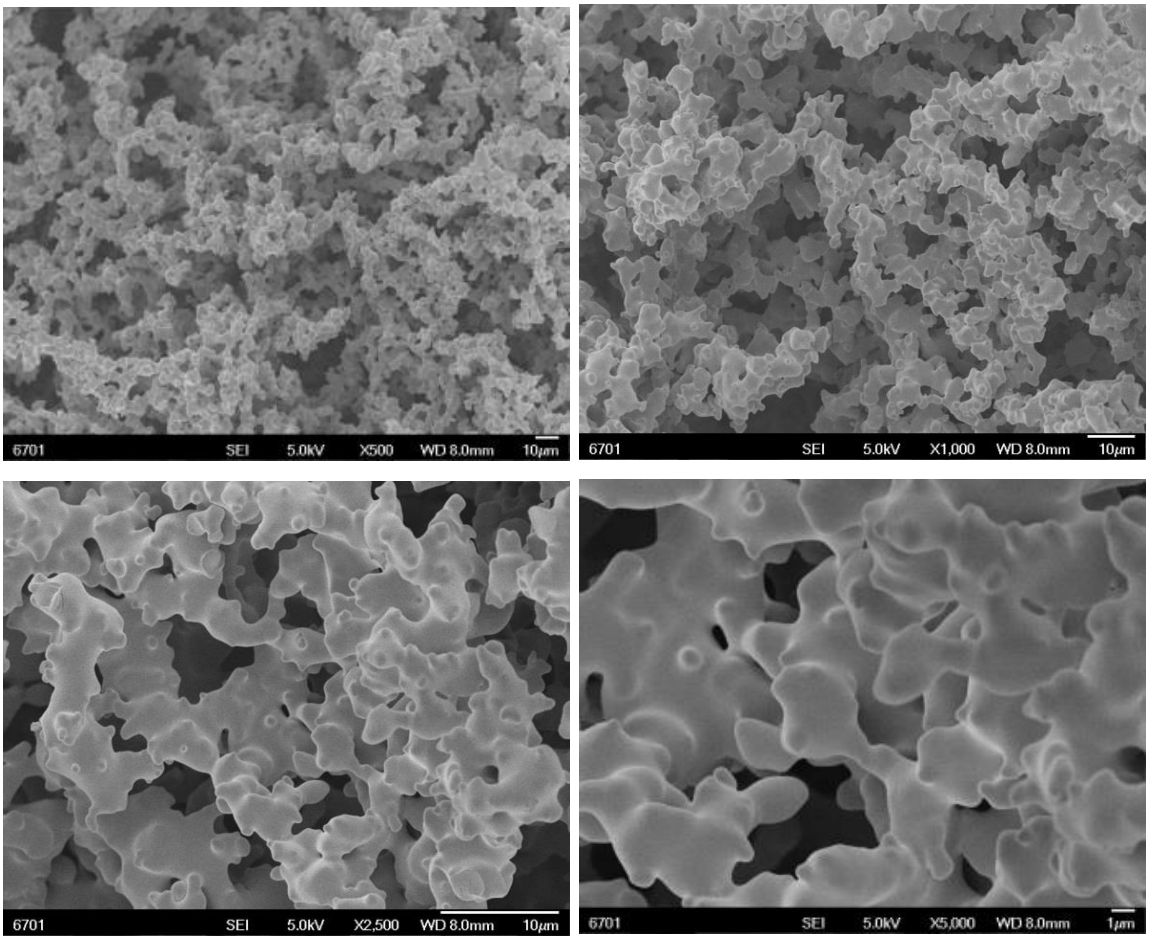

Figure S5. SEM images of the ANSA-3#.

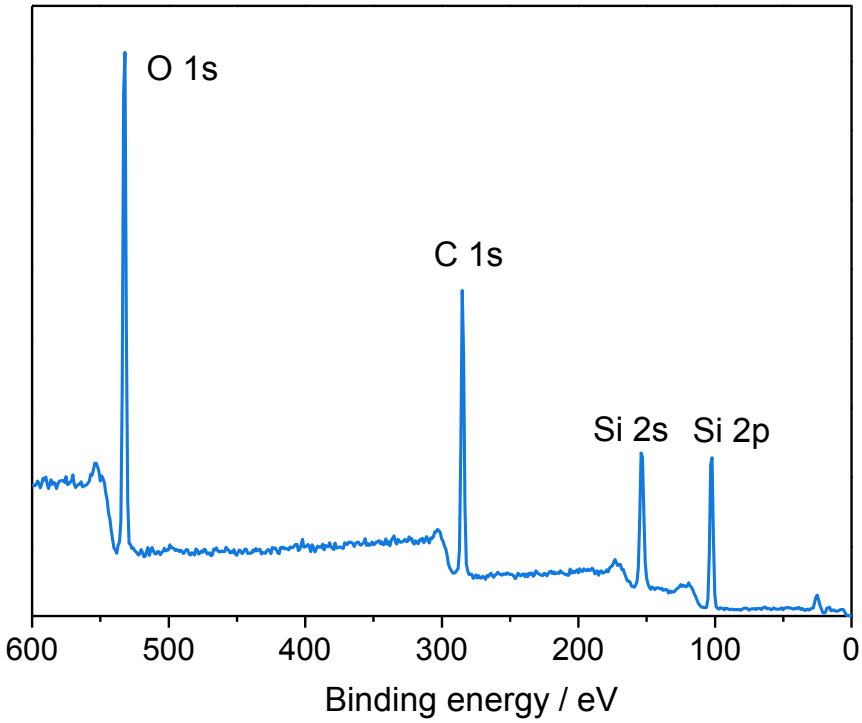

Figure S6. XPS spectrum of the ANSA-3#.

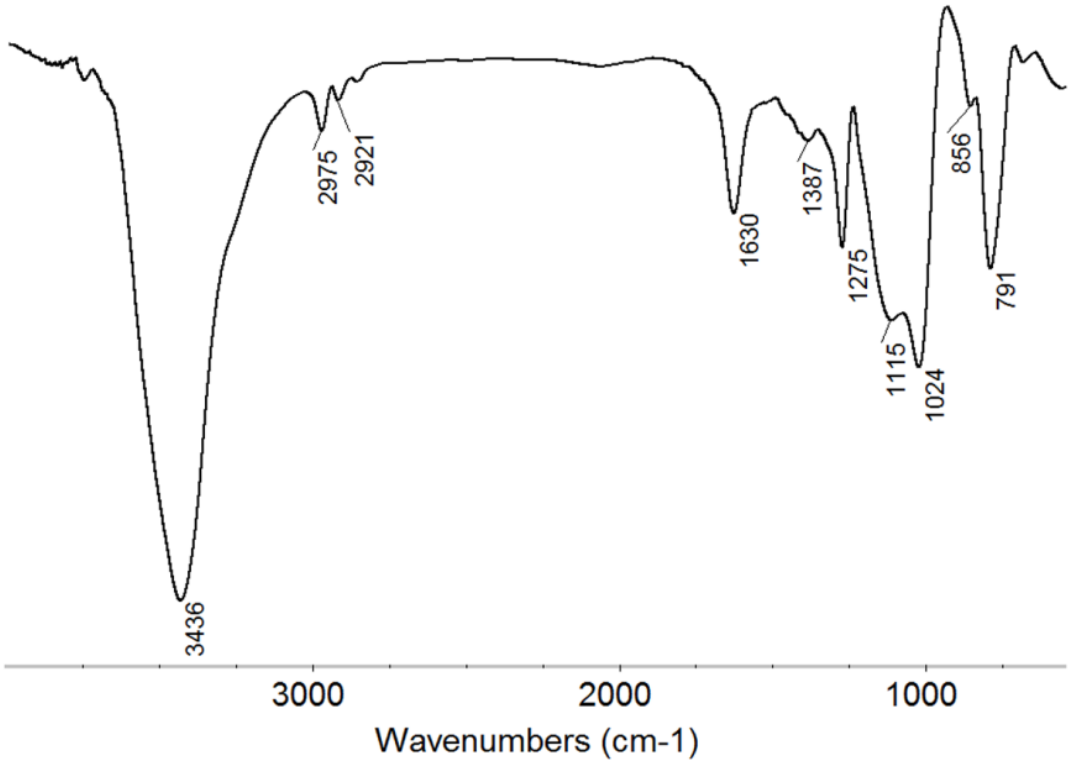

Figure S7. Infrared spectrum of the ANSA-3#. The absorption band at 1024 cm^{-1} is attributed to asymmetric stretching of linear and branched Si-O-Si.[1] The band at 1115 cm^{-1} is attributed to Si-O-Si asymmetric stretching of polycyclic oligomers. The bands at 1387 and 1275 cm^{-1} are assigned to methyl asymmetric deformations. The bands at 856 and 791 cm^{-1} are attributed to methyl rocking of Si-$(CH_3)_2$ and Si-CH_3 as well as C-Si asymmetric stretching.[2] The bands at 2975 and 2921 cm^{-1} are assigned to methyl stretching. The band at 1630 cm^{-1} is due to -OH groups of physical adsorbed water. The broad band at 3436 cm^{-1} is due to -OH groups of physical adsorbed water and the Si-OH groups of the ANSA.[3]

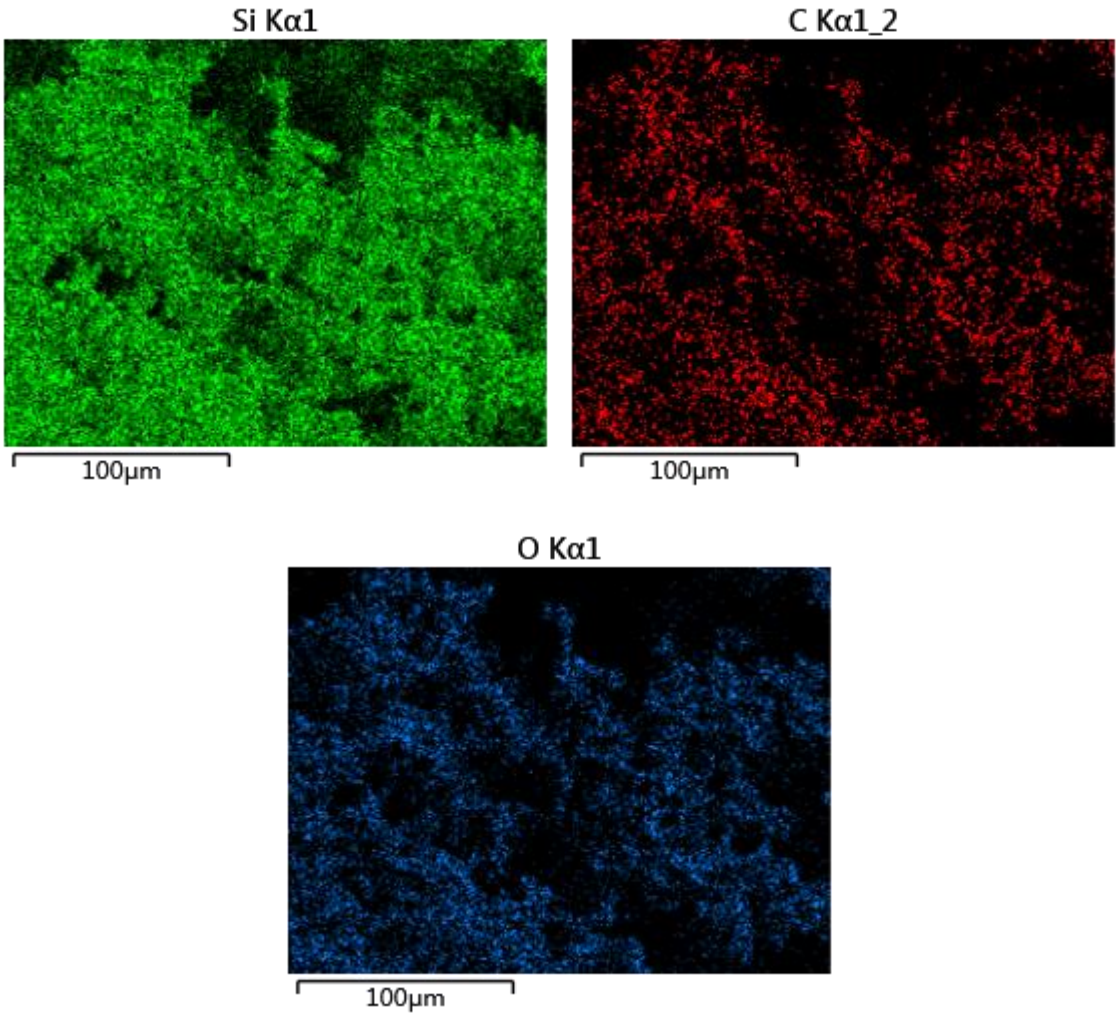

Figure S8. Elemental maps of Si, C and O of the ANSA-3#.

Figure S9. Preparation of the ANSA in the absence of HAc and Na_2CO_3 (ANSA-0#).

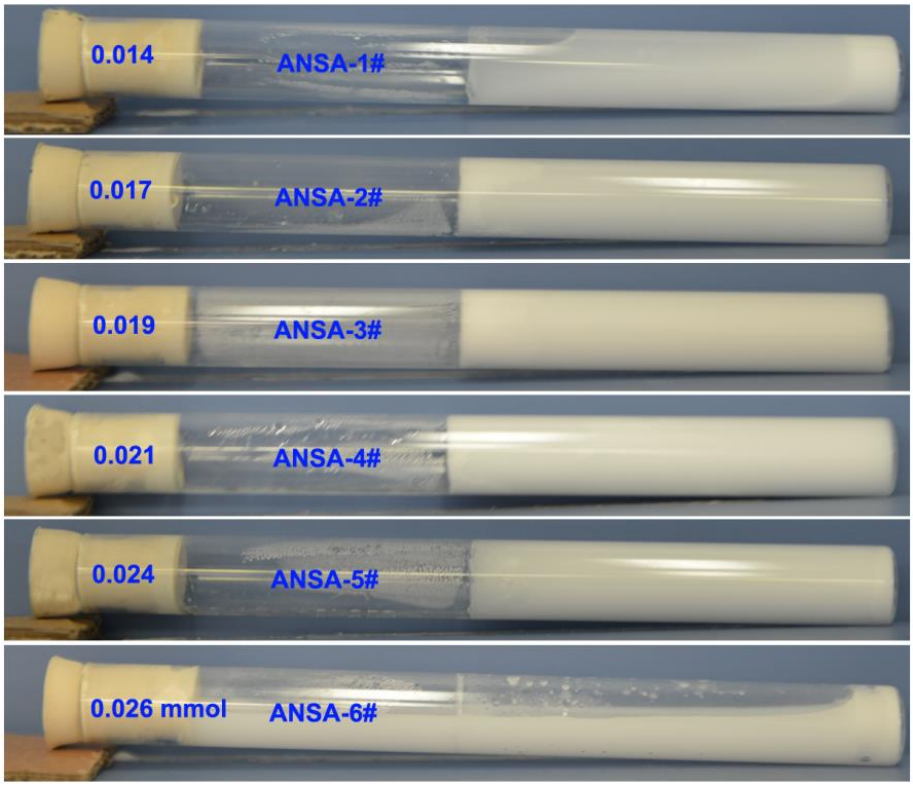

Figure S10. Preparation of the ANSAs with different content of Na_2CO_3.

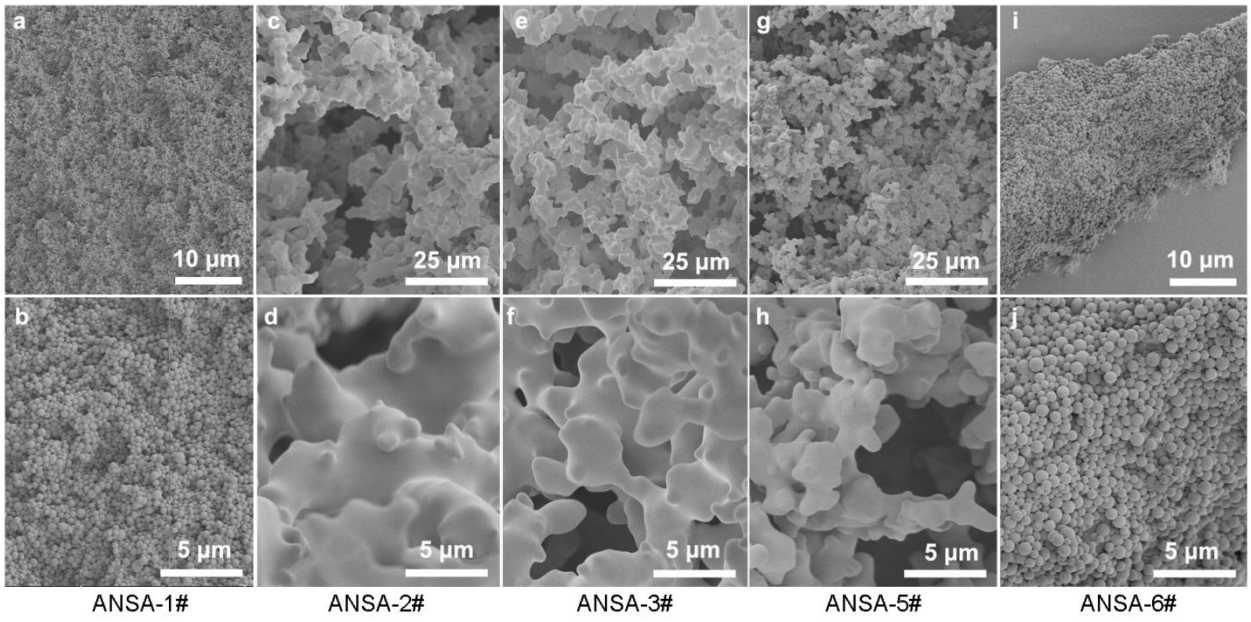

Figure S11. SEM images of the ANSAs prepared with a-b) 0.014 mmol, c-d) 0.017 mmol, e-f 0.019 mmol, g-h) 0.024 mmol and i-j) 0.026 mmol of Na_2CO_3.

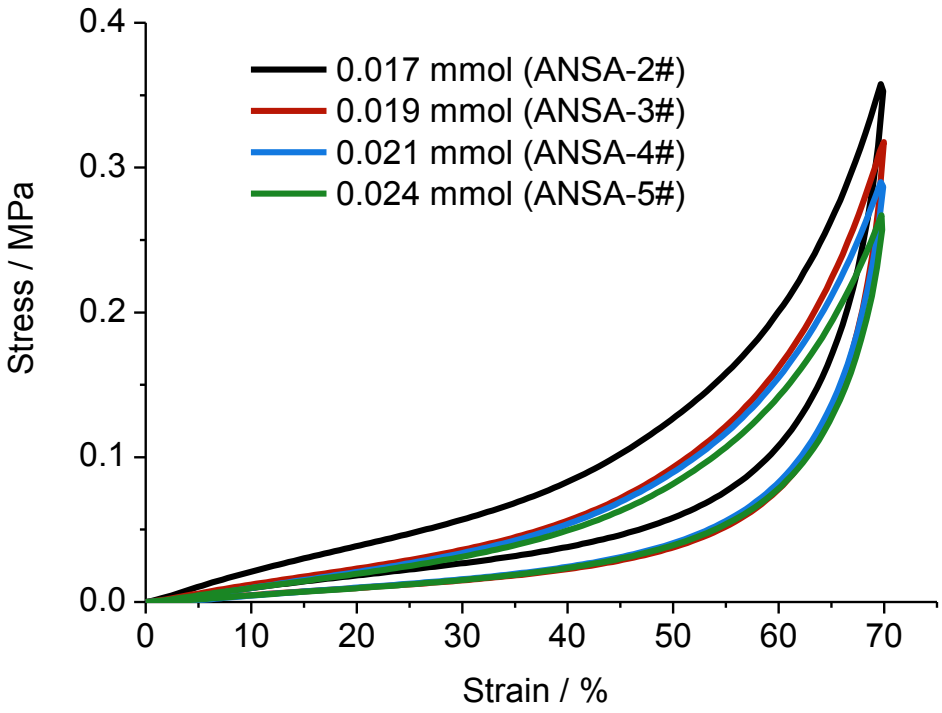

Figure S12. Compressive stress-strain curves of the ANSAs prepared with different Na_2CO_3 contents, i.e., different pH.

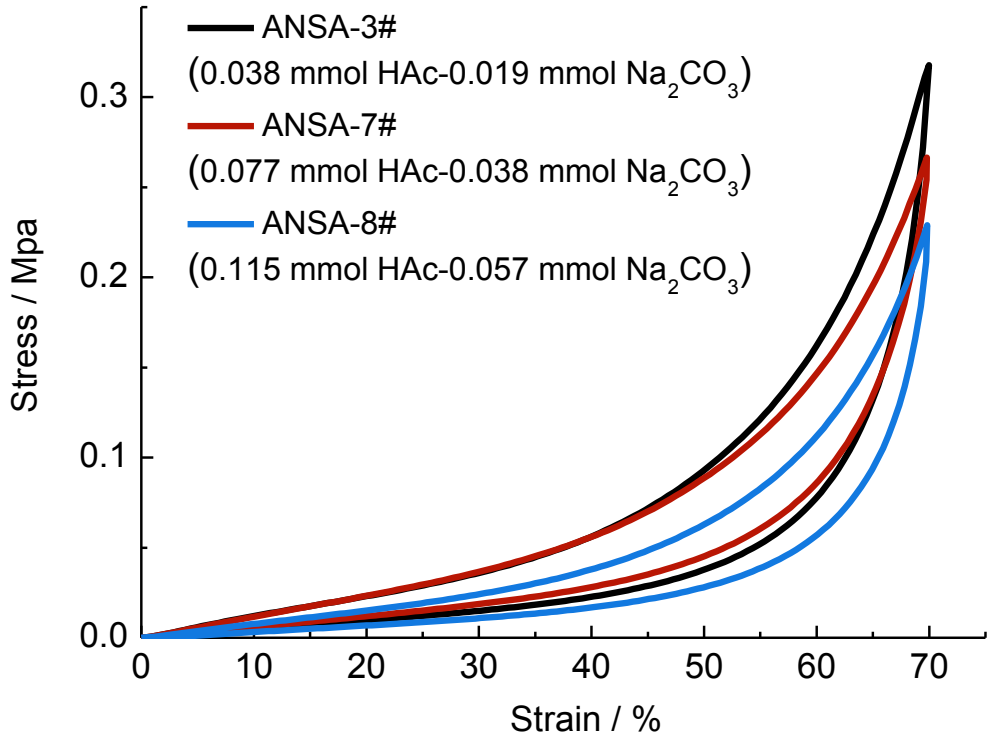

Figure S13. Compressive stress-strain curves of the ANSAs prepared with different HAc and Na_2CO_3 contents, i.e., different concentrations of the HAc-NaAc buffer solution.

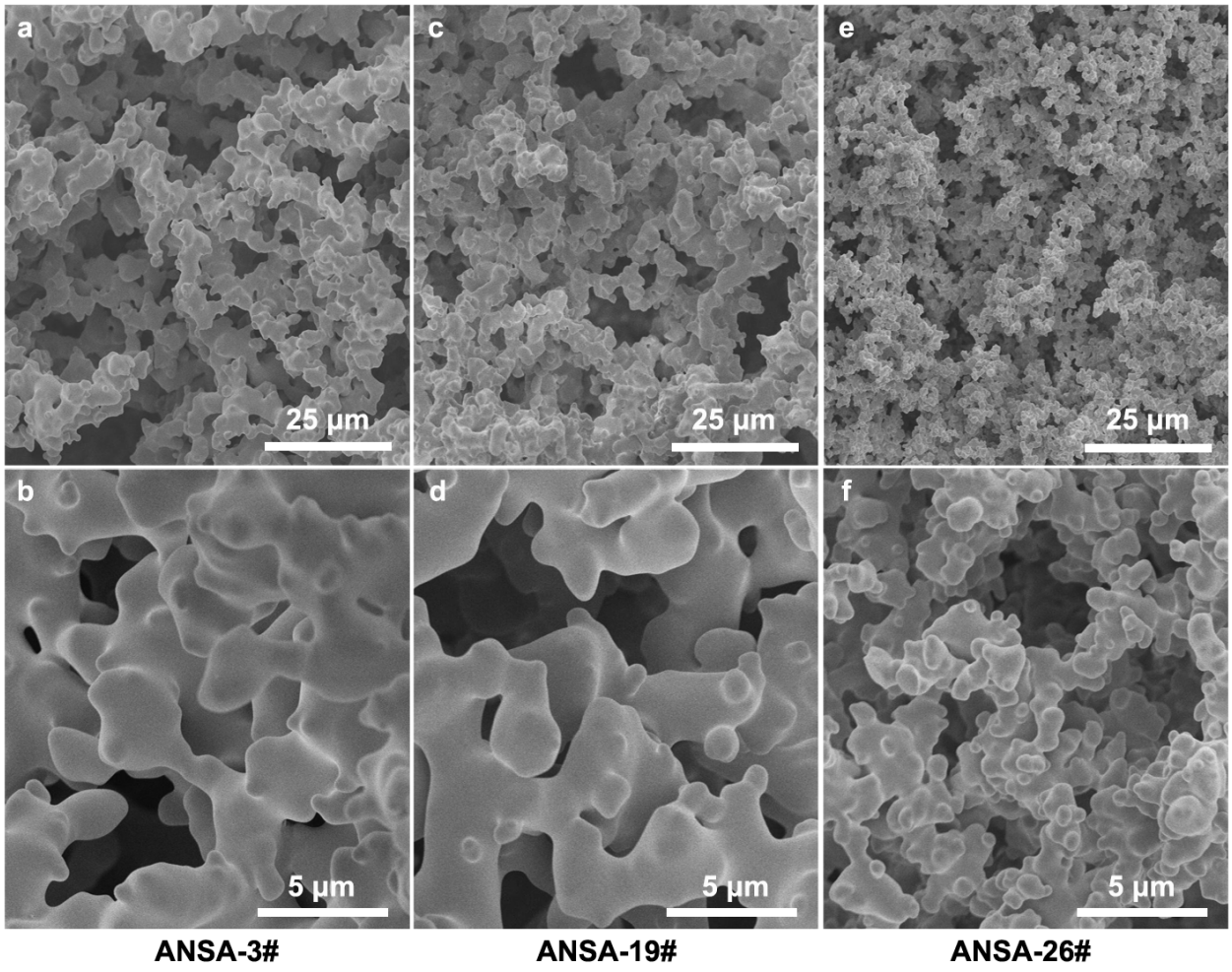

Figure S14. SEM images of the ANSAs prepared with a-b) Na_2CO_3, c-d) $NaHCO_3$, and e-f) ammonia.

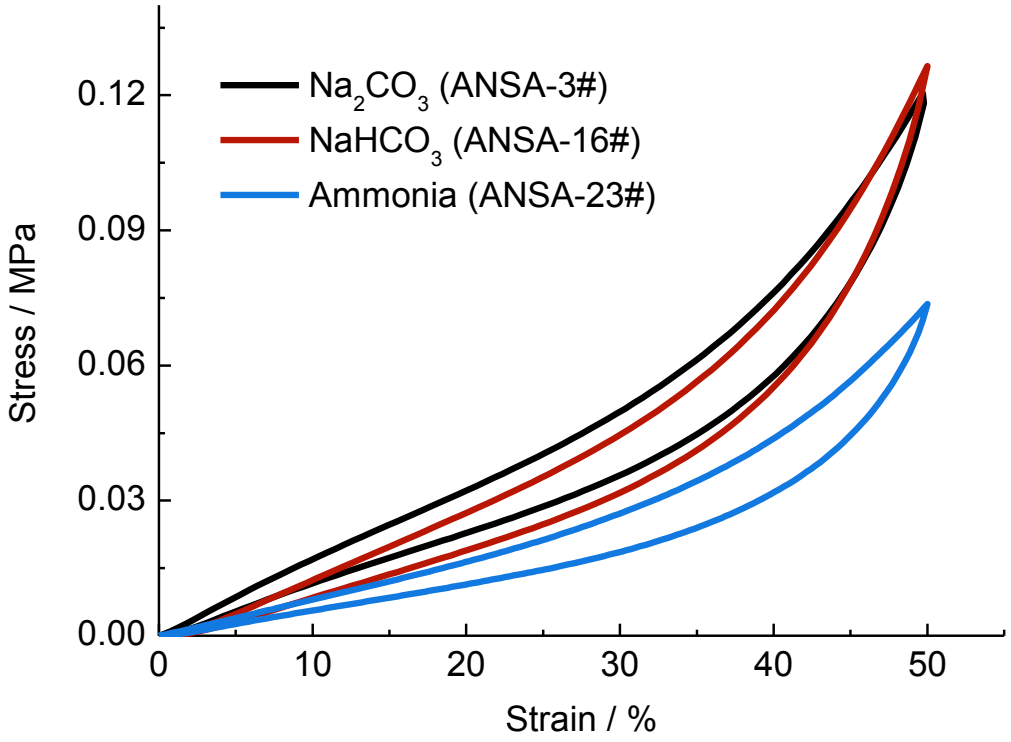

Figure S15. Compressive stress-strain curves of the ANSAs prepared using different buffer solutions. The buffer solutions were prepared using HAc and different alkalis including Na_2CO_3, $NaHCO_3$ and ammonia.

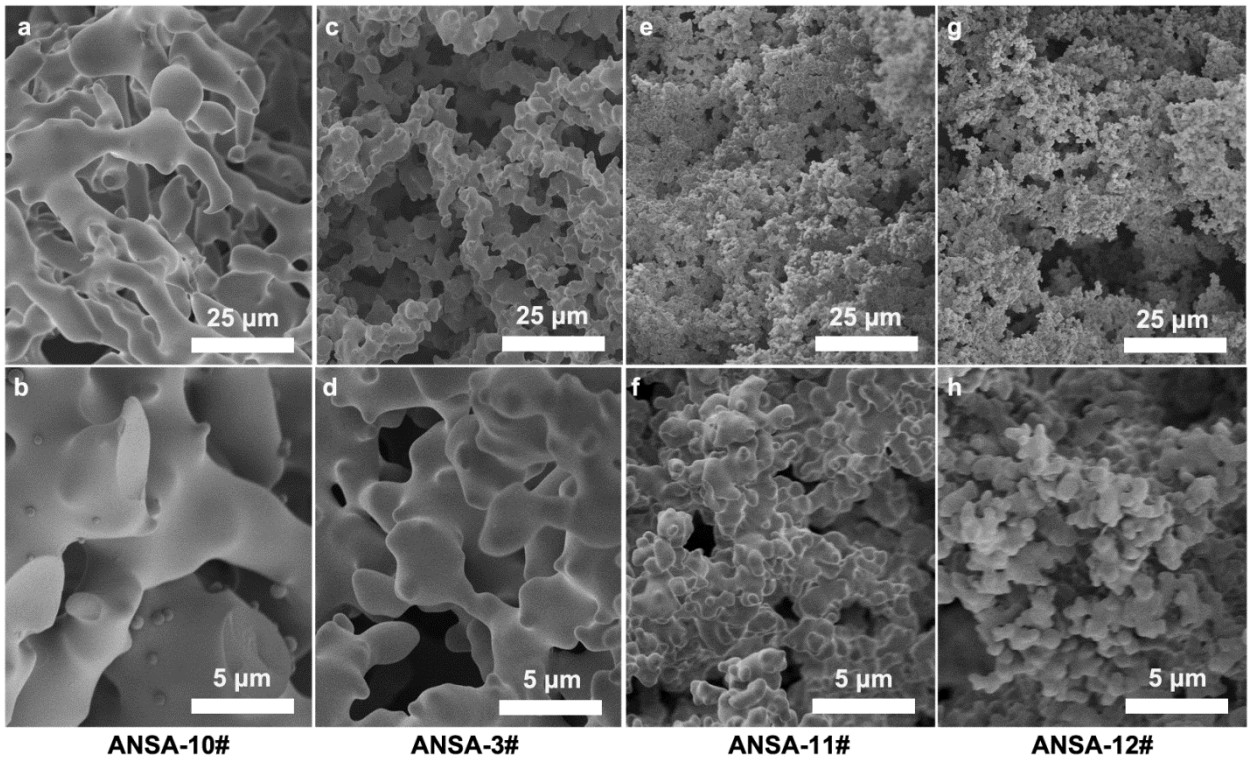

Figure S16. SEM images of the ANSAs prepared with a-b) 0.0025 mmol, c-d) 0.0034 mmol, e-f) 0.0042 mmol and g-h) 0.0050 mmol of DHDAB.

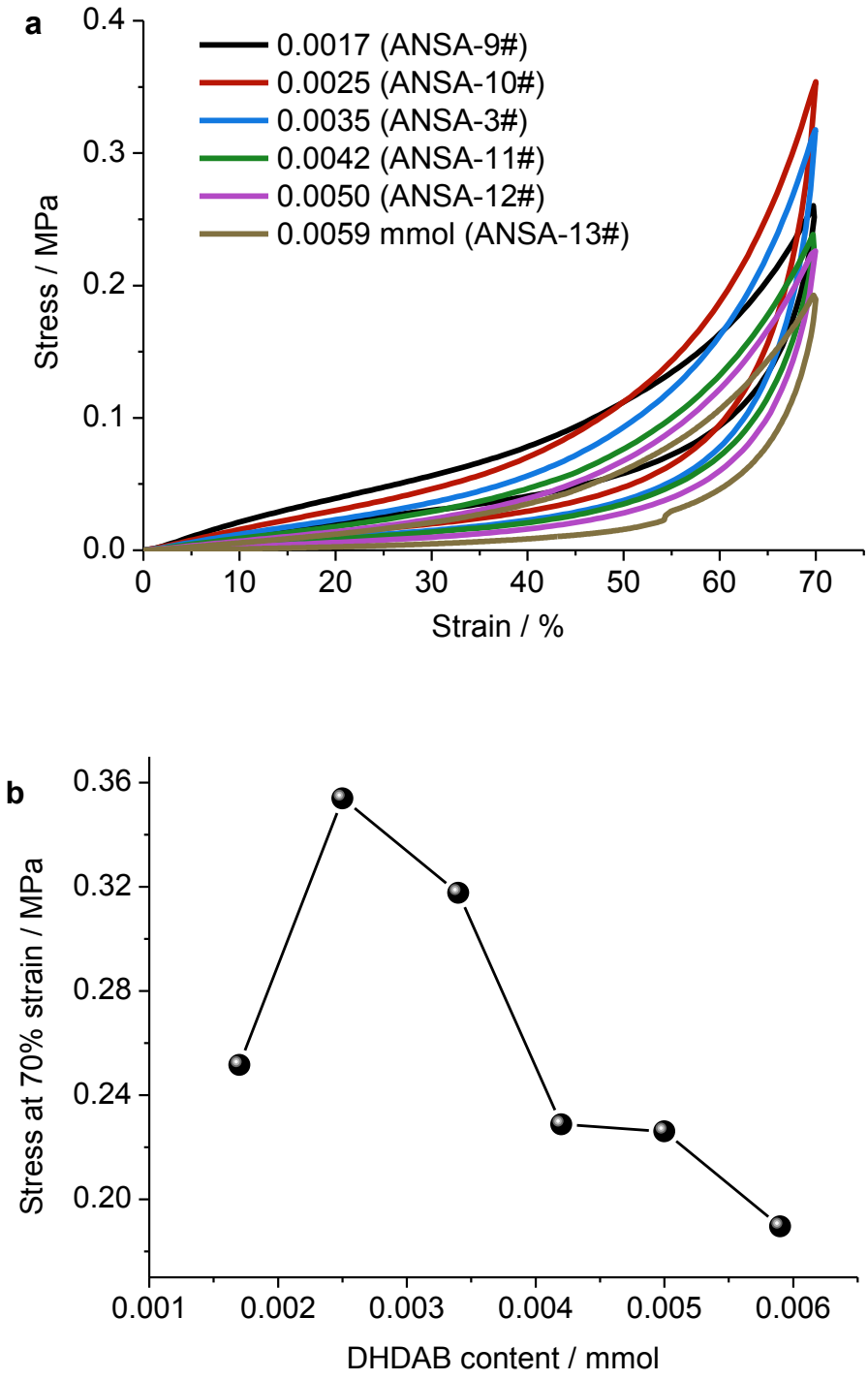

Figure S17. a) Compressive stress-strain curves of the ANSAs prepared with different DHDAB contents. b) Variation of compressive stress of the ANSAs at 70% strain with the DHDAB content.

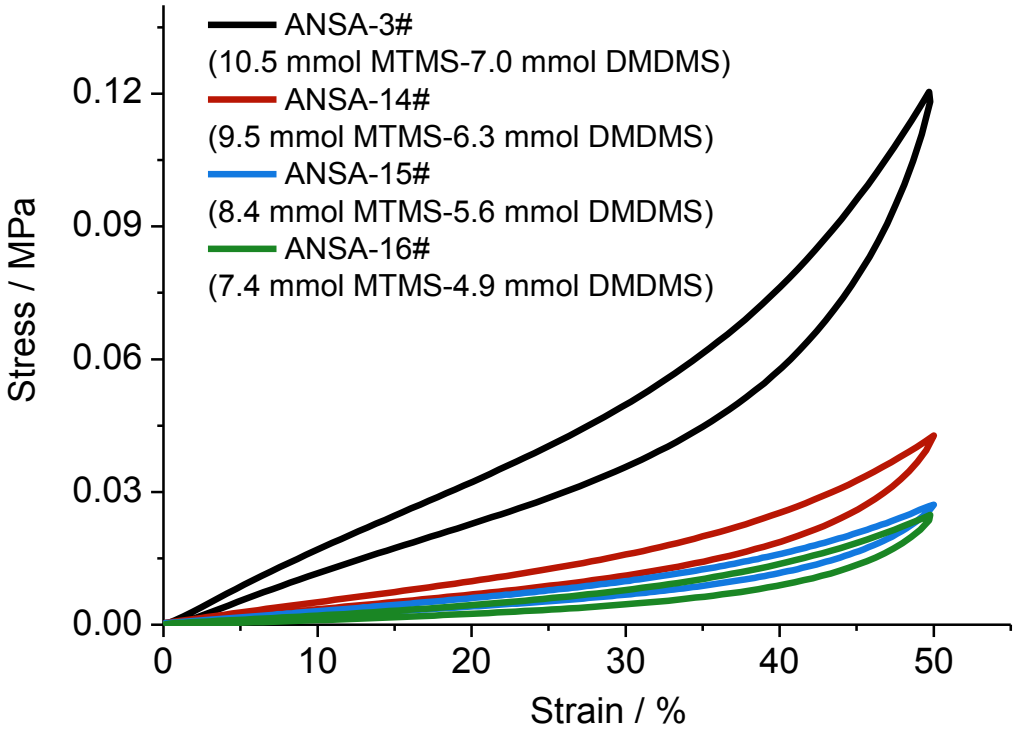

Figure S18. Compressive stress-strain curves of the ANSAs prepared with different contents of MTMS and DMDMS.

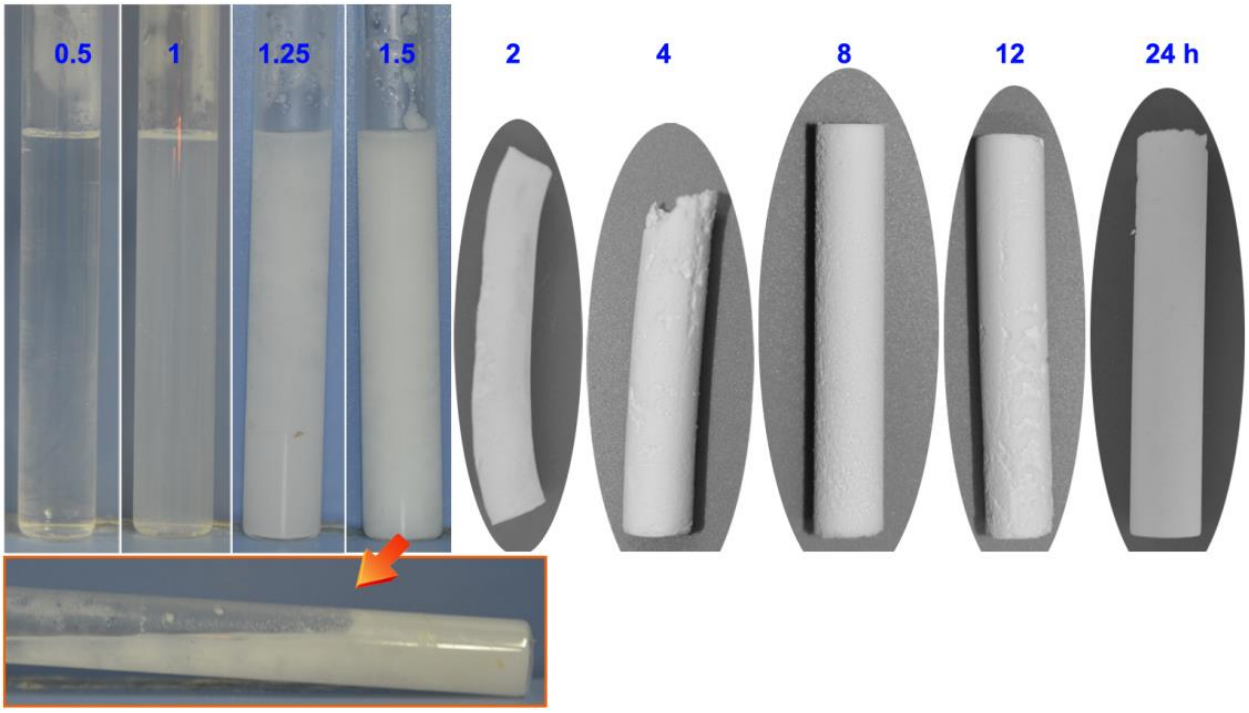

Figure S19. Preparation of the ANSAs (ANSA-3# series) with different sol-gel transition and phase separation time.

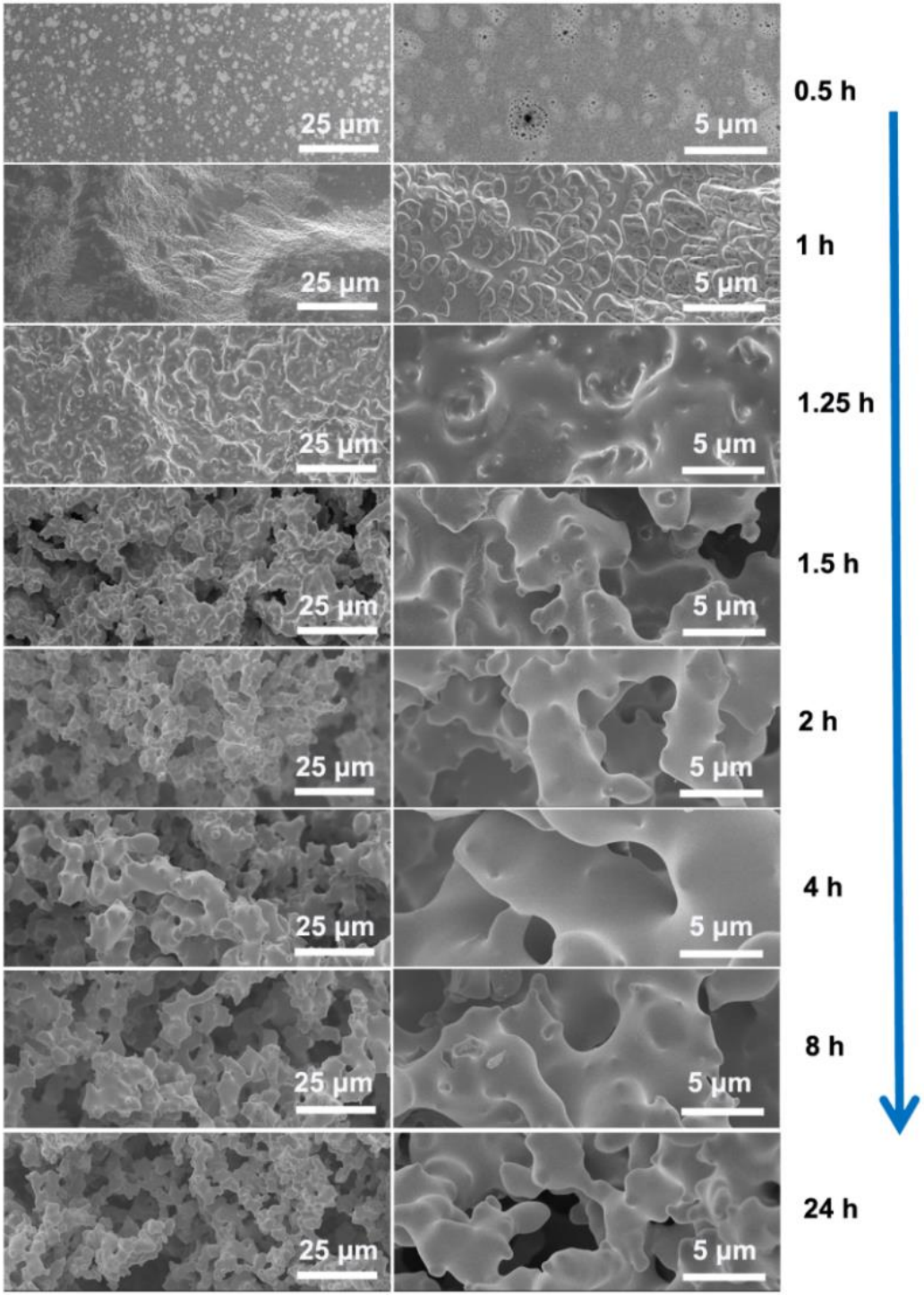

Figure S20. SEM images of the ANSAs (ANSA-3# series) with different sol-gel transition and phase separation time.

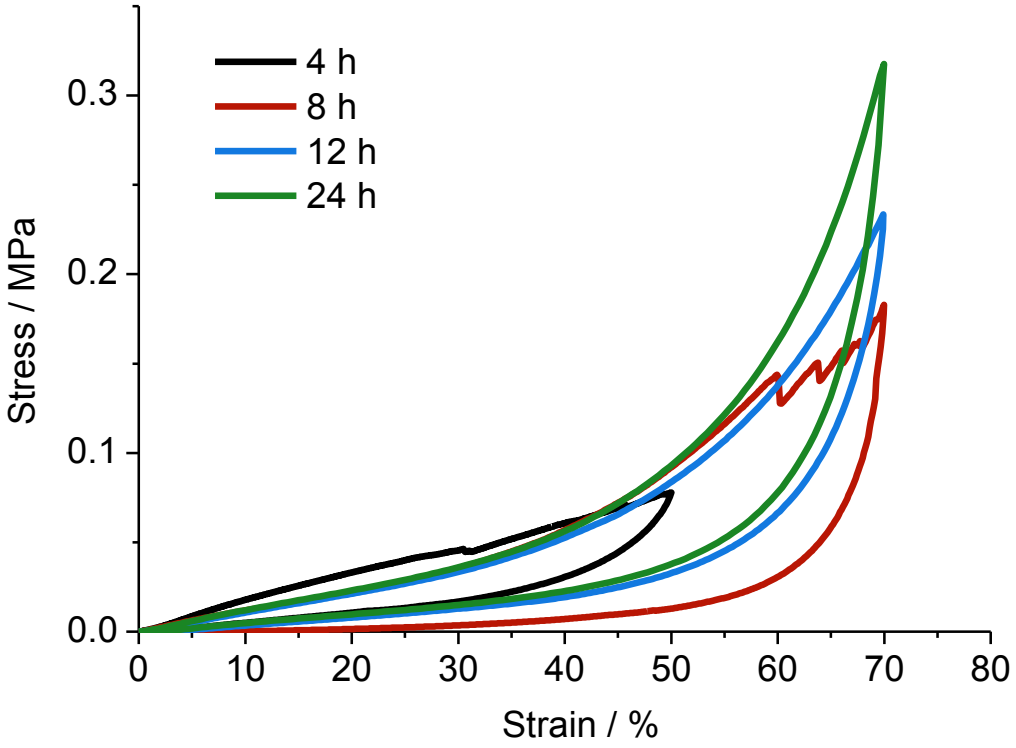

Figure S21. Compressive stress-strain curves of the ANSAs (ANSA-3# series) with different sol-gel transition and phase separation time.

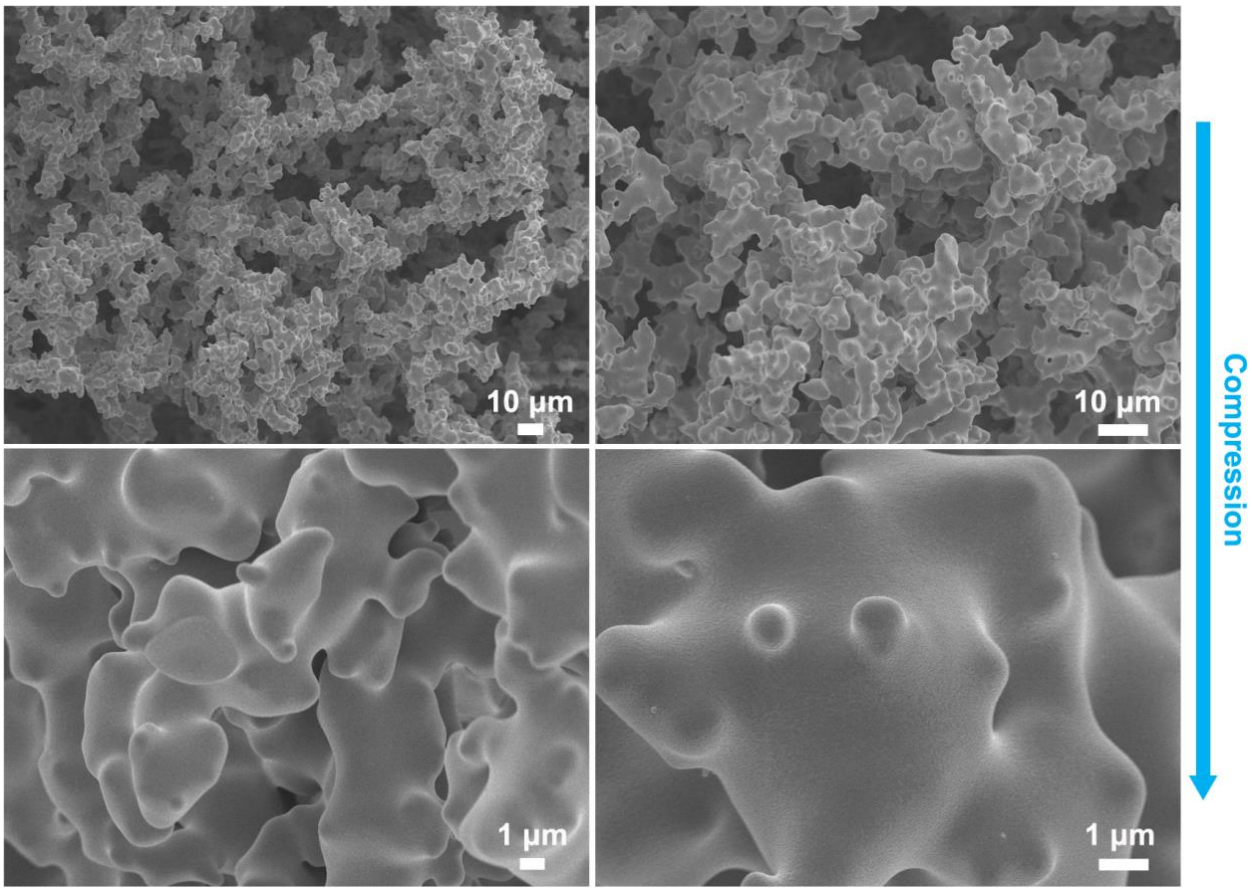

Figure S22. SEM images of the ANSA-3# normal to the compression direction after 500 successive cyclic compressive fatigue tests of 50% strain.

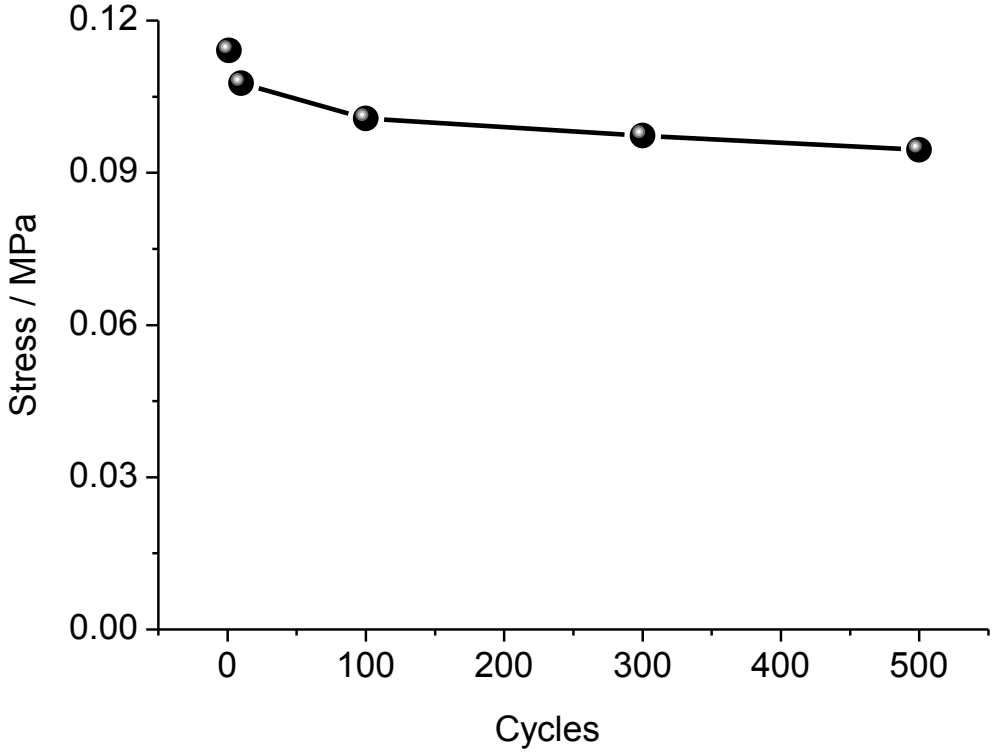

Figure S23. History of the compressive stress at 50% strain of the ANSA-3# as a function of compressive test cycles.

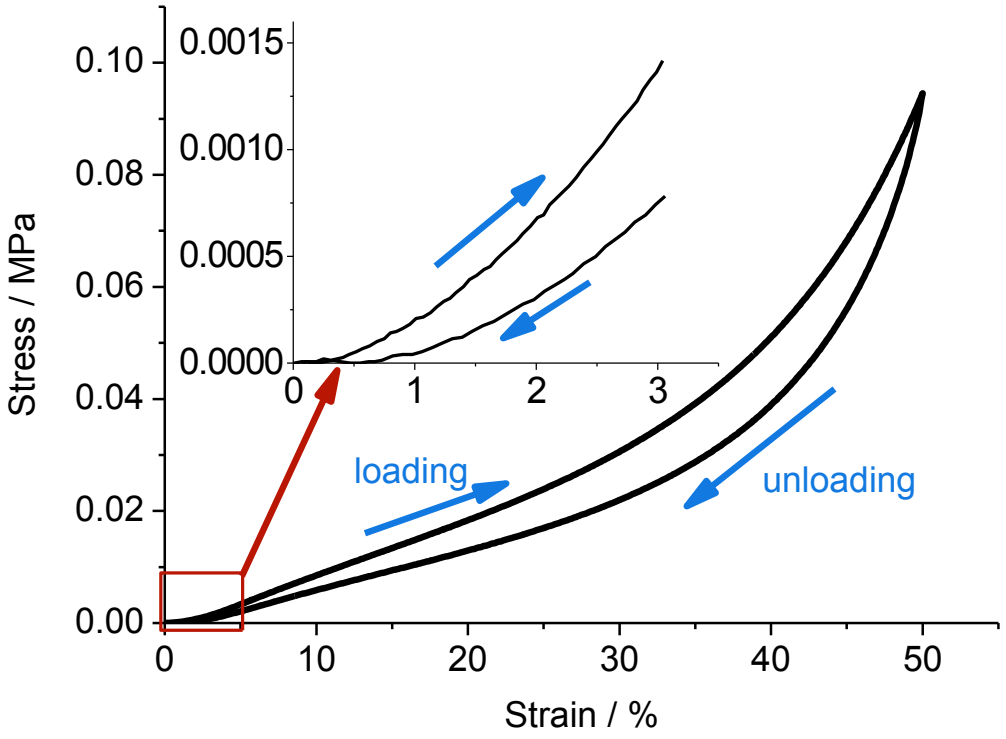

Figure S24. Compressive stress-strain curve of the ANSA-3# in the 500th successive cyclic compressive fatigue test of 50% strain. Inset: the loading at the beginning and unloading at the end of the 500th cycle.

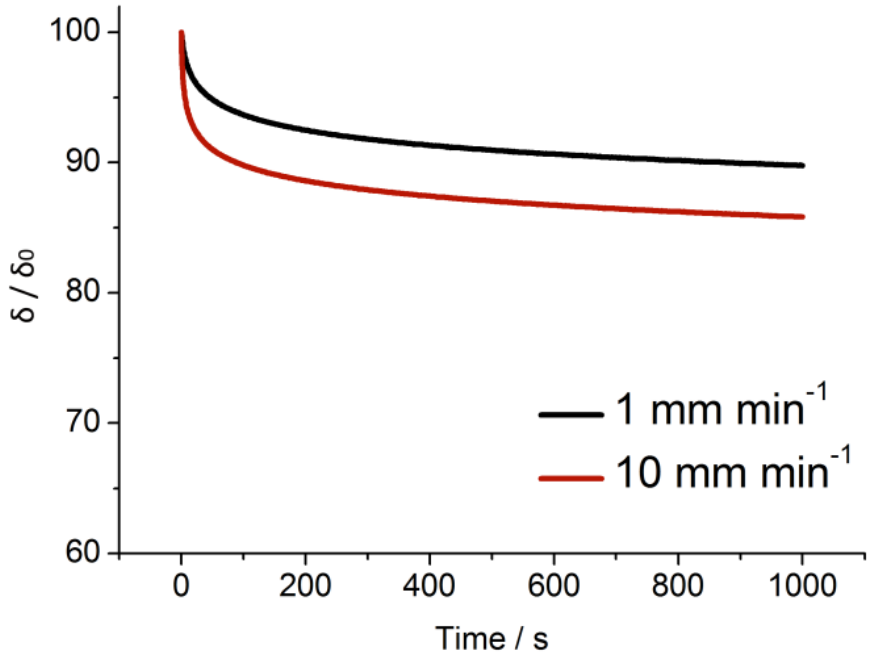

Figure S25. Stress relaxation of the ANSA-3#. The ANSA-3# was compressed at 1 and 10 mm min^{-1} to 50% strain at which the compressive stress is δ_0, and subsequent decrease in the stress δ was recorded for 1000 s while keeping 50% strain.

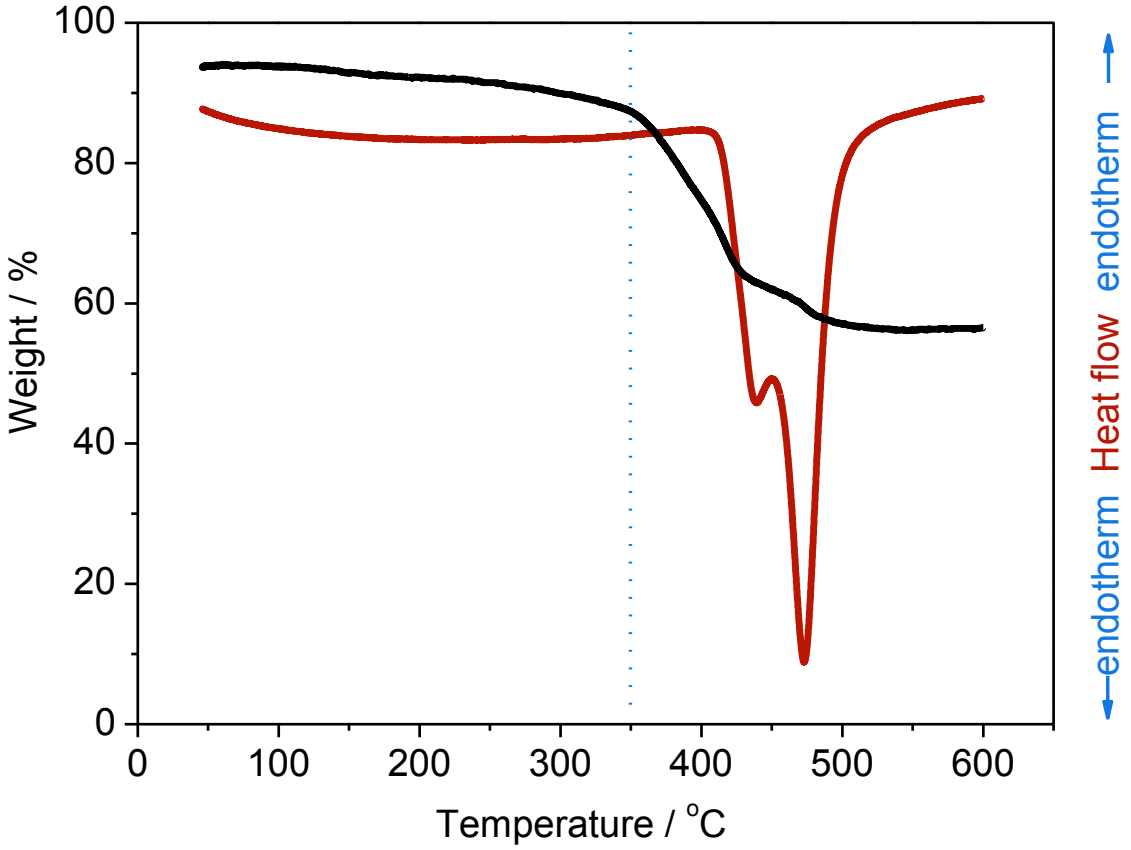

Figure S26. TGA and DSC curves of the ANSA-3# under air atmosphere.

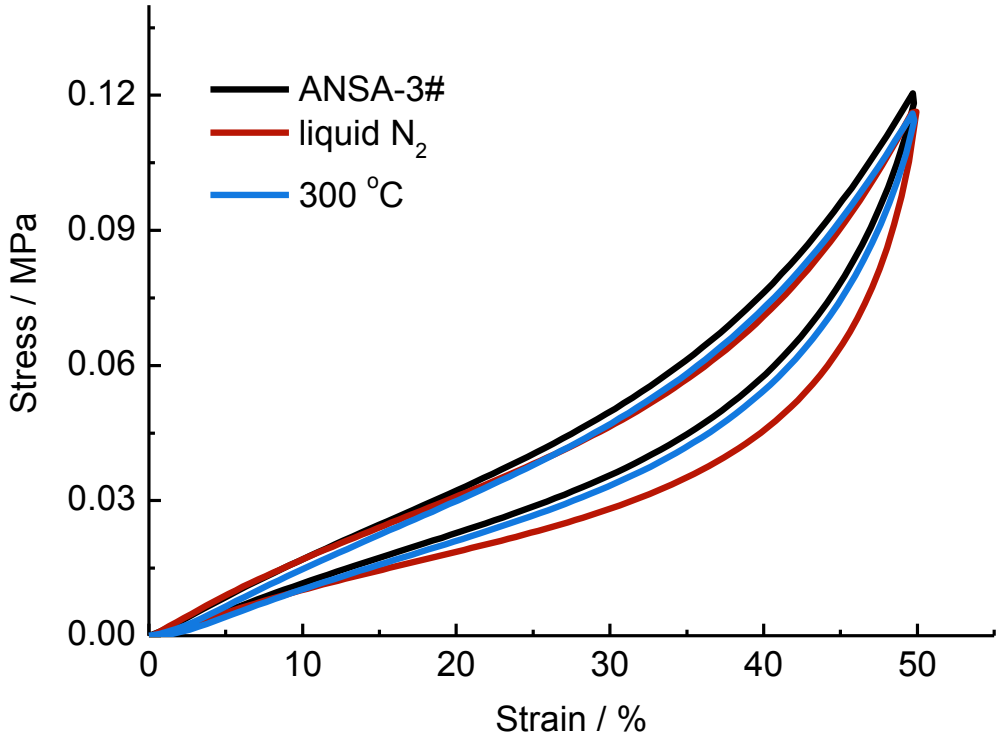

Figure S27. Compressive stress-strain curves of the ANSA-3# after kept in liquid N_2 for 20 min or in an oven at 300 ℃ for 6 h.

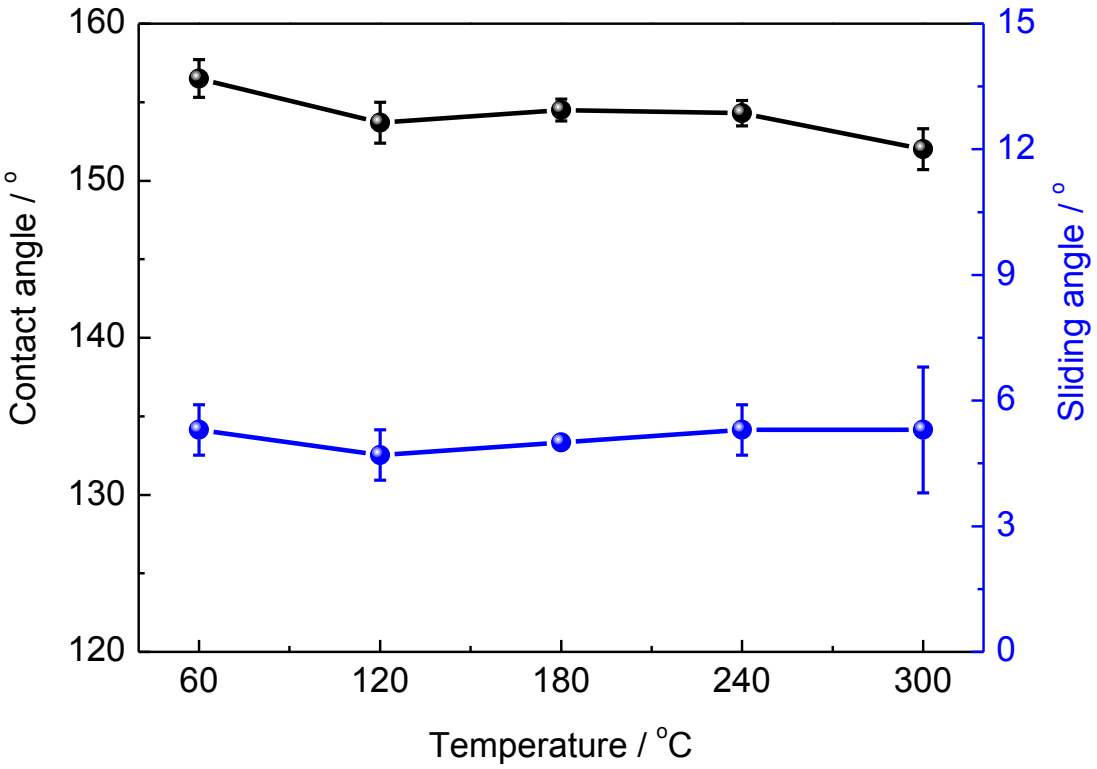

Figure S28. Water contact angles and sliding angles of the ANSA-3# after kept at different temperatures for 6 h.

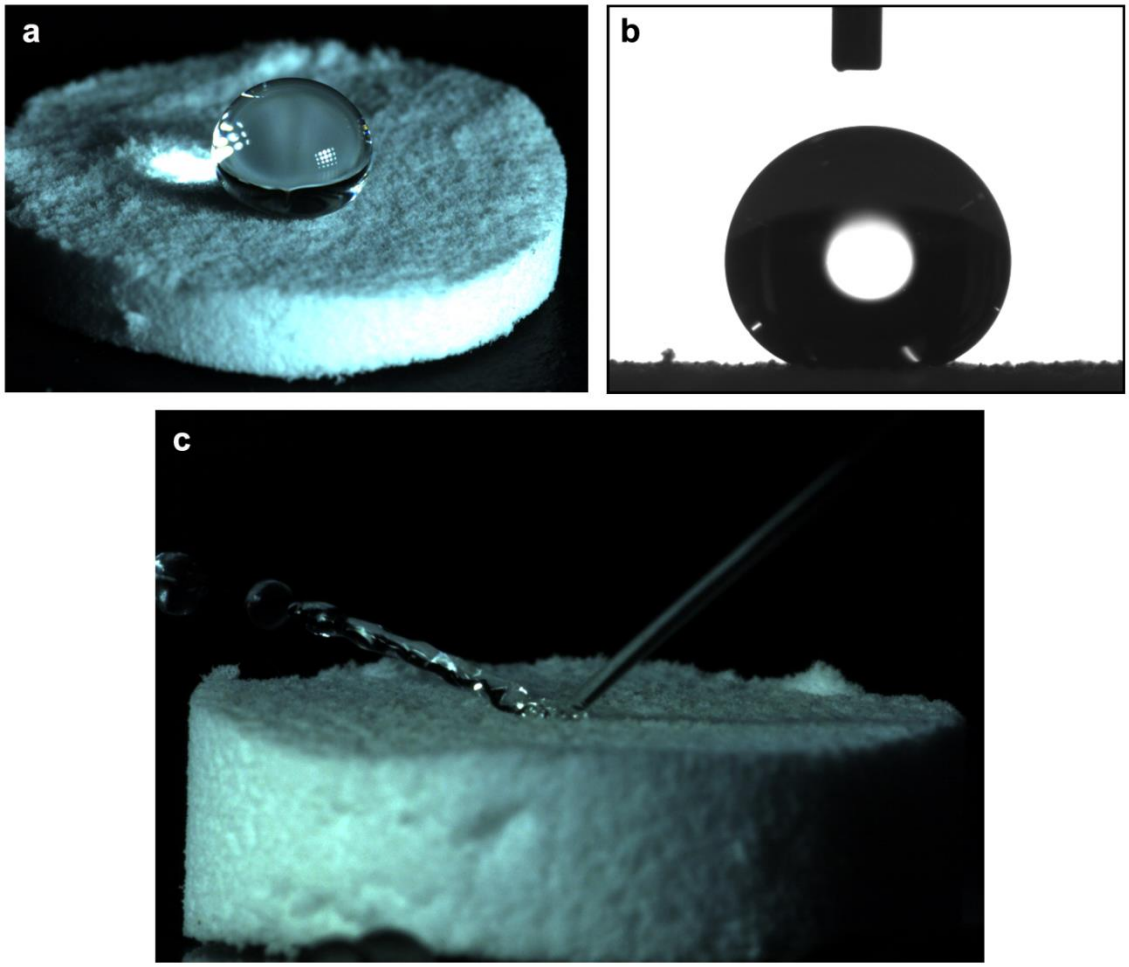

Figure S29. a-b) Photographs of a water droplet on the surface of the ANSA-3#. c) A jet of water bouncing off the surface of the ANSA-3#.

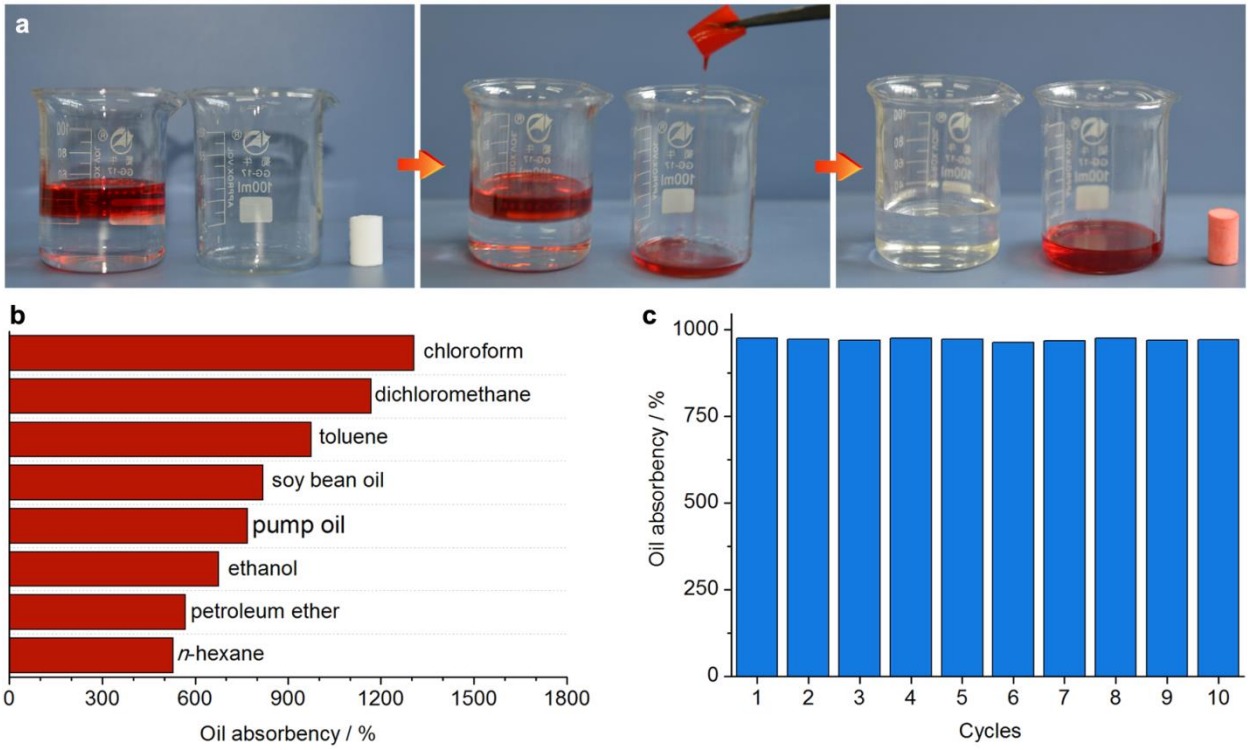

Figure S30. a) Absorption and collection of immiscible oil from water using the ANSA-3#. Oil was dyed with oil read O. b) Absorbency of the ANSA-3# for different organic liquids. **c)** Variation of absorbency of the ANSA-3# for toluene with absorption cycles. The absorbed oil was stored in the micropores of the ANSA and can be squeezed out by hand. No dripping of the absorbed oil was observed in the handling process. The absorbency depends on the density of the organic liquids. The equilibrium absorbency can be achieved within a few seconds regardless of the density and viscosity of the organic liquids. The unique wettability insures efficient oil/water separation, and the macroporous superelastic network promotes absorption/desorption of oils.

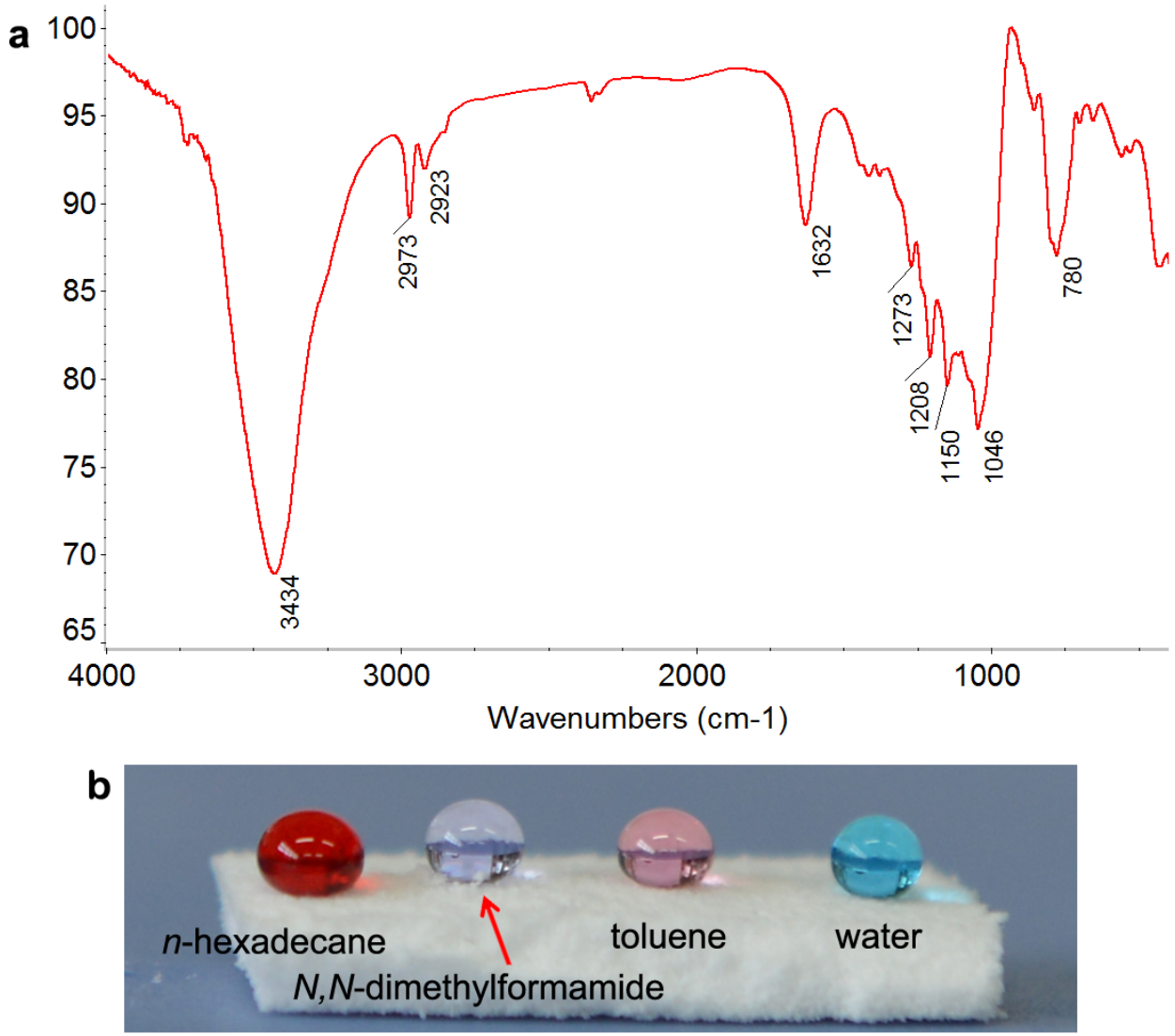

Figure S31. a) Infrared spectrum of the superamphiphobic ANSA-3# and b) a photograph of various liquid droplets on the surface of the superamphiphobic ANSA-3#. Water was dyed with methylene blue. Toluene and *n*-hexadecane were dyed with oil red O. After modification with *1H,1H,2H,2H*-perfluorodecyltriethoxysilane and tetraethoxysilane, the C-F band at 1208 cm^{-1} was easily recognized.[4] The band at 1150 cm^{-1} is attributed to the possible silsesquioxane bands stemming from the co-condensation of hydrolyzed *1H,1H,2H,2H*-perfluorodecyltriethoxysilane and tetraethoxysilane.

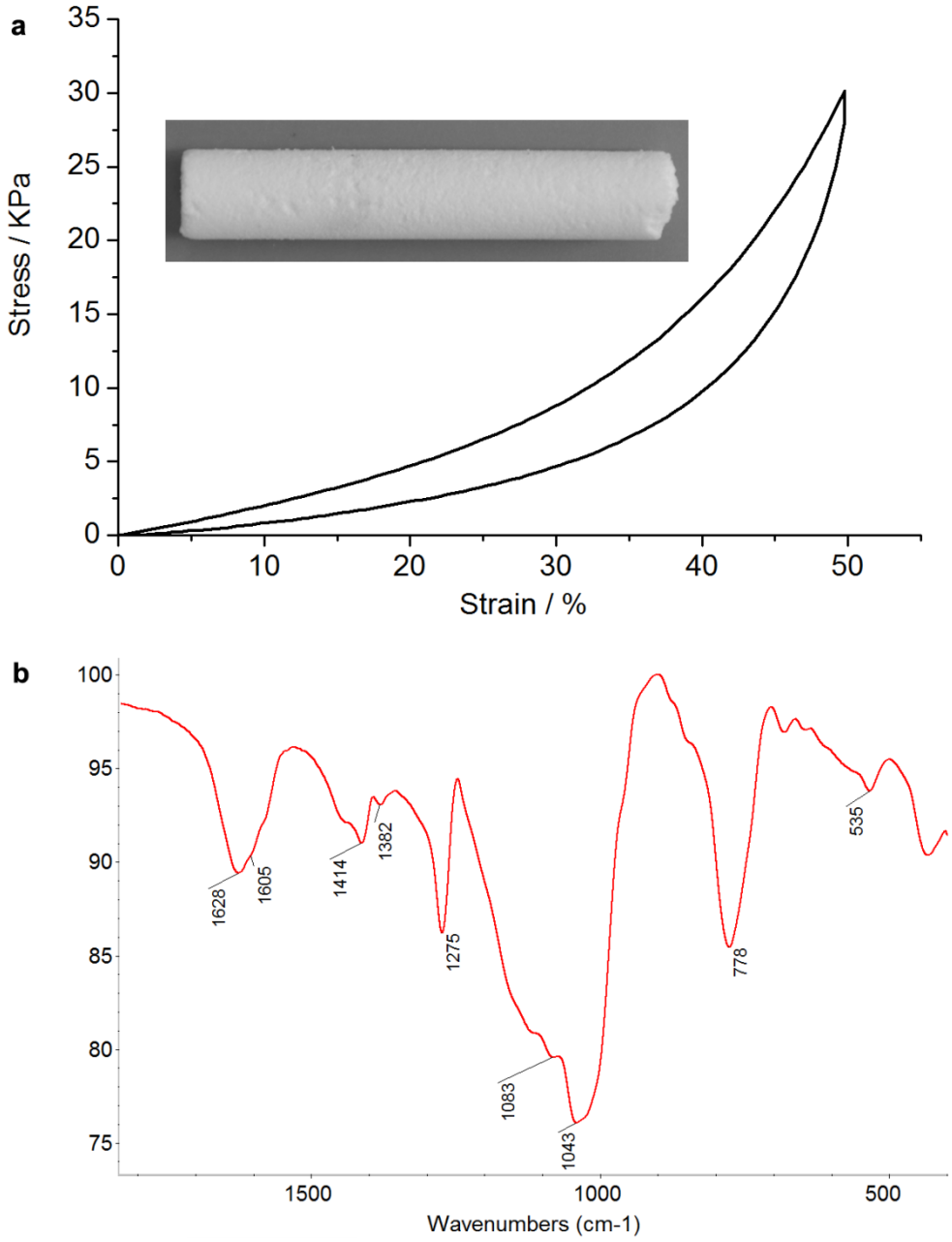

Figure S32. a) Compressive stress-strain curve and a photograph, and b) infrared spectrum of the ANSA prepared using MTMS and methylvinyldimethoxysilane. The bands of the vinyl group were detected at 1605 cm^{-1} (C=C stretching) and 1414 cm^{-1} (=CH_2 scissor stretching). The broad band in the range 970-1050 cm^{-1} is attributed to asymmetric stretching of linear and branched Si-O-Si, =CH_2 wagging and C=C twisting.[5]

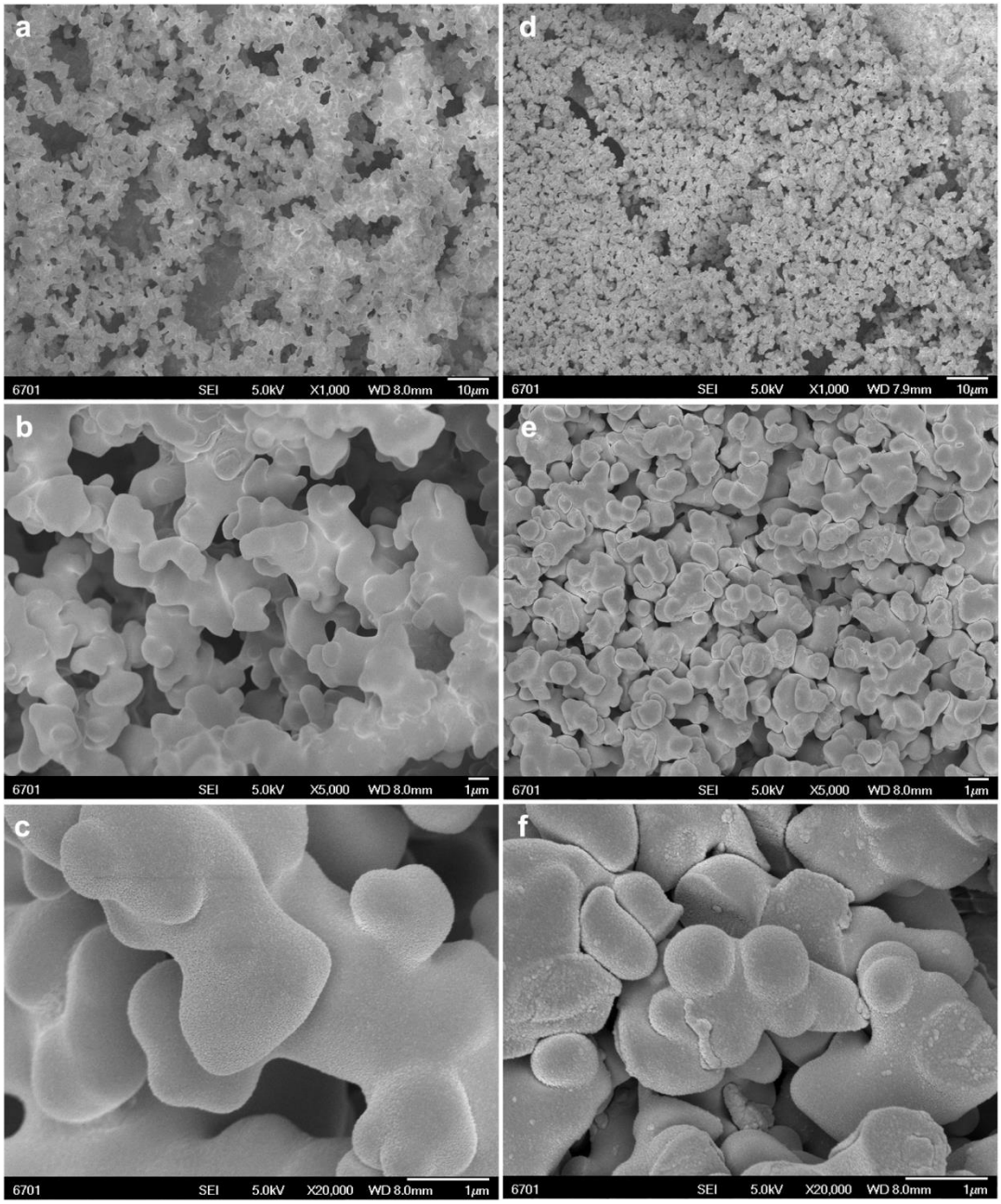

Figure S33. SEM images of the ANSA coatings on a-c) glass slide and d-f) PTFE plate.

Table S1. Starting compositions for preparation of the ANSAs and the products. √ means monolithic ANSAs were formed, whereas × means silicone nanoparticles were formed.

Samples	**HAc / mmol**	**Na_2CO_3 / mmol**	**DHDAB / mmol**	**MTMS / mmol**	**DMDMS / mmol**	**H_2O / g**	**Products**
ANSA-0#	0	0	0.0034	10.5	7.0	7.7	×
ANSA-00#	0.0385	0	0.0034	10.5	7.0	7.7	×
ANSA-1#	0.0385	0.014	0.0034	10.5	7.0	7.7	×
ANSA-2#	0.0385	0.017	0.0034	10.5	7.0	7.7	√
ANSA-3#	0.0385	0.019	0.0034	10.5	7.0	7.7	√
ANSA-4#	0.0385	0.021	0.0034	10.5	7.0	7.7	√
ANSA-5#	0.0385	0.024	0.0034	10.5	7.0	7.7	√
ANSA-6#	0.0385	0.026	0.0034	10.5	7.0	7.7	×
ANSA-7#	0.0770	0.038	0.0034	10.5	7.0	7.7	√
ANSA-8#	0.1155	0.057	0.0034	10.5	7.0	7.7	√
ANSA-9#	0.0385	0.019	0.0017	10.5	7.0	7.7	√
ANSA-10#	0.0385	0.019	0.0025	10.5	7.0	7.7	√
ANSA-11#	0.0385	0.019	0.0042	10.5	7.0	7.7	√
ANSA-12#	0.0385	0.019	0.0050	10.5	7.0	7.7	√
ANSA-13#	0.0385	0.019	0.0059	10.5	7.0	7.7	√
ANSA-14#	0.0385	0.019	0.0034	9.5	6.3	7.7	√
ANSA-15#	0.0385	0.019	0.0034	8.4	5.6	7.7	√
ANSA-16#	0.0385	0.019	0.0034	7.4	4.9	7.7	√
Samples	**HAc / mmol**	**$NaHCO_3$ / mmol**	**DHDAB / mmol**	**MTMS / mmol**	**DMDMS / mmol**	**H_2O / g**	**Products**
ANSA-17#	0.0385	0.030	0.0034	10.5	7.0	7.7	×
ANSA-18#	0.0385	0.033	0.0034	10.5	7.0	7.7	√
ANSA-19#	0.0385	0.036	0.0034	10.5	7.0	7.7	√
ANSA-20#	0.0385	0.039	0.0034	10.5	7.0	7.7	√
ANSA-21#	0.0385	0.042	0.0034	10.5	7.0	7.7	√
ANSA-22#	0.0385	0.045	0.0034	10.5	7.0	7.7	×
Samples	**HAc**	**Ammonia**	**DHDAB**	**MTMS**	**DMDMS**	**H_2O**	**Products**

	/ mmol	/ mmol	/ mmol	/ mmol	/ mmol	/ g	
ANSA-23#	0.0385	0.030	0.0034	10.5	7.0	7.7	×
ANSA-24#	0.0385	0.033	0.0034	10.5	7.0	7.7	√
ANSA-25#	0.0385	0.037	0.0034	10.5	7.0	7.7	√
ANSA-26#	0.0385	0.040	0.0034	10.5	7.0	7.7	√
ANSA-27#	0.0385	0.043	0.0034	10.5	7.0	7.7	√
ANSA-28#	0.0385	0.047	0.0034	10.5	7.0	7.7	√
ANSA-29#	0.0385	0.050	0.0034	10.5	7.0	7.7	×

Table S2. pH of the sols (after hydrolysis at 30 ℃ for 1 h) prepared with different amount of Na_2CO_3.

Samples	Na_2CO_3 / mmol	pH
ANSA-00#	0	2.75
ANSA-1#	0.014	4.36
ANSA-2#	0.017	4.52
ANSA-3#	0.019	4.76
ANSA-4#	0.021	4.98
ANSA-5#	0.024	5.32
ANSA-6#	0.026	5.78

Table S3. Density of the ANSAs prepared with different contents of MTMS and DMDMS.

Samples	MTMS / mmol	DMDMS / mmol	MTMS + DMDMS / mmol	Density / g cm^{-3}
ANSA-3#	10.5	7.0	17.5	0.122
ANSA-14#	9.5	6.3	15.8	0.110
ANSA-15#	8.4	5.6	14.0	0.104
ANSA-16#	7.4	4.9	12.3	0.092

Table S4. Length (*L*) and diameter (*D*) of the as-prepared hydrogels, after washing via different methods and the ANSAs (ANSA-3# series). "–" means not applicable.

Washing methods	**As-prepared hydrogels**		**After washing**		**ANSAs**	
	L / mm	*D* / mm	*L* / mm	*D* / mm	*L* / mm	*D* / mm
Water & ethanol	78.5	12.1	79.6	12.7	78.3	12.4
Water	78.3	12.5	78.8	12.6	78.4	12.6
Without washing	77.2	12.7	–	–	76.8	12.8

Table S5. Contact angles and sliding angles of liquids droplets (5 μL) with different surface tension on the surface of the superamphiphobic ANSA-3# at 25 ℃.

Liquids	Contact angles / °	Sliding angles / °	Surface tension (mN m^{-1}, 20 ℃)
water	159.8 ± 2.5	1.0 ± 0.0	72.8
diiodomethane	162.4 ± 1.4	1.0 ± 0.0	50.8
N,*N*-dimethylformamide	152.8 ± 2.4	19.3 ± 0.5	37.1
toluene	158.5 ±2.0	15.0 ± 1.0	28.4
n-hexadecane	159.7 ± 0.6	21.0 ± 1.0	27.5

Movie S1. Ambient pressure drying of the alcogel washed with water and ethanol, and the hydrogel without washing (ANSA-3# series) at 60 ℃ for 4.5 h. The play speed of the video is 500 times of the original. This video highlights that the silicone hydrogel full of water can be dried directly at ambient pressure without any temporary shrinkage.

Movie S2. Compression and release of the ANSA-3# by 50% strain at a strain rate of 500 mm min^{-1}. This video highlights superelasticity and ultrafast resilience of the ANSA.

Movie S3. Water droplets bouncing on the surface of the ANSA-3# and a jet of water bouncing off the surface of the ANSA-3#. The video was taken using a high-speed camera (FASTCAM Mini UX100, Photron, Japan) at the frame rate of 4,000 fps. This video highlights superhydrophobicity of the ANSA.

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