# **Electronic Supplementary information**

# Amphiphilic superabsorbent cellulose nanofibril aerogels

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#### Synthesis of cellulose nanofibrils

Cellulose nanofibrils (CNFs) were isolated from pure rice straw cellulose via combined TEMPO mediated oxidation and mechanical blending. Briefly, rice straw cellulose (1.0 g) was oxidized in aqueous solution containing 0.016 g of TEMPO, 0.1 g of NaBr and 5 mmol NaClO at pH 10.0. After centrifugation and dialysis, the TEMPO oxidized cellulose was blended (Vitamix 5200) at 37,000 rpm for 30 min, yielding clear suspensions containing cellulose nanofibrils. The clear suspension was centrifuged at 5,000 rpm for 15 min to remove larger aggregates and the supernatant was concentrated using a rotary evaporator (Buchi rotavapor R-114) to over 0.6 wt% concentration, then stored at 4 °C for future use.

#### Fabrication and silanization of CNF aerogel

Aqueous CNF suspension (10 mL, 0.1-0.6 wt%) in a conical shaped centrifuge glass tube (14 mm inner diameter) was slowly frozen in a freezer (-20 °C) for 15 h, followed by lyophilizing in a freeze-drier (-50 °C, FreeZone 1.0L Benchtop Freeze Dry System, Labconco, Kansas City, MO) for 2 days to yield CNF aerogels. Silanization of 0.2CNF aerogel was carried out using triethoxyl(octyl) silane in a beaker-in-bottle set-up (Figure S7) under vacuum at 120 °C for 12 h

# Characterization

### Density, porosity and liquid absorption capacity of CNF aerogels

Cylindrical CNF aerogel was cut into approximately 10 mm long sections. The dimensions (length and diameter) and mass were measured using a digital caliper and balance to 0.01 mm and 0.1 mg resolution, respectively, to calculate the density of aerogel ( $\rho_a$ ).

Porosity of each aerogel was calculated as,

Porosity (%) = 
$$\left(1 - \frac{\rho_a}{\rho_c}\right) \times 100\%$$
 (1)

where  $\rho_c$  is the density of cellulose take as 1.6 g·cm<sup>-3</sup>.

For liquid absorption capacity, each CNF aerogel was immersed in 20 mL liquid and allowed to saturate. Upon taking out of the liquid, each saturated gel was blotted with filter paper to remove surface liquid and weighed. The absorption capacity (g/g) was calculated as,

Absorption capacity = 
$$\frac{(w_e - w_0)}{w_0}$$
 (2)

Where  $w_e$  and  $w_o$  are weights of fully saturated and dry CNF aerogels, respectively.

## Scanning electron microscopy (SEM)

CNF aerogel was cut along the cross and longitudinal sections of the cylinder with a sharp razor, mounted with conductive carbon tape, sputter coated with gold and imaged by a field emission scanning electron microscope (FE-SEM) (XL 30-SFEG, FEI/Philips, USA) at a 5 mm working distance and 5-kV accelerating voltage.

# Energy-dispersive x-ray spectroscopy (EDS)

Elemental analysis of chemically modified 0.2CNF aerogel was conducted using the EDS (EDAX, AMETEK, Inc.) on the FE-SEM. The samples were scanned at a 1000 magnification with a 5-kV accelerating voltage and a 5 mm working distance.

### BET specific surface area

The specific surface and pore characteristics of 0.2CNF aerogel were determined by  $N_2$  adsorption at 77K by a surface area and porosity analyzer (ASAP 2000, Micromeritics, USA). The sample was degassed at 35 °C to below 16 mmHg. The specific surface was determined by the Brunauer-Emmett-Teller (BET) method from linear region of the

isotherms in the 0.06-0.20 relative  $P/P_0$  pressure range. Pore size distributions were derived from desorption branch of the isotherms by the Barrett–Joyner–Halenda (BJH) method.

#### *X*-ray diffraction and crystallinity

XRD spectra for 0.2CNF aerogel was collected on a Scintag XDS 2000 powder diffractometer using a Ni-filtered Cu K $\alpha$  radiation ( $\lambda$ =1.5406 Å) at an anode voltage of 45 kV and a current of 40 mA. Diffractograms were recorded from 5° to 40° at a scan rate of 2°/min. Crystallinity index (CrI) was calculated from the intensity of the 200 peak (I<sub>200</sub>, 2 $\theta$  = 22.6°) and the intensity minimum between 200 and 110 (I<sub>am</sub>, 2 $\theta$ =18.7°) peaks using the empirical equation:<sup>[1]</sup>

$$CrI = \frac{I_{200} - I_{am}}{I_{200}} \times 100$$
(3)

## Compressive properties of CNF aerogels

Compressive tests were performed on 10 mm long cylindrical CNF aerogels using Instron 5566 equipped with a 2.5 N load cell and two flat-surface compression stages. The loading and unloading compressive rates were set to the same constant 1 mm/min. For compressive test in water, CNF aerogel was placed in a beaker filled with water, with the water level is slightly higher than the hydrogel to ensure complete immersion under water.



Figure S1. a) Photograph of cylindrical shaped aerogels frozen and freeze-dried from aqueous suspensions of various CNF concentrations (0.1-0.6 wt%); b) diameters of cylindrically shaped aerogels from varying CNF concentrations, showing similar dimensions at concentrations at and above 0.2 wt%, the dash line marks the tube inner diameter (ID), suggesting some contraction oft he aerogels; c) 0.2CNF aerogels fabricated with two tube sizes: Left, 14 mm ID; Right, 27 mm ID), showing scaling up potential.



Figure S2. 0.2CNF aerogel dimensions and weight: (a) 28.27 mm length; (b) 11.86 mm diameter; (c,d) 8.3 mg weight.





Figure S3. SEM images of 0.1 (a,b), 0.3 (c,d), 0.4 (e,f) and 0.5 (g,h) CNF aerogels at cross sections.



Figure S4. SEM images of 0.2CNF aerogel at longitudinal sections.



distribution.

Samples	0.2CNF	0.4CNF	0.6CNF
Densities (mg/cm <sup>3</sup> )	2.7	5.2	8.1
Yield strain	0.04	0.11	0.19
Young's modulus (kPa)	13.2	19.7	54.5
Maximum stress at ε=0.8 (kPa)	8.5	13.8	25.3

Table S1. Mechanical properties of CNF aerogels with various densities.



Figure S6. Loading and unloading compressive stress-strain curves of 0.2CNF aerogel at 0.4, and 0.8 set strains, showing 15 and 7.5% recovery, respectively.



Figure S7. Set-up for organosilane vapor deposition of 0.2 CNF aerogels: A small beaker containing 0.5 mL triethoxyl(octyl) silane in the center of a capped bottle containing aerogels.





Figure S9. Unmodified 0.2CNF aerogel could be completely wetted by water and submerges but afloat under water surface.

Materials	Preparation method	Chloroform absorption capacity (g/g)	Drawbacks	Ref.
Carbon aerogel	Freeze-drying carbon nanotube and graphene oxide suspension followed by hydrazine vapor reduction	580	Expensive raw materials, chemical vapor reduction	[2]
Graphene framework	Hydrothermal treatment of graphene oxide and pyrrole at 180 °C for 12 h, then freeze-dried and pyrolysis at 1050 °C	480	Expensive raw materials, high temperature treatment, material loss during carbonization	[3]
Carbon nanofiber aerogels	Pyrolysis of bacterial cellulose aerogel at 700-1300 °C	290	Material loss from pyrolysis, high temperature treatment	[4]
Carbon nanotube aerogels	Chemical vapor deposition of ferrocene in dichlorobenzene at 860 °C	180	Expensive raw materials, complicated processing method	[5]
Graphene based sponge	Adsorption of graphene onto commercially available melamine sponges	160	expensive template, expensive raw materials	[6]
Carbonaceo us nanofibers	Hydrothermal carbonization of glucose at 180 °C for 12-48 h, using Te nanowire as template and was removed by chemical etching afterwards. Aerogel was derived by freeze- drying	115	expensive template, material loss during carbonization	[7]
Graphene sponge	Hydrothermal treatment of graphene oxide in water/ammonia at 180	90	Using of solvent, expensive raw materials, high temperature	[8]

Table S2. Preparation methods, absorption capacity, and drawbacks of various carbonand bio-based aerogels

	°C for 24 h, followed by freeze-drying		treatment	
Nanocellul ose aerogel	Freeze-drying carboxymethylated and high pressure homogenized nanocellulose, chemical vapor silanization	45	Low absorption capacity	[9]
Nanocellul ose aerogel	Freeze-drying mechanically homogenized nanocellulose, atomic layer deposition coating of TiO <sub>2</sub>	40	Low absorption capacity	[10]
Cellulose nanofibril aerogels	Freeze-drying TEMPO oxidized cellulose nanofibrils, chemical vapor silanization	356		Current study



Figure S10. Cyclic absorption and distillation of octane (a) and cyclohexane (b) with silane-modified 0.2CNF aerogel.



Movie S1. Video showing 0.2CNF aerogel could fly toward a plastic tube by static electricity.

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