Supplementary Information (SI) for Green Chemistry.

Supplementary Information for

P-N synergy with lignocellulosic biomimetic flame-retardant aerogel for effective fire-safe and thermal insulation

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1. Materials methods

Materials: Lignin, separated from the Eucalyptus pre-hydrolysis liquor, was kindly provided by Jining Mingsheng New Material Co., Ltd., China. Softwood pulp was purchased from Asia Pacific Senbo (Shandong) Pulp & Paper Co., Ltd., China. Sodium alginate (SA, AR), 2-(3,4-dihydroxyphenyl) ethylamine hydrochloride (dopamine hydrochloride), 1,4-dioxane, phosphorus pentoxide (P_2O_5, AR), urea (H_2NCONH_2, AR), tris(hydroxymethyl) aminomethane (Tris), sodium hydroxide (NaOH, 96%), and hydrochloric acid (HCl, 36% ~ 38%) were purchased from Energy Chemical Reagent Co., Ltd. (Anhui, China). All these chemical reagents were analytically pure.

Pretreatment of lignin and phosphating modification of lignin: First, 20 g of pre-hydrolyzed lignin was dissolved in 1,4-dioxane solution and stirred for 4 h. Next, the volume of the lignin mixed solution was concentrated to 1/3 of the original volume by rotary evaporator. The obtained lignin concentrate was added dropwise to acid water with pH = 2 and allowed to stand in a refrigerator at 4 ºC for 24 h. The supernatant was then removed by vacuum filtration and continuously rinsed with deionized water. The obtained precipitate was freeze-dried to obtain the purified pre-hydrolyzed lignin (L).

Typically, 3.0 g of lignin, 6.0 g of P_2O_5, and 1.0 g of urea were mixed in a 250 mL zirconia jar and ground at 250 rpm for 8 h using a zirconia ball with a diameter of 10 mm. Then, the obtained sample was evenly dispersed in deionized water. Afterwards, the mixed solution was purified using a dialysis tube with a molecular weight cutoff of 1000 Da. Finally, phosphorylated lignin (PL) was obtained by lyophilization.

Pretreatment of softwood fiber pulp and fabrication of dopamine-modified lignocellulose (PDA@LCF): First, the softwood pulp board was mechanically dispersed to obtain fiber slurry, and then the wet fibers were filtered and stored in a refrigerator at 4 °C. Next, a more dispersed fiber is obtained by means of simple mechanical ball milling. Specifically, the dispersed 6.0 g lignocellulose was packed in 250 mL zirconia tank, and the zirconia ball with a diameter of 10 mm was ground for 2 h at 400 rpm. Finally, the obtained lignocellulose (LCF) was pretreated.

The dopamine modification of lignocellulose was carried out through a typical step with modified cellulose. Typically, 0.4 g Tris was dissolved in 100 mL water and gradually added to 0.1 mol/L HCl solution until the pH reached 8.5. Then 0.4 g of dopamine hydrochloride was added to get the PDA precursor solution. LCF was then immersed in the solution for 48 h to obtain lignocellulose surface loaded with polydopamine (PDA@LCF).

Preparation of lignin composite aerogel: To fabricate lignin composite aerogel, 4.0 g PL and 2.0 g PDA@LCF were uniformly dispersed in an aqueous solution with pH 12. Then, 4.0 g SA was added and stirred at 200 rpm for 4 h. After that, it is introduced into a special mold and unidirectional freezing with liquid nitrogen. Subsequently, the monoliths were lyophilized at -40 ºC under 0.1 Pa for 3 days to obtain the lignin composite aerogel. The final product was named as SA/PDA@LCF-PL40, of which SA represented sodium alginate, PDA@LCF represented dopamine-modified lignocellulose, PL represented phosphorylated lignin, and the subscripts represented PL contended. The other samples were prepared by the same method.

2. Characterization

Fourier transform infrared spectroscopy (FT-IR). FT-IR spectra of lignin were recorded using a Perkin-Elmer spectrophotometer. The spectra of powdered lignin supported by KBr pellets were recorded in the range of 400 to 4000 cm^{-1} with 32 scans averaged at 4.0 cm^{-1} resolution at room temperature.

Nuclear magnetic resonance (NMR). All NMR spectra were recorded on a Bruker Ascend-400 MHz spectrometer instrument (Bruker, Germany). 2D 1H-31P was carried out using the heteronuclear multiple bond correlation (HMBC) technique with 128-time domains with 16 scans. ^{31}P NMR samples were prepared and analyzed according to procedures reported by Argyropolous in 2019.[1]

^{1}H NMR Quantitative test. 30 mg of epoxidized lignin and 5.0 mg of internal standard (*p*-nitrobenzaldehyde) were dissolved in 0.5 mL of DMSO-d_6 and proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded at 25 ºC on a Bruker Ascend-400 MHz NMR spectrometer.

Scanning electron microscope (SEM). A scanning electron microscope (SEM, JEOL JSM-7800F) was used to analyze the surface and cross-sectional characteristics of PVA composite film with different lignin contents. Before the SEM observation, the samples were sputtered with a thin layer of gold coating.

Thermal analysis. The thermal stability of lignin samples and mass loss of epoxy polymers were determined by a Q500 thermogravimetric analyzer (TA Instruments). Approximately 10.0 mg sample in a small crucible were performed under a nitrogen atmosphere with temperature ranging from 25 to 800 ºC at a heating rate of 10 ºC min^{-1}. Glass transition temperature (T_g) was determined by a differential scanning calorimetry (DSC) on a DSC6000 equipment (TA Instruments) by subjecting epoxy polymers to a heat-cool-heat cycle from 80 to 150 ºC at 10 ºC/min under a nitrogen atmosphere. Meanwhile, the thermal degradation behavior of polymers was characterized using thermogravimetric analysis (TGA 25). 5-20 mg of the polymer was loaded into a platinum pan and heated under continuous N_2 flow (10 mL/min). The sample was heated to 800 ºC at a rate of 10 ºC/min.

The limiting oxygen index (LOI) values were tested on a JF-3 oxygen index meter (Jiangning, China) according to GB/T 2046.2-2009. The vertical burning test (UL-94) was performed on a CZF-4 instrument (Jiangning, China) according to GB/T 8333-2008, and the dimensions of all samples are 100 mm × 10 mm × 10 mm. The combustion behaviors were measured by a cone calorimeter device (FTT0402). Samples with a size of 100 mm × 100 mm × 10 mm were tested under a heat flux of 35 kW/m^2.

Raman spectroscopies of residual chars after cone calorimetry tests were performed on a Lab RAM HR800 Raman spectrometer (SPEX Co., USA) with a 532 nm laser line.

The X-ray photoelectron spectroscopies (XPS) were performed on XSAM 800 spectrometer (Kratos Co., UK), with Al Kα excitation radiation (1486.6 eV), operated at 12 kV and 15 mA.

Thermogravimetry-infrared spectrometer (TG-IR) was performed using a NETZSCH TGA (209 F1) thermogravimetric analyzer linked with a Nicolet 6700 FT-

IR spectrophotometer at a 20 ºC/min heating rate from 40 ºC to 700 ºC under nitrogen atmosphere.

3. XPS data details of the lignin samples

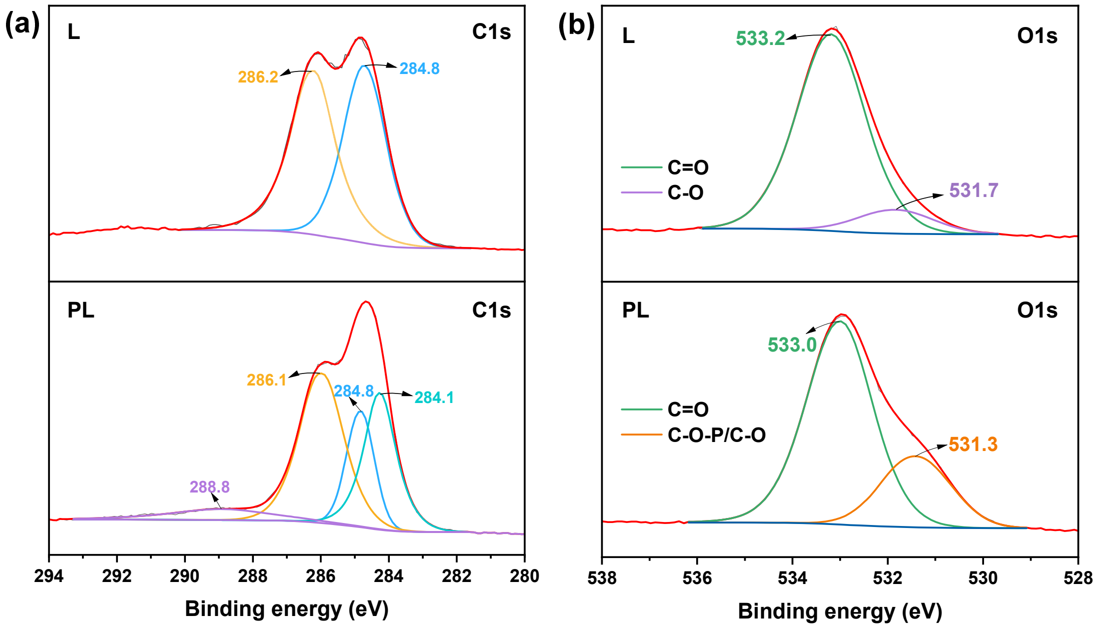

Fig. S1. (a) and (b) were the C1s and O1s XPS spectra of PL and L, respectively.

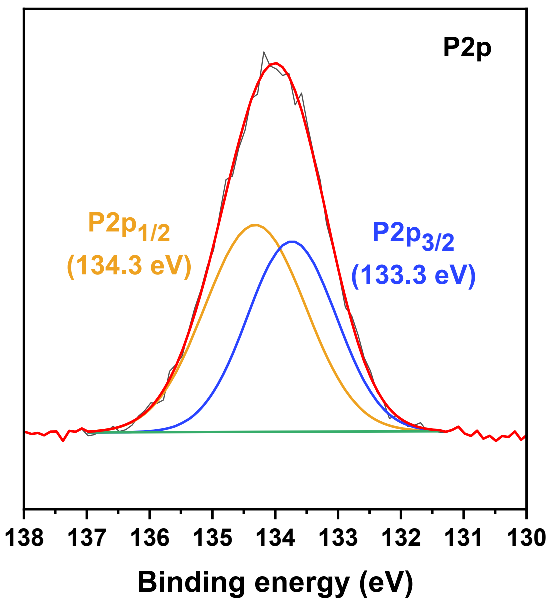

Fig. S2. P2p XPS spectrum of phosphorylated lignin (PL).

4. FT-IR spectral characterization of the lignin samples

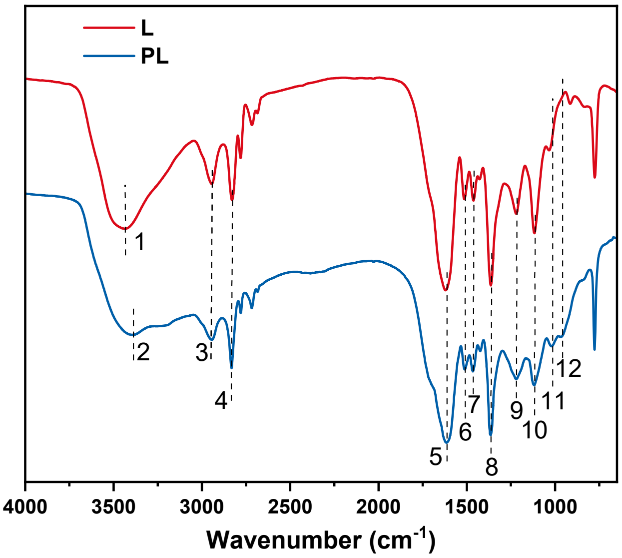

Fig. S3. FT-IR spectra of PL and L.

Table S1 Signal assignments of the FT-IR spectra of L and PL.

Band number	Wavenumber (cm^{-1})	Assignments
1	3432/3392	Stretching vibration of alcohol and phenol hydroxyl groups
2	2943	Stretching vibration of C−O in methoxy group ($–OCH_3$)
3	2832	Asymmetric C−H vibration
4	1618	The ester group vibration of acetyl group
5	1506	Stretching of C=C skeleton of lignin aromatic ring
6	1463	Aromatic C−H deformation; asymmetric in −CH and $−CH_2−$
7	1362	The aromatic ring vibration of S-type were accompanied by the condensation of G-type
8	1219	Aromatic ring C−H vibration of syringaldehyde
9	1114	Skeleton C−H vibration of S-type aromatic ring
10	1013	P=O stretching vibration
11	961	Vibrational stretching of the P−O−H and P−O−C

5. TGA data of different samples

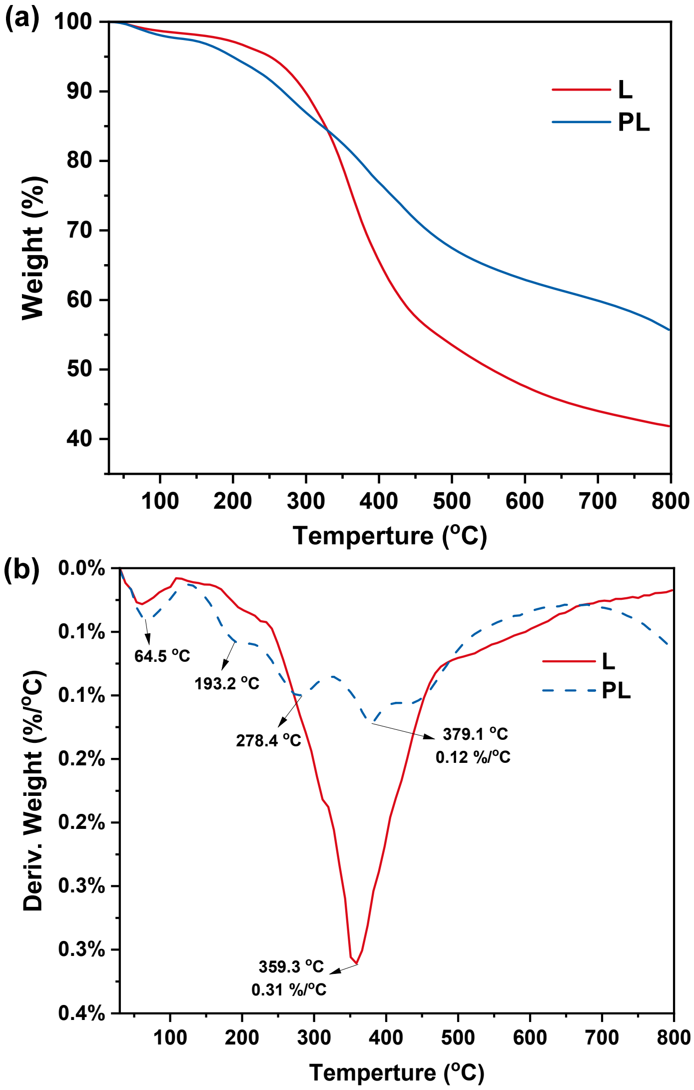

Fig. S4. Distribution of (a) TGA and (b) DTG in different lignin samples.

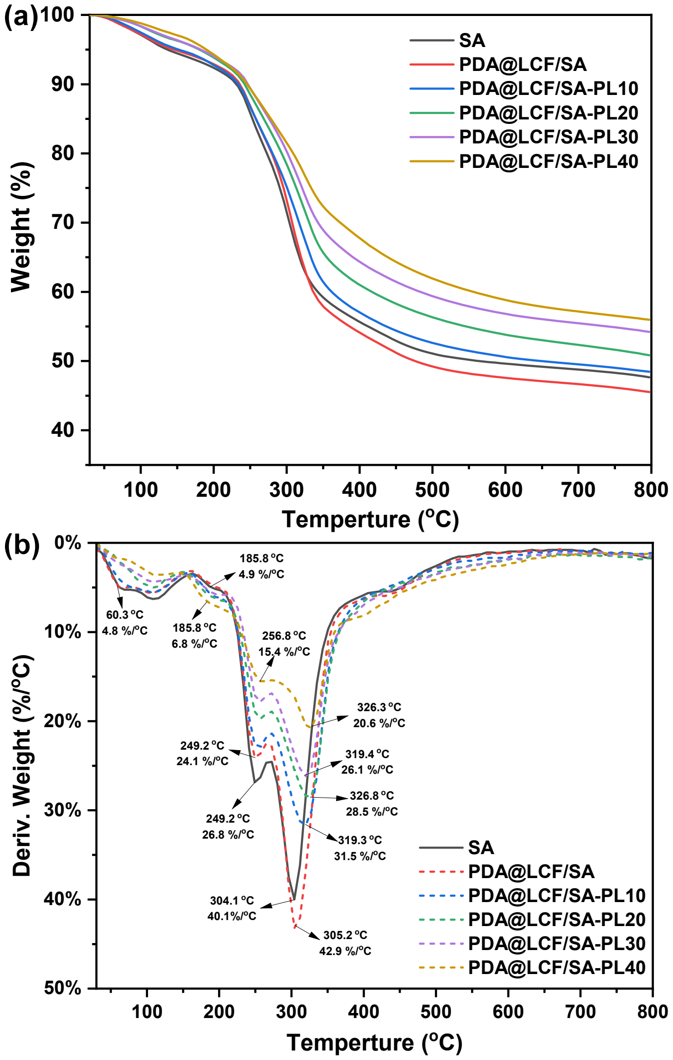

Fig. S5. (a) TGA and (b) DTG distribution of different aerogel samples.

Table S2 Compared with the results of thermogravimetric analysis of lignin as polymer flame-retardants.

Sample	T_i (°C)[a]	T_{max} (°C)[b]	Residues (%)	Ref.
SA	249	304	48	This work
PDA@LCF	249	305	45	
PDA@LCF/SA-PL10	257	326	48	
PDA@LCF/SA-PL20	257	319	50	
PDA@LCF/SA-PL30	256	326	54	
PDA@LCF/SA-PL40	253	319	56	
PLA	315	373	2	2
PLA/MCAPP/LIG	321	368	17.2	
PLA/APP/DK1	291	374	13.4	
PLA/APP/DK2	284	370	17.4	
PLA/APP/DK4	303	376	14.3	
PLA/APP15/Lig5	320	373	8.9	3
PLA/Lig-Si/APP	322	376	13.1	
PP/Lig	316	472	12.5	4
PP/20 PN-Lig	325	479	12.4	
PP/30 PN-Lig	361	483	21	

[a] The T_i was defined as the initial decomposition temperature.

[b] The T_{max} was defined as the maximum weight-loss temperature.

6. Detailed data diagram of vertical combustion of composite aerogel

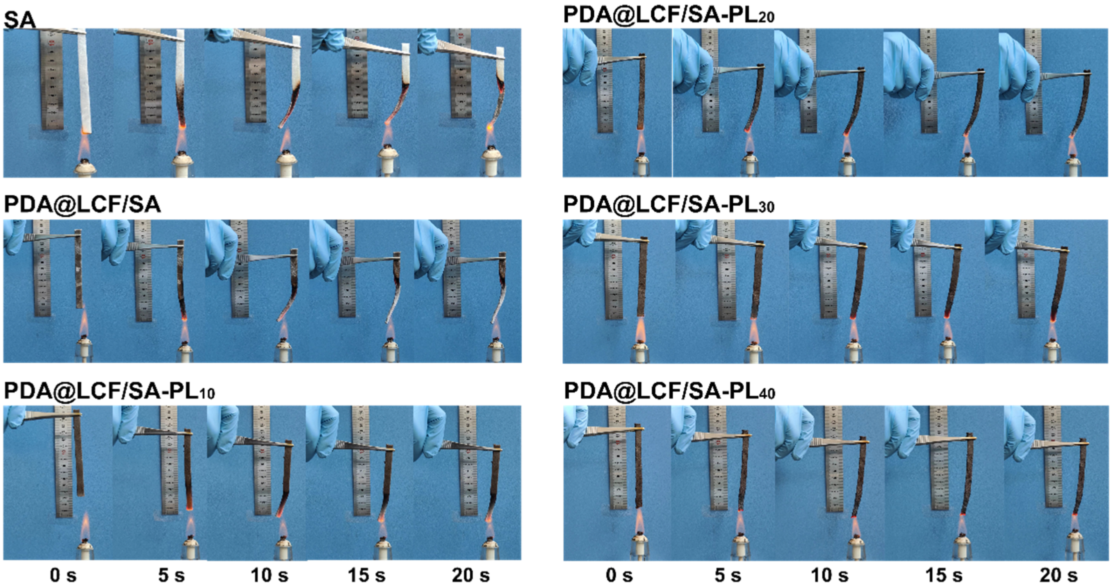

Fig. S6. Images of different aerogel samples undergone 20 s vertical combustion test.

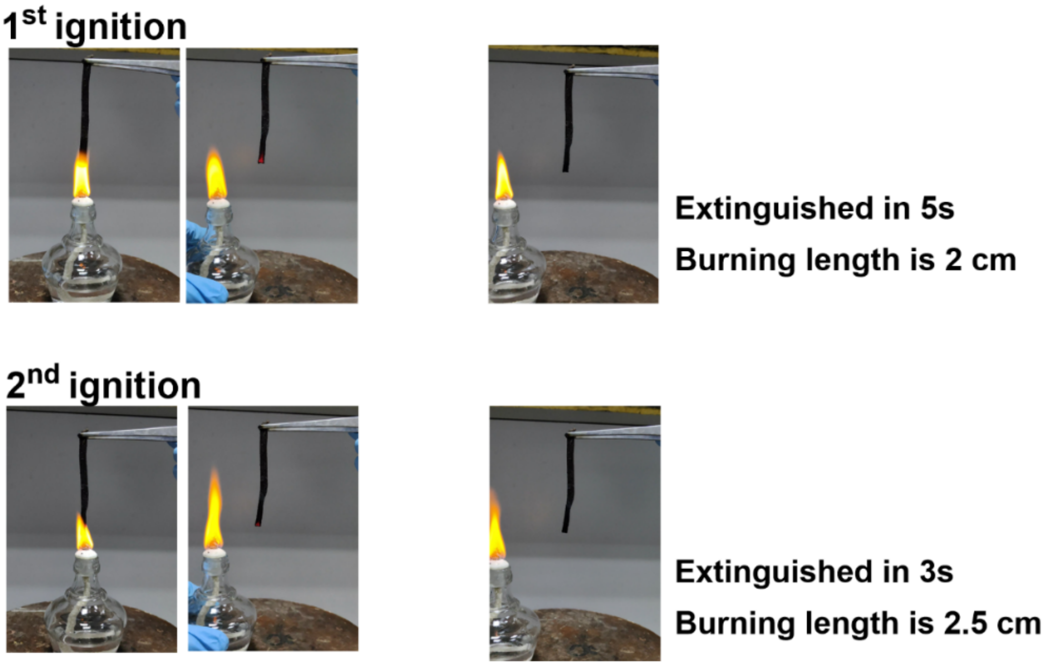

Fig. S7. The UL-94 vertical combustion test image of PDA@LCF/SA-PL40 aerogel sample.

7. Detailed SEM image and EDS data of carbon residue after vertical combustion of composite aerogel

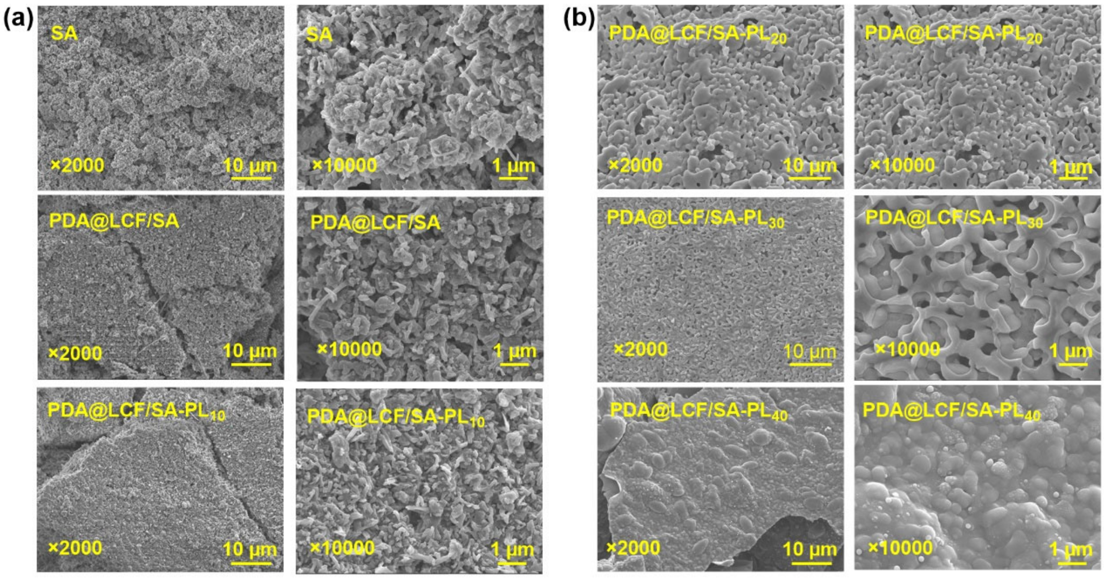

Fig. S8. SEM images of carbon residue of different aerogel samples.

Table S3 The displayed were detailed data on the content of different elements of PDA@LCF/SA-PL40.

Element	Line type	Apparent Concentration	Wt% (%)	Atomic (%)
C	K series	30.15	46.02	56.87
N		2.84	1.97	2.09
O		45.05	31.56	29.28
Na		30.26	11.77	7.60
P		33.21	8.68	4.16

8. Detailed UV resistance data of composite aerogel

Table S4 Presented were the data of UV protection performance of pure SA and PDA@LCF/SA-PL40.

Sample	UPF	T (UVA) (%)	T (UVB) (%)	STD-T(UVA) (%)	COV-T (UVA) (%)	STD-T (UVB) (%)	COV-T (UVB) (%)
SA	174.2	2.79	0.41	0.9	32.28	0.26	64.76
PDA@LCF/SA-PL40	2000	0.05	0.05	–	–	–	–

9. Composite aerogel detailed hydrophobic photographs and contact angle data

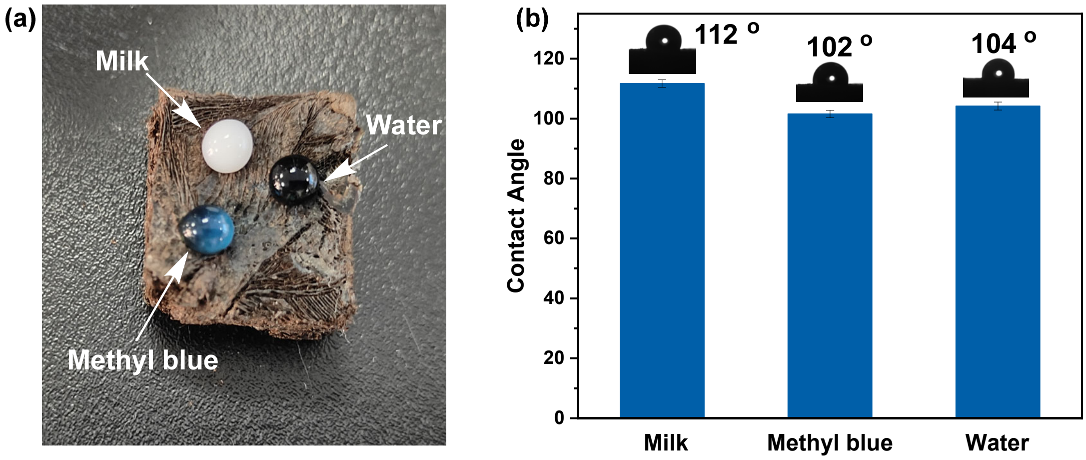

Fig. S9. Photographs of (a) and (b) displayed hydrophobic and static contact angles, respectively.

10. References

[1] X. Meng, C. Crestini, H. Ben, N. Hao, Y. Pu, A. J. Ragauskas and D. S. Argyropoulos, *Nat. Protoc.*, 2019, 14, 2627-2647.

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