【Electronic Supplementary Information】

Control of rheological properties of clay nanosheet hydrogel with guanidinium-attached calix[4]arene binder

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1. Rheological measurements

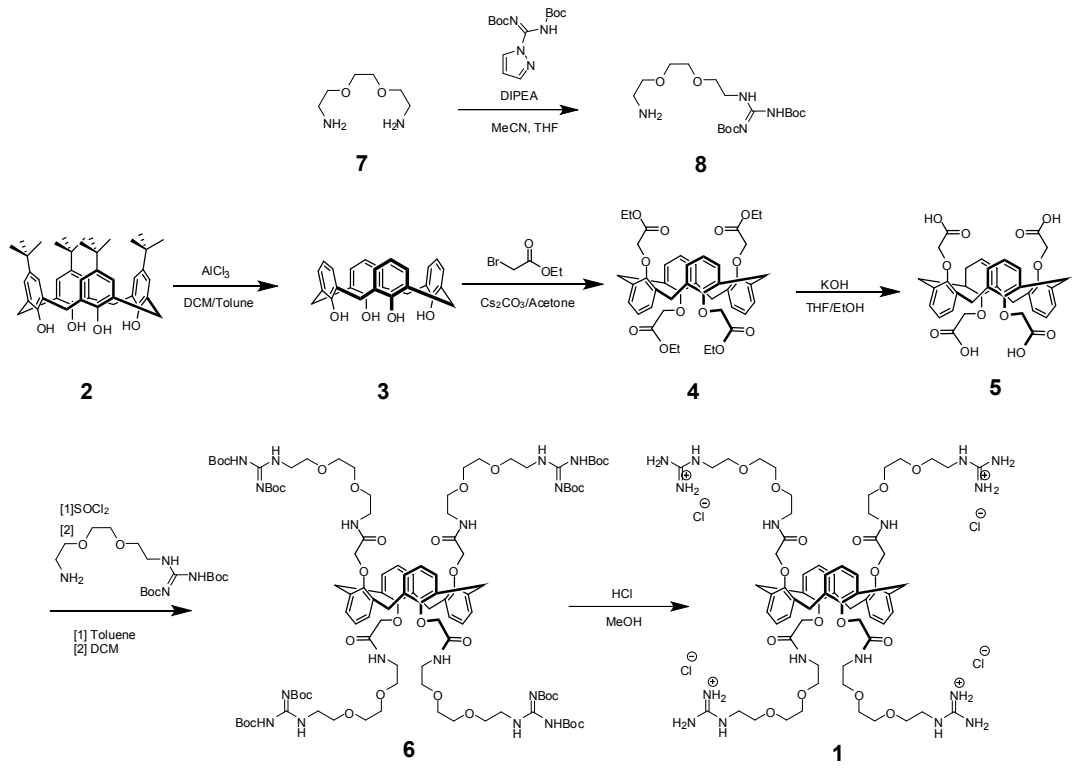
Rheological test of gels were carried out by using An AR-2000ex (TA Instruments Ltd., New Castle, DE, USA) was implemented with a 40-mm diameter parallel plate that was attached to a transducer. The gap in the setup for rheological testing of the gels was 1.0 mm and experiments were conducted at 25 ^{o}C. Strain sweep tests were performed with increasing amplitude oscillation up to 100 % apparent strain on shear. The recovery properties of the gels in response to applied shear force were investigated with the following 1500 sec procedure: 0.5% (300s)→100% (300s-600s)→0.5% (600s-900s)→100% (900s-1200s)→0.5% (1200s-1500s).

2. SEM observation

An FE-SEM, Philips XL30 S FEG field emission scanning electron microscope was used to obtain images of freeze-dried gel samples using an accelerating voltage 5–15 kV and an emission current of 10 μA. Prior to SEM observation, the gels were transferred into liquid N_2 for 10min and subsequently freeze-dried for 24h at -40^{o}C in a 0.1 Pa vacuum to thoroughly remove the water. Samples were observed from the side after cutting.

3. Preparation of hydrogels

Typically, CNS (60 mg)) was portion-wise added at 20 °C to water, upon stirring magnetically (2400 μL, 1000 rpm), and an aqueous solution of ASSP (0.3 - 0.7wt%, 600 μL) were added to the resulting suspension. After stirring (500 rpm) for 10 min at 20 °C, an aqueous solution of molecular binder **1** (3.0 - 5.0 wt%, 126 μL) was added to the resultant dispersion, and the mixture was immediately stirred by a vortex mixer for 10 sec and then allowed to stand at 20 °C.



Synthesis of **8** : To an CH_3CN/THF (45 mL, v/v = 2/1) solution of **7** (0.238mL, 1.61 mmol) were successively added diisopropylethylamine (DIPEA, 1 mL) and N,N'-bis (tert-butoxycarbonyl)-1H-pyrazol-1-carboxamide (0.5g, 1.61 mmol) in CH_3CN/THF (20 mL, v/v = 2/1) was added dropwise by syringe pump at 0.15mL/min. After being stirred for 2h at -20°C, the reaction mixture was evaporated to dryness, and the residue was dissolved in MC (100 mL), and washed with brine (100 mL). The organic extract was dried over Na_2SO_4, evaporated to dryness, and the residue was subjected to recycling preparative HPLC with MeOH/MC (v/v =1:10) as an eluent to allow isolation of **8** in 37% yield (0.234g). NMR (300 MHz, DMSO-d_6) δ ppm 11.48 (s, 1H), 8.62 (s, 1H), 3.68-3.60 (m, 8H), 3.53 (t, 2H), 2.87 (t, 2H), 1.502 (m, 18H); ^{13}C NMR (75 MHz DMSO-d_6) δ ppm 160, 158, 154, 85, 79, 73, 70, 42, 31, 28; ESI-MS: Calculated for $C_{17}H_{34}N_4O_6$ $[M]^+$: 390.25, Found 390.92; Anal. Calcd for C, 52.29; H, 8.78; N, 14.35; O, 24.58, Found: C, 52.27; H, 8.80; N, 14.35; O, 24.58

Synthesis of **2** : *p-tert*-Butyl phenol (150 g, 1 mol) and NaOH (1.8 g, 45 mmol) was dissolved in 37% formaldehyde (100.7 g, 1.24 mol). The reaction mixture was refluxed at 120 °C for 12 h. After the solution was cooled to room temperature, H_2O was removed *in vacuo*, and then to it was added diphenyl ether (450 mL) and toluene (150 mL). The reaction mixture was refluxed at 250 °C, again. The color of the reaction mixture changed to dark brown. Then, the crude product was recrystallized from ethyl acetate (300 mL) and was washed with acetic acid (100 mL) to give the white crystalline solid **2** in 57% yield. mp. 343 °C; IR (KBr pellet): 3176, 2958, 2866, 1603, 1482, 1361, 1242, 1200, 1042, 871, 816, 783; ^{1}H NMR (300 MHz, DMSO-d_6) δ ppm 10.36 (s, 4H), 7.07 (s, 8H), 3.52 (s, 4H), 1.23 (s, 36H); ^{13}C NMR (75 MHz DMSO-d_6) δ ppm 147.62, 143.63, 126.96, 125.74, 34.52, 33.1, 31.2; ESI-MS: Calculated for $C_{44}H_{56}O_4$ $[M+H]^+$ 649.42, Found 649.35; Anal. Calcd for $C_{44}H_{56}O_4$: C, 81.44; H, 8.70. Found: C, 81.75; H, 8.65.

Synthesis of **3**: A suspension of $AlCl_3$ (24 g, 180 mmol) and toluene (150 mL) was stirred in a 1 L three-necked round-bottom flask. The contents of the flask were poured into a suspension of compound **2** (20 g, 30.8 mmol), CH_2Cl_2 (200mL), and toluene (50 mL). After the reaction mixture was stirred for 0.5 h, CH_2Cl_2 (100 mL) and 10% aqueous HCl (400 mL) solution was added to the reaction mixture in an ice bath. Finally, the reaction mixture was extracted with CH_2Cl_2 (3 x 200 mL), washed twice with water, dried over anhydrous $MgSO_4$, and the solvent was removed *in vacuo*. The crude product was recrystallized from CH_2Cl_2/ethyl ether (1:30, v/v) to give a beige crystalline solid **3** in 67% yield (8.7 g). mp. 315 °C; IR (KBr pellet): 3160, 2935, 2870, 1594, 1465, 1448, 1244, 752; ^{1}H NMR (300 MHz, DMSO-d_6) δ ppm 9.76 (br, 4H), 7.16 (d, 8H), 6.66 (t, 4H), 3.89 (s, 4H); ^{13}C NMR (75 MHz DMSO-d_6) δ ppm 149.8, 129.2, 129.0, 121.7, 31.1; ESI-MS: Calculated for $C_{28}H_{24}O_4$ $[M+H]^+$ 425.17, Found 425.28; Anal. Calcd for $C_{28}H_{24}O_4$: C, 79.22; H, 5.70. Found: C, 79.25; H, 5.67.

Synthesis of **4** : Compound **3** (5.00 g, 11.78 mmol) and Cs_2CO_3 (38.4 g, 11.78 mmol) were suspended in dry acetone (250 mL) and added to the solution of ethyl 2-bromoacetate (11.81 g, 70.68 mmol) in dry acetone (25 mL). The reaction mixture was refluxed for an additional 4 h. After cooling to room temperature, the salt was filtered and the solvent (acetone) was removed *in vacuo*. To the resulting pale yellow oil, 10% aqueous HCl (100 mL) solution and CH_2Cl_2 (100 mL) were added and the organic layer was separated and washed twice with water, dried over anhydrous $MgSO_4$, and the solvent was removed *in vacuo*. The crude product was recrystallized from CH_2Cl_2/*n*-hexane (1:30, v/v) to give a white crystalline solid **4** in 46% yield (4.12 g). mp. 118 °C; IR (KBr pellet): 3062, 2980, 2938, 1758, 1453, 1180, 1095, 1060, 769; ^{1}H NMR (300 MHz, DMSO-d_6) δ ppm 7.07 (d, 8H), 6.65 (t, 4H), 4.17 (q, 8H), 3.96 (s, 8H), 3.79 (s, 8H), 1.23 (t, 12H); ^{13}C NMR (75 MHz DMSO-d_6) δ ppm 169.9, 158.2, 133.8, 130.6, 122.7, 69.8, 60.7, 35.7, 14.5; ESI-MS: Calculated for $C_{44}H_{48}O_{12}$ $[M+Na]^+$ 791.30, Found 791.25; Anal. Calcd for $C_{44}H_{48}O_{12}$: C, 68.74; H, 6.29. Found: C, 68.72; H, 6.30.

Synthesis of **5** : A solution of compound **4** (2 g, 2.6 mmol) in the mixture of THF (40 mL) and EtOH (40 mL) was heated to reflux temperature. The reaction mixture was then added to aqueous KOH (1 mL, 26 mmol). After refluxing for 4 h, the organic solvents were removed in vacuo, and water (10 mL) was added. The remaining aqueous solution was acidified to pH 1 by addition of 6 N HCl. The resulting precipitate was filtered and washed with water. The precipitation was dried under vacuum to give compound **5** as a white solid in 80% yield (1.36 g). mp 303 °C; IR (KBr pellet) 3448, 3015, 2925, 1731, 1460, 1356, 1322, 1195, 1058, 767; ^{1}H NMR (300 MHz, DMSO-d_6) δ ppm 12.48 (br, 4H), 7.12 (d, 8H), 6.69 (t, 4H), 4.12 (s, 8H), 3.83 (s, 8H); ^{13}C NMR (75 MHz DMSO-d_6) δ ppm 169.5, 154.4, 134.7, 124.1, 122.7, 72.5, 34.1; ESI-MS: calculated for $C_{36}H_{32}O_{12}$ $[M + K]^+$ 695.15, $C_{36}H_{32}O_{12}$ $[M + Na]^+$ 679.17,

found 695.25, 679.50; anal. calcd for $C_{36}H_{32}O_{12}$: C, 65.85; H, 4.91. Found: C, 66.21; H, 4.97.

Synthesis of **6** : A solution of compound **5** (0.7 g, 1.06 mmol) in toluene (30mL) was refluxed at 80^{o}C. The reaction mixture was then added $SOCl_2$ (12 mL, 26 mmol) and DMF 2-3 drops. After refluxing for 2h, the organic solvents were removed in vacuo, and compound **8** (2g, 5.12 mmol, 4.8 equivalent) in dichlorimethane (10 mL) and TEA (3mL) were added. The resulting precipitate was filtered and washed with ethyl ether. The crude product thus obtained was purified by column chromatography (eluent: MeOH/DCM =1:10) to brown solid in 83.5% yield (1.9g).). ^{1}H NMR (300 MHz, DMSO-d_6) δ ppm 11.48 (s, 4H), 8.42 (s, 4H), 7.14 (d, 8H), 6.69 (t, 4H), 6.45 (s, 4H), 4.81 (s, 8H), 4.79 (s, 8H), 3.4-3.6 (m, 40H), 3.18 (s, 8H), 1.45 (s, 38H), 1.38 (s, 38H); ^{13}C NMR (75 MHz DMSO-d_6) δ ppm 168, 160, 158, 155, 154, 134, 125, 124, 85, 80, 70, 68, 43, 37, 32, 28; ESI-MS: calculated for $C_{104}H1_{60}N_{16}O_{32}$ $[M]^{+}$ 2145.14 Found $[M]^{+}$ 2145.14; anal. calcd for $C_{104}H1_{60}N_{16}O_{32}$: C, 58.19; H, 7.51; N, 10.44; O, 23.85. Found: C, 58.18; H, 7.52; N, 10.45; O, 23.84

Synthesis of **1**: A solution of compound **6** (0.3g, 0.14mmol) in MeOH/con-HCl (1:1) was stirred for 10h. The reaction mixture solution was removed in vacuo, added H_2O and was filtered in 94% yield (0.178g). ^{1}H NMR (300 MHz, DMSO-d_6) δ ppm 7.8 (m, 4H), 7.6-7.2 (br, 14H), 7.15 (m, 8H), 6.68 (t, 4H), 6.52 (t. 4H), 4.6-4.4 (br, 16H), 4.83 (m, 16H), 3.6-3.5 (m, 24H), 3.45 (m, 8H), 3.32 (m, 8H), 3.18 (m, 8H); ^{13}C NMR (75 MHz DMSO-d_6) δ ppm 168, 158, 154, 134, 125, 123,71, 70, 67, 41, 39, 32; ESI-MS: calculated for $C_{64}H_{100}Cl_4N_{16}O_{16}$ $[M\ ]^{+}$ 1488.63 Found $[M]^{+}$ 1488.61; anal. calcd for $C_{64}H_{100}Cl_4N_{16}O_{16}$: C, 51.54; H, 6.76; Cl, 9.51; N, 15.03; O, 17.16. Found: C, 51.53; H, 6.77; Cl, 9.51; N, 15.02; O, 17.14.

Fig. S1 Photograph of CNS hydrogel with binder **1**.

Fig. S2 Photograph of CNS hydrogel without binder **1**.

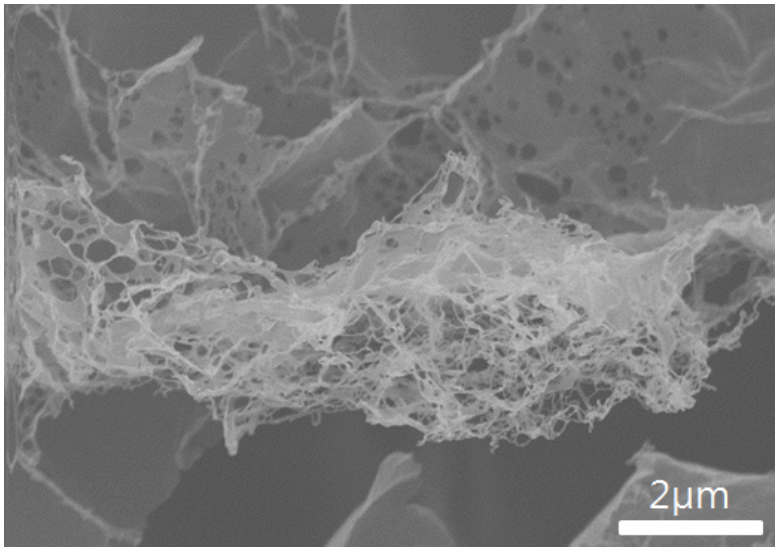


Fig. S3 SEM images of hydrogel of CNS (60 mg) with different concentrations ASSP 0.7 wt% in the presence of binder **1**(magnification ratio: 10000 times).

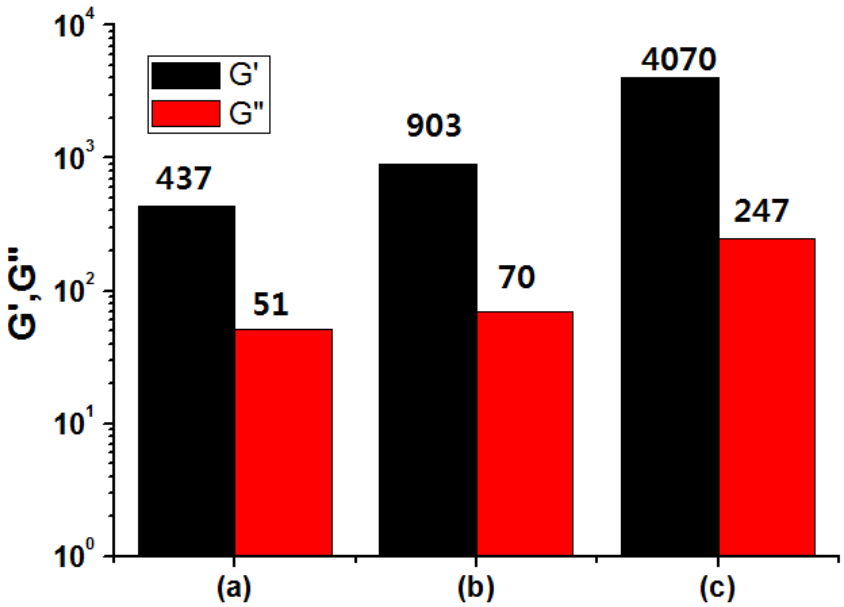


Fig. S4 Graph of G′ and G″ at γ =0.1% in figure 2A(a-c).

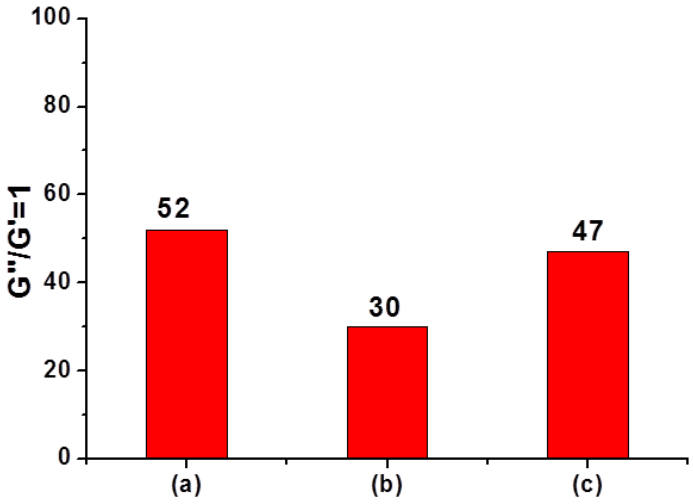


Fig. S5 Graph of γ values at G″/G′=1 in figure 2B (a-c).

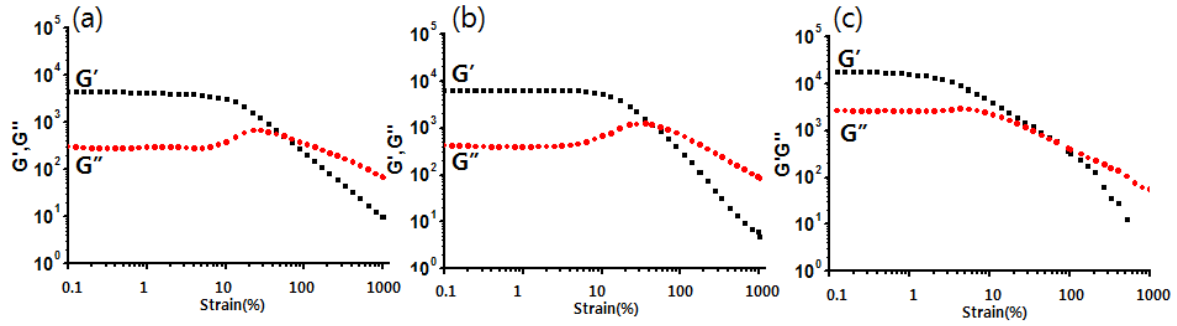


Fig. S6 Strain sweep at 0.1%-1000% (frequency =1 rads^{-1}) of CNS gels with **1** (a: 0 wt%, b: 3.0 wt% and c: 5.0 wt%).

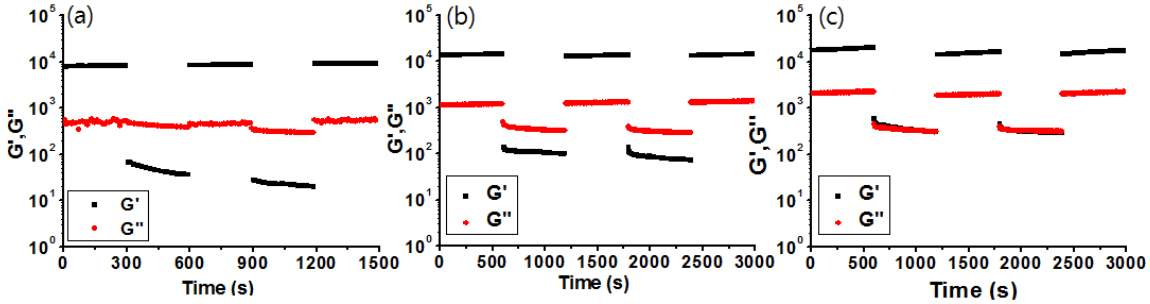


Fig. S7 Continuous step strain measurements at 0.5% and 100% of CNS gels with **1** (a: 0 wt%, b: 3.0 wt% and c: 5.0 wt%).

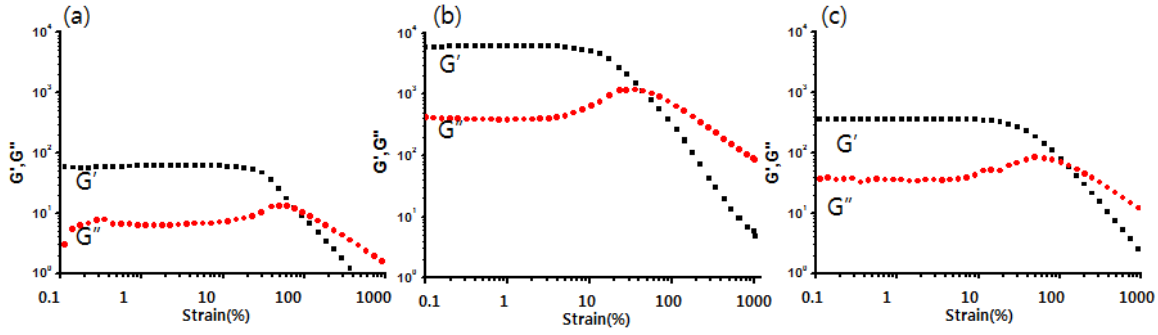


Fig. S8 Strain sweep at 0.1%-1000% (frequency =1 rads^{-1})of CNS hydrogels with ASSP and binder **1** at different pH values (a) pH 3, (b) pH 7, (c) pH 11. (d) Graph of γ values of CNS gels at G″/G′=1.

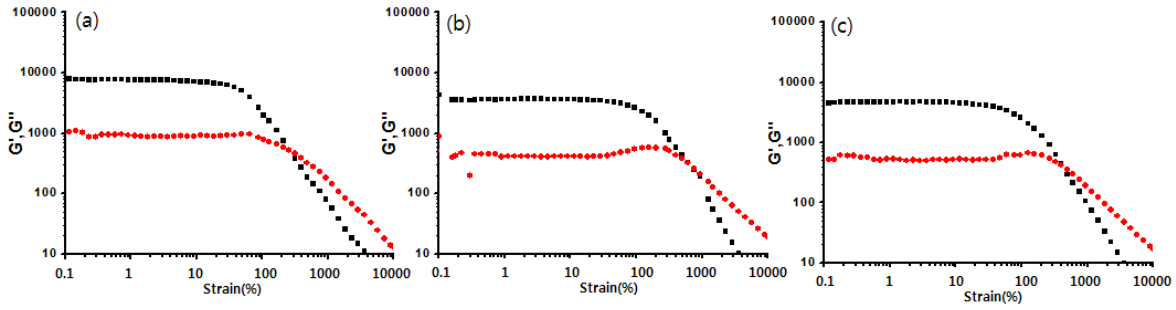


Fig. S9 Strain sweep at 0.1%-1000% (frequency =1 $rads^{-1}$)of CNS hydrogels with ASSP and binder **1** upon addition (a) 0.125 mol, (b) 0.5 mol and (c) 5 mol of Na^{+} ion.

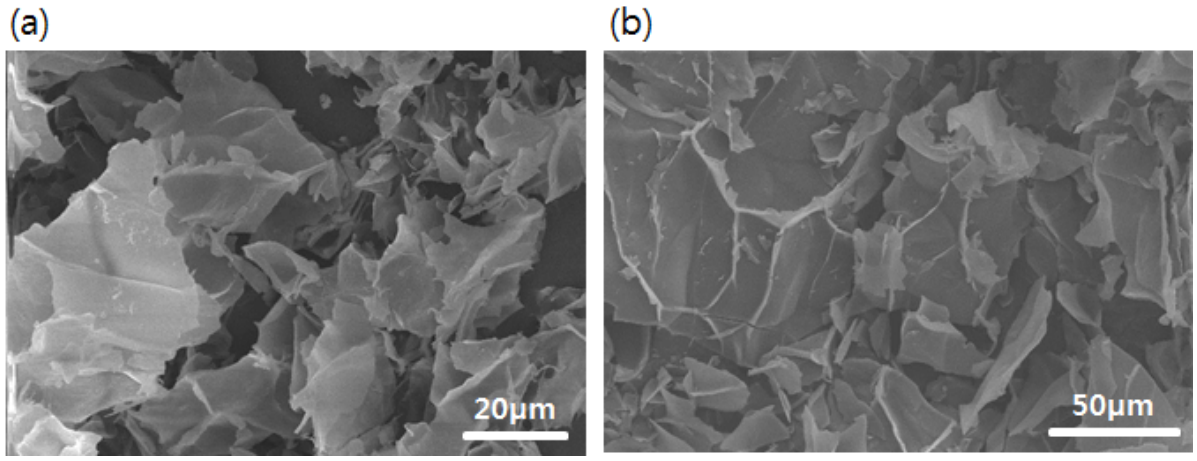


Fig. S10 SEM images of CNS hydrogels with ASSP (0.7 wt%) and binder **1** (5 wt%) at different pH (a) 3 and (b) 11.

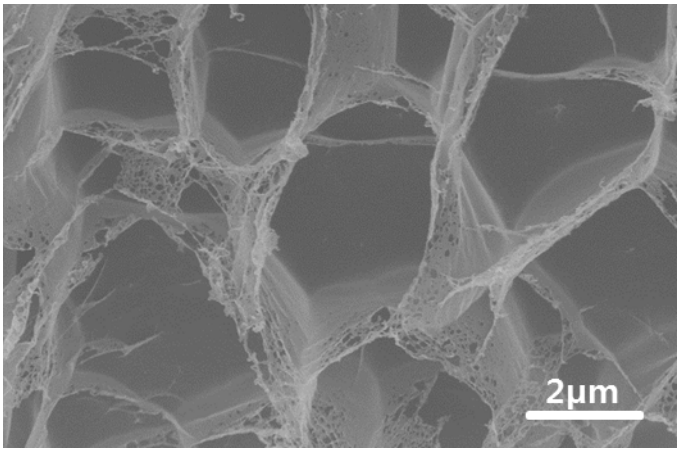


Fig. S11 SEM image of CNS hydrogel with ASSP (0.7 wt%) and binder **1** (5 wt%) in the present of Na^{+} ion (0.125 mmol).