Electronic Supplementary Information

Metal Oxide Cluster-Assisted Assembly of Anisotropic Cellulose Nanocrystal Aerogels for Balanced Mechanical and Thermal Insulation Properties

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Materials and methods

Preparation of CNCs. The dried sisal pulp is used as raw material (20 g), which is dispersed into 60 wt% of sulfuric acid solution (160 mL) in an ice-water bath for 30 min. Then the hydrolysis of the pulp is conducted at 50 ^{o}C for 1 h. After hydrolysis, the obtained suspension is washed with deionized water (DI water, 160 mL) and filtered to remove the free acid. After filtration, the obtained solids are diluted with DI water (750 mL) to form a suspension, which is further neutralized with sodium hydroxide solution. The neutralized suspension is stirred and sheared with a high-speed mixer (JK-818) for 4 min, forming a translucent dispersion. The translucent dispersion is centrifuged at 12000 rpm for 8 min to obtain CNC dispersion. The separated CNC dispersion is stored and frozen in a freezer. Then the frozen CNC dispersion is thawed at room temperature, washed, and filtered to obtain CNC suspension (8.0 wt%), which is further stirred and sheared with a high-speed mixer for 2 min. The finally obtained CNC suspension is directly used in this work.

For A-CNC, the mole contents of N element is equal to that of Si. Therefore, Si content inside A-CNC sample is calculated to be 8.2×10^{-4} mmol/g based on the element analysis data.

SAXS data fitting models

E.q. S1

$$I(q) = \frac{B}{1 + (\xi_2 q)^m} + bg \ (1)$$

which the Lorentz term represents the network at the larger dimension scale in the CNC aqueous suspension, q is scattering vector.

E.q. S2

$$I(q) = \frac{A}{(1+\xi_1 q)^n} + \frac{B}{1+(\xi_2 q)^m} + bg \quad (2)$$

which the first Lorentzian term represents the network at the larger dimension scale in the hydrogel, the second Lorentzian term represents the network in the smaller dimension scale, q is scattering vector.

E.q. S3

$$I(q) = \frac{A}{(\xi_1 q)^n} + \frac{B}{1+(\xi_2 q)^m} + bg \quad (3)$$

which the first Porod term represents the formed CNC aggregates at the larger dimension scale, the second Lorentzian term represents the relatively homogenous network in a smaller dimension scale, ζ represents the correlation length in a network.

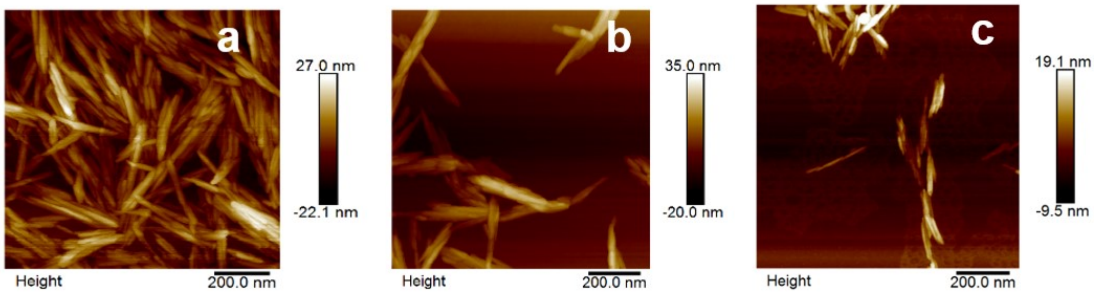

Fig. S1 AFM images of hydrogels CNC (a), CNC/PTA (b), and A-SCNC/PTA (c).

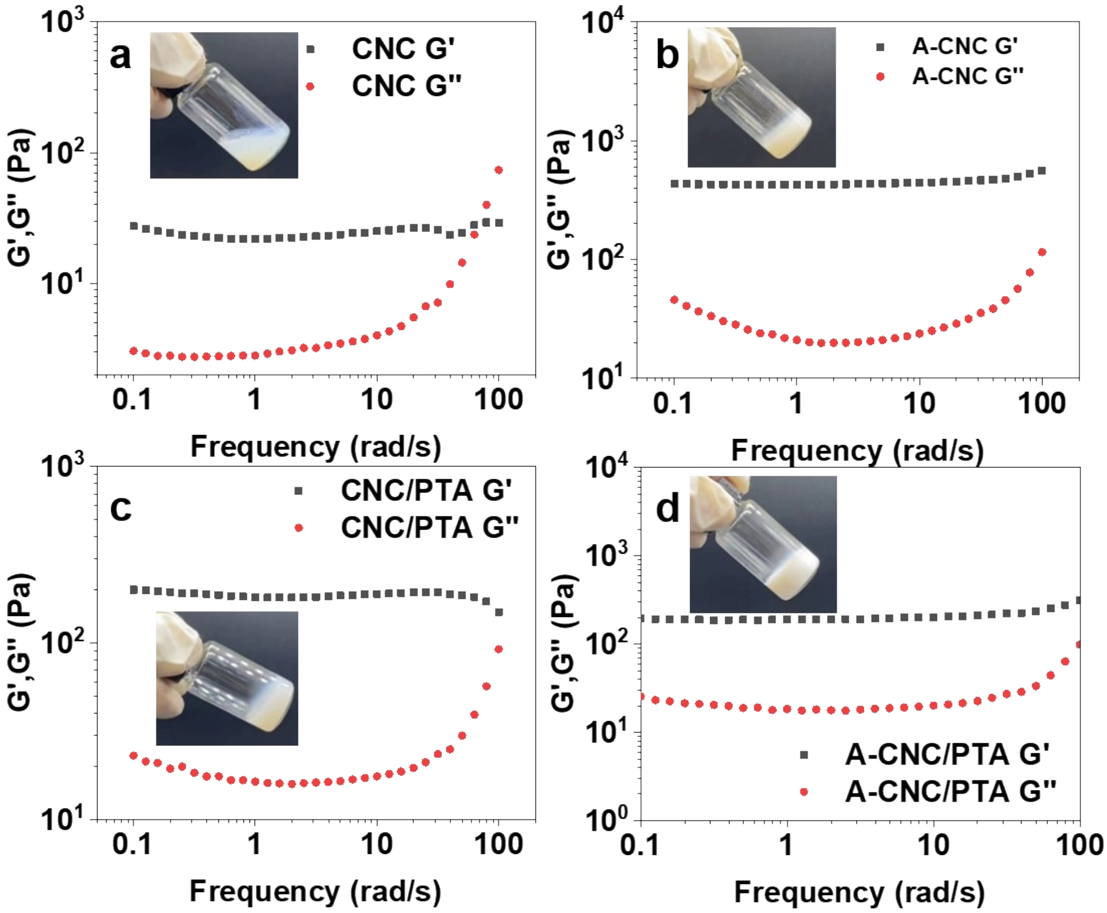

Fig. S2 Storage and loss modulus of samples CNC (a), CNC/PTA (b), A-CNC (c), and A-CNC/PTA (d) in the aqueous media.

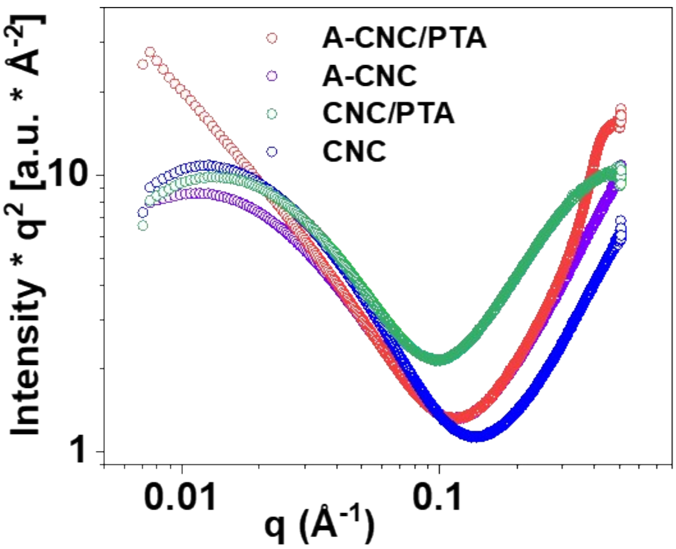

Fig. S3 Lorentz-corrected intensities ($I \times q^2$) against the scattering vector q of CNC dispersions.

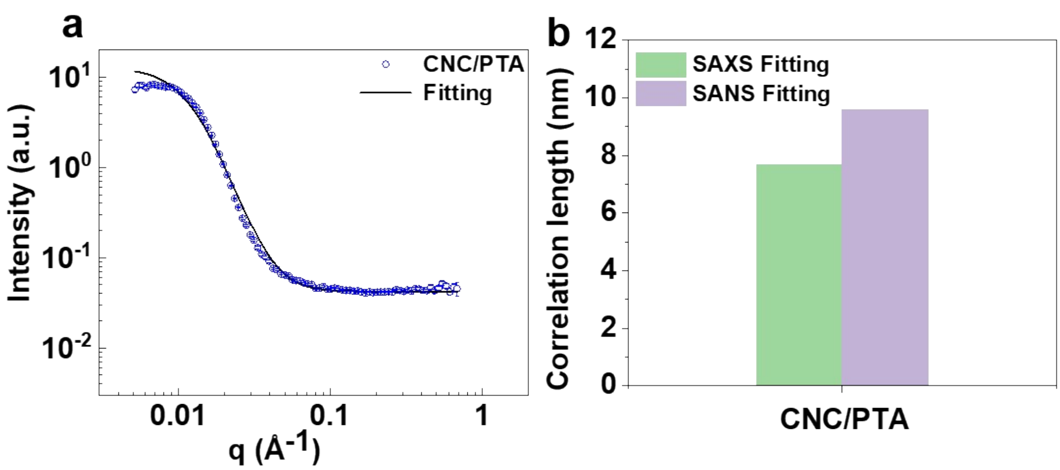

Fig. S4 (a) SANS and the Lorentzian model fitting data of sample CNC/PTA in the aqueous media. (b) Comparison of the fitted correlation lengths of sample CNC/PTA in the aqueous media from SAXS and SANS data.

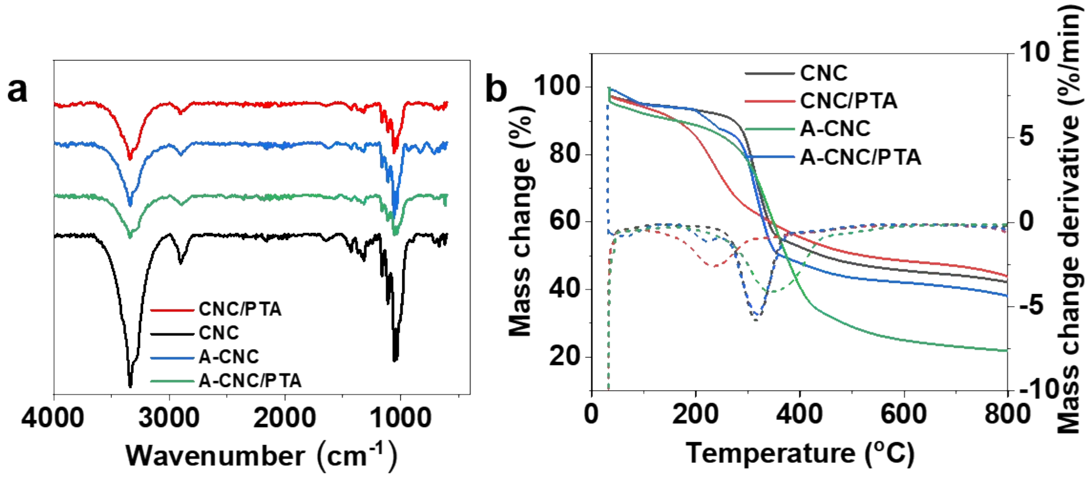

Fig. S5 (a) FT-IR spectra of the four aerogels. (b) Thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) curves of the four aerogels.

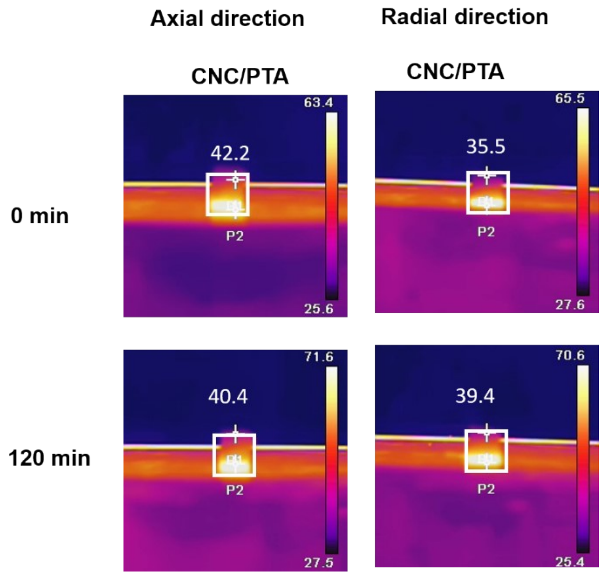

Fig. S6 Infrared images (axial and radial direction) of the aerogel CNC/PTA placed on the hot disk at 70 ^{o}C.

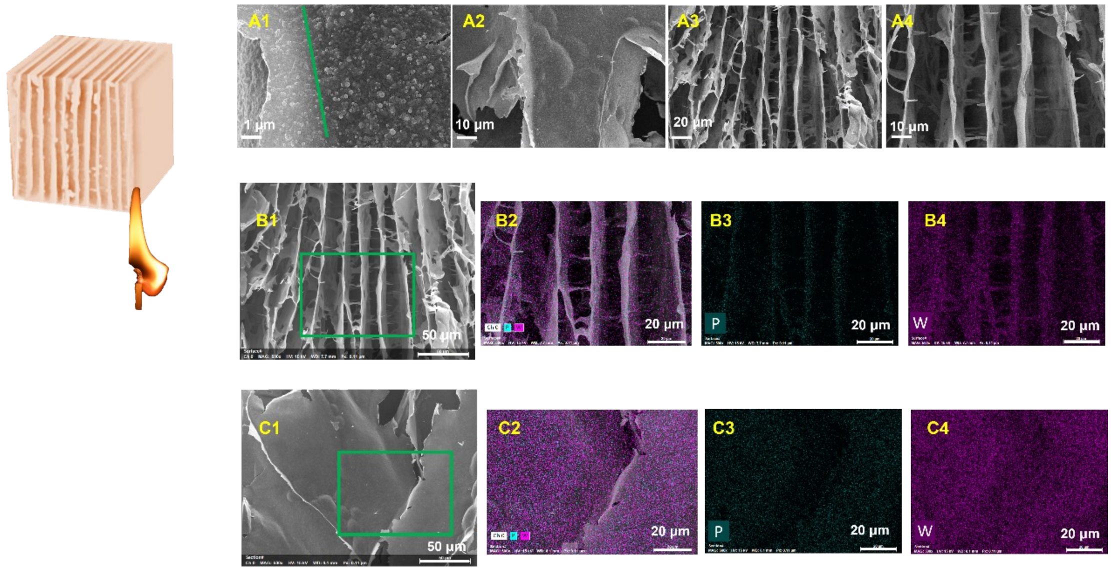

Fig. S7 Microstructure of the burned aerogel A-CNC/PTA (A1-A4), and mapping images (B1 to B4, C1 to C4).

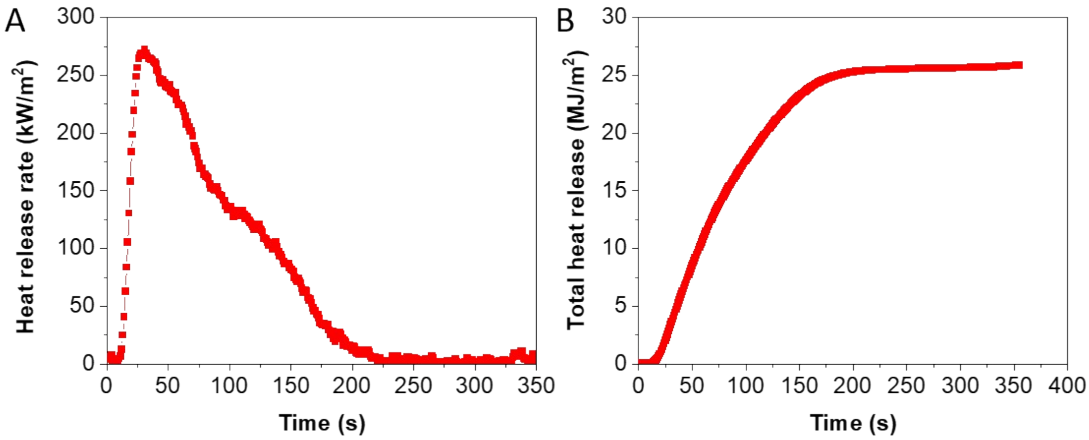

Fig. S8 (A) Plots of heat-release rate (HRR) and (B) total heat release (THR) for the aerogel A-CNC/PTA.

Table S1. Apparent density of CNC based aerogels

Samples ID	Apparent density (g/cm^3)
CNC	0.023±0.01
CNC/PTA	0.036±0.01
A-CNC	0.029±0.02
A-CNC/PTA	0.034±0.01

Table S2. Specific surface area and pore dimension of the four CNC aerogels

Samples	BET surface area (m^2 g^{-1})	t-plot external surface area (m^2 g^{-1})	BJH average pore diameter (nm)	BJH desorption average pore diameter (nm)
CNC	34.3	33.6	8.9	4.8
CNC/PTA	4.9	2.9	23.7	14.7
A-CNC	16.1	15.0	17.1	9.5
A-CNC/PTA	38.3	35.9	23.5	16.5

Table S3. Two Lorentzian model fitting parameter of the four CNC hydrogels

Samples	Lorentzian length 1 (Å)	Lorentzian exp 1 (n)	Lorentzian length 2 (Å)	Lorentzian exp 2 (m)
CNC	78.0	3.4	0	0
CNC/PTA	76.9	3.4	2.4	2.9
A-CNC	81.1	3.4	0	0
A-CNC/PTA	123.6	3.5	0	0

Table S4. Two Lorentzian model fitting parameter of the four CNC aerogels

Samples	Lorentzian length 1 (nm)	Lorentzian exp 1 (n)	Lorentzian length 2 (nm)	Lorentzian exp 2 (m)
CNC	6.9	3.6	0	0
CNC/PTA	8.5	3.2	0	0

A-CNC	11.5	3.6	0	0
A-CNC/PTA	12.3	3.7	0	0

Table S5. pH value and zeta potential of CNCs in aqueous media

Samples	pH value	Zeta potential (eV)
CNC	7.27±0.01	-37.07±2.78
CNC/PTA	3.41±0.01	-44.23±2.21
A-CNC	9.45±0.01	-28.01±0.01
A-CNC/PTA	8.72±0.01	-48.33±3.67

Table S6. Elemental analysis of A-CNC samples

Sample ID	N (%)[a]	C (%)[a]	H (%)[a]
A-CNC	1.15±0.014	40.37±0.21	6.64±0.45

[a] Mass percentage.

Table S7. Combustion parameters from the cone calorimetry analysis for the aerogels

Samples	TTI (s)	PHRR (kW m^{-2})	TTPHRR (s)	THR (MJ m^{-2})	TSR (m^2)
Cellulose-Si[a]	1	175.36	5	34.34	0.0385
A-CNC/PTA	9	272.24	23	25.85	35.80

[a] data from the previous literature (*ACS Sustainable Chem. Eng.* **2018**, *6*, 7168−7180); TTI: time to Ignition; HRR: heat-release rate; PHRR: peak heat release rate; TTPHRR: time to peak heat release rate; THR: total heat release rate; TSR: total smoke release.