Supplementary Information

A scalable *waste-free* biorefinery inspires revenue from holistic lignocellulose valorization

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S1. Materials and methods

S1.1. Synthesis of N, S co-doped CDs from autohydrolysate in the presence of amino acid

With regard to a normal procedure, the preparation of CDs was carried out through the hydrothermal treatment of eucalyptus autohydrolysate (a color of light yellow) with the addition of *L*-cysteine (2 wt%) at 200 °C for a period of 6 h. After heating, the N, S-doped CDs was successfully formed in the solution. The purification of the N, S-doped CDs was carried out with the use of a dialysis tube (500 Da, molecular weight cut off) for a period of approximately 48 h. Moreover, the final N, S-doped CDs was stored at a temperature of 4 °C for further experiments.

S1.2. Cellulose enzymatic hydrolysis

Enzymatic hydrolysis of eucalyptus cellulose was performed according to the Laboratory Analytical Procedures that was reported by the National Renewable Energy Laboratory (NREL) (Selig et al., 2008). Cellulose enzymatic hydrolysis of eucalyptus was conducted in a 25 mL flask using 50mM sodium citrate buffer (pH 4.8) and 2% (g/mL) dry matter at 50 °C with an agitation speed of 150 rpm on a thermostatic shaker for 0–72 h at the cellulase loading of 20 FPU/g dry substrate. Enzymatic hydrolysate of 500 μL was suctioned from the hydrolysis mixture to detect the released glucose by a high performance anion exchange chromatography (HPAEC, Dionex ICS-3000, USA). The samples were filtered through a 0.45 μm Nylon filter and diluted with ultrapure

water for 50-folds volume before HPAEC analysis. After reaction for 72 h, the mixture was centrifuged to eliminate the hydrolyzed carbohydrates, and then the residue was freeze-dried and denoted as cellulose enzymatic lignin (CEL). Eventually, the well-defined CEL was acted as a resource to synthesis of lithium-sulfur (Li-S) cathode *via* carbonization.

References

Selig, M., Weiss, N., Ji, Y., 2008. Enzymatic saccharification of lignocellulosic biomass (Technical report NREL/TP-510-42629). Laboratory Analytical Procedures (LAP), National Renewable Energy Laboratory (NREL), Golden, Colorado.

S1.3. A dual-templating approach to prepare lignin-derived hierarchically porous heteroatom-doped carbon materials for Li-S cathode

Lignin (CEL), *L*-cysteine, $Mg_5(OH)_2(CO_3)_4$ and $ZnCl_2$ are mixed and ground for about 15 min, then the mixture is pyrolyzed at 800 °C for 3 h under nitrogen atmosphere with a temperature ramping rate of 3 °C min^{-1}. Afterwards, the obtained product is immersed in 2.0 M HCl solution for 24 h to remove any inorganic impurities, and then washed with water several times and dried at 60 °C overnight to recover lignin activated carbon (LAC). The LAC/S composite was synthesized *via* a facile melt-diffusion strategy with minor modifications. The as-prepared product (LAC/S) was eventually installed as a cathode for the fabrication of Li-S cell.

In brief, the as-prepared carbon (LAC) and sublimed sulfur with a weight ratio of

1:3 were mixed together and placed in a sealed vessel, and the mixture was heated to 155 °C for 24 h with the heating rate of 5 °C min^{-1}, followed by another heat treatment in a tube furnace at 300 °C for 2 h under N_2 atmosphere to remove the excess sulfur on the surface of biochar LAC. The obtained product was denoted as LAC/S for the fabrication of Li-S cathode. Typically, 80 wt% of sulfur composites, 10 wt% of acetylene black and 10 wt% of polyvinylidene difluoride (PVDF) binder were dispersed in N-methyl-2-pyrrolidone (NMP). The slurry was coated on an aluminum foil and vacuum dried at 60 °C overnight to fabricate the working electrode. CR2032 coin cells were assembled in an argon-filled glove box with the composite LAC/S as cathode, lithium metal as anode, and Celgard 2400 polypropylene membrane as separator. Electrolyte consisted of 1.0 mol/L lithium bis(trifluoromethanesulfonyl)imide in the mixed solvent of 1,3-dioxolane and dimethoxymethane (v/v=1:1, with 1 wt% of $LiNO_3$ additive) was prepared, and 15 μL electrolyte added into each Li-S cell.

S1.4. Analytic methods

S1.4.1 Determination of XOS, monosaccharaides, byproducts, and molecular weight for eucalyptus autohydrolysate with the assistance of L-cysteine

High-performance anion-exchange chromatography (HPAEC) was used to quantify the monosaccharides and oligosaccharides by a Dionex ICS-3000 system. The molecular weight distribution was determined by gel permeation chromatography (GPC, Agilent 1200 series, Agilent Technologies, USA) system. The generation of byproducts from

eucalyptus *via* the process of *L*-cysteine-assisted hydrothermal pretreatment was also quantitatively analyzed using a GPC system with a C18 column (Agilent 1200 series). The contents of XOS (DP 2–6) were quantified by HPAEC (Dionex ICS 3000) using a Carbopac^{TM} PA-100 column (4×250 mm, Dionex) in combination with a PA-100 guard column (4×50 mm, Dionex). A sample volume of 2 μL was taken for each injection *via* an AS50 autosampler. The flow rate of the gradient elution was 0.4 mL/min and the temperature of column was 30 °C. The gradient was 0–80 mM sodium acetate in 100 mM NaOH (carbonate free and purged with nitrogen) for 15 min, followed by 80–300 mM of NaAc gradient in 100 mM NaOH for 10 min. Before each injection, a 10 min elution with 100 mM NaOH was used to re-equilibrate the column. The concentrations of XOS were calculated by the peak areas in correlation with those for the standard curves of xylobiose (X2), xylotriose (X3), xylotetraose (X4), xylopentaose (X5) and xylohexose (X6). The standard chemicals of XOS were purchased from Megazyme Ltd. (Ireland). In addition, the content of XOS with the DP>6 was determined by an extended acid hydrolysis method.

Weight-average (M_w), number-average (M_n) molecular weights and polydispersity (M_w/M_n) of the dilute acid filtrate (mainly hemicelluloses-derived products) were determined by GPC equipped with a differential refractive index detector (RID), using a PL aquagel-OH 50 column (300 × 7.7 mm, Polymer Laboratories Ltd.). The data were calibrated with PL pullulan polysaccharide standards. The eluent was 0.02 M NaCl in 0.005 M sodium phosphate buffer (pH 7.5), and the flow rate was 0.5 mL/min.

S1.4.2. Structural characterization of N, S-doped CDs

The transmission electron microscopy (TEM) images of CDs were observed on a JEM-2100 apparatus operating at 200 kV. The determination of particle diameter and self-aggregation behavior of CDs were performed by dynamic light scattering method using Malvern DLS instrument (Malvern Zetasizer ZS90) at 298 K. The Raman spectrum was measured using a 532 nm laser on a Renishaw inVia-reflex spectroscopy. The X-ray photoelectron spectroscopy (XPS) measurements were made on an AXIS UL TRA DLD system to analyze the surface chemical states. The Fourier transformed infrared (FTIR) spectrum was acquired on a Nicolet 6700 FTIR spectrometer in the range of 400–4000 cm^{-1}. The Ultraviolet-visible (UV–vis) absorption and photoluminescence (PL) spectra were monitored by UV-3101PC and Hitachi F-7000 spectrophotometers.

S1.4.3. Structural characterization of lignin and eucalyptus

The crystallinity, morphological and structural properties of eucalypytus were determined by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The weight average (M_w), number-average (M_n) molecular weights, and polydispersity index (PI, M_w/M_n) of lignin were recorded by GPC (Agilent 1200, USA). The HSQC and ^{31}P NMR spectra of lignin were plotted using a Bruker AVIII 400 MHz spectrometer.

The weight average (M_w) and number-average (M_n) molecular weights of the lignin were determined by GPC with an ultraviolet (UV) detector at 280 nm wavelength. The column used was a PL-gel 10 mm mixed-B 7.5 mm *i.d.* column, which was calibrated

with PL polystyrene standards. Initially, four milligrams of lignin was dissolved in 2 mL of tetrahydrofuran (THF), and then filtered through a 0.22 μm organic membrane before injection. Lignin/THF solution of 20 μL was injected by automatic sampler equipped with GPC. The analytical column was operated at ambient temperature and eluted with THF at a flow rate of 1.0 mL min^{-1}.

The NMR spectra were acquired on a Bruker Avance 400 MHz spectrometer fitted with a 5 mm gradient probe with inverse geometry (proton coils closest to the sample). The lignin preparation of 25 mg were dissolved in 0.5 mL of DMSO-d_6 respectively. The central solvent peak at δC/δH 39.5/2.49 was used as an internal reference. The standard Bruker implementations of one- and two-dimensional (gradient-selected, ^{1}H-detected HSQC) NMR experiments were used for structural characterization and assignment authentication. For 2D-HSQC spectra, the Bruker pulse program "hsqcetgpsi" was used and the parameters used is listed as below: the number of collected complex points was 1 K for the ^{1}H dimension with d_1 (2 s), number of scanning is 64, and 256 time increments were always recorded.

^{31}P NMR spectra were acquired at 25 °C on a Bruker AVIII 400 MHz spectrometer after the reaction of lignin with 2-chloro-1,3,2 dioxaphospholanyl chlorides. Lignin of 20 mg was dissolved in 500 μL of anhydrous pyridine and deuterated chloroform (1.6 : 1, v/v) under stirring. This was followed by the addition 100 μL of cyclohexanol (10.85 mg mL^{-1} in anhydrous pyridine and deuterated chloroform 1.6:1, v/v) as an internal standard and 100 μL of chromium(III) acetylacetonate solution (5 mg/mL in anhydrous pyridine and deuterated chloroform 1.6 : 1, v/v) as a relaxation reagent. The mixture

was reacted with 100 μL of phosphitylating reagent (2-chloro-4,4,5,5-tetramethyl-1,3,2- dioxaphospholane, TMDP) for 20 min and then transferred into a 5 mm NMR tube for subsequent NMR analysis. The standard ^{31}P NMR experiment was selected from Bruker Program Library and the parameters used were listed as follows: the 30° pulse angle, 2 s relaxation delay (d_1), 64 K data points, and 1024 scans. The content of hydroxyl groups in lignin was determined *via* integration of the following spectral regions: aliphatic hydroxyls (149.0–146.0 ppm), condensed syringyl (CS) phenolic hydroxyls (144.5–143.2 ppm), syringyl (S) phenolic hydroxyls (143.2–142.17 ppm), condensed guaiacyl (CG) phenolic hydroxyls (142.17–141.42 ppm), guaiacyl (G) phenolic hydroxyls (140.17–138.79 ppm), *p*-hydroxyphenyl (H) phenolic hydroxyls (138.4–137.1 ppm), and carboxylic acids (135.5–134.2 ppm).

S1.4.4. Characterization of lignin-derived Li-S cathode

The morphology, microstructure, elemental analysis, surface chemical states, sulfur content and specific surface area of CEL-derived cathode material were performed with SEM, transmission electron microscopy (TEM, Tecnai G2 F30, Netherlands), XRD, thermogravimetric analysis (TGA), and nitrogen adsorption-desorption isotherms respectively. The galvanostatic charge/discharge measurements, cyclic voltammotry (CV), and electrochemical impedance spectroscopy (EIS) test were also performed to monitor the electrochemical performances of CEL-derived Li-S cathode.

XRD patterns were collected on a Rigaku MiniFlex 600 instrument. In order to determine the sulfur content of LAC/S composite, TGA analysis was conducted using

a TA SDT Q600 with a heating rate of 10 °C min^{-1} in N_2 flow. Nitrogen adsorption-desorption isotherms were carried out using automatic specific surface area and porosity analyzer (JWBK122W, JWGB Ltd., China), and analyzed with Brunauer−Emmett−Teller (BET) model.

The galvanostatic charge/discharge measurements were performed with a voltage window of 1.7–2.8 V *vs.* Li^+/Li using a LAND CT2001A test system. All the capacities were calculated on the basis of the sulfur mass in the cathode. CV test was conducted using an electrochemical workstation (Biologic, VSP 300, France) by potential cycling between 3 V and 1.5 V with a sweeping rate of 0.2 mV s^{-1}. EIS measurement at open-circuit potential was carried out in the frequency range of 100 kHz to 0.01 Hz with an AC modulation amplitude of 5 mV using the same electrochemical workstation (Biologic, VSP 300, France).

Figure captions

Figure S1. (a) Three building blocks and their structural composition of lignocellulose eucalyptus. (b) The chemical components (columns), crystallinity index (lines), (c-d) SEM images (scale bar 20 μm), and (e) enzymatic hydrolysis of feedstock. Control: original eucalyptus; HTT: hydrothermally treated eucalyptus.

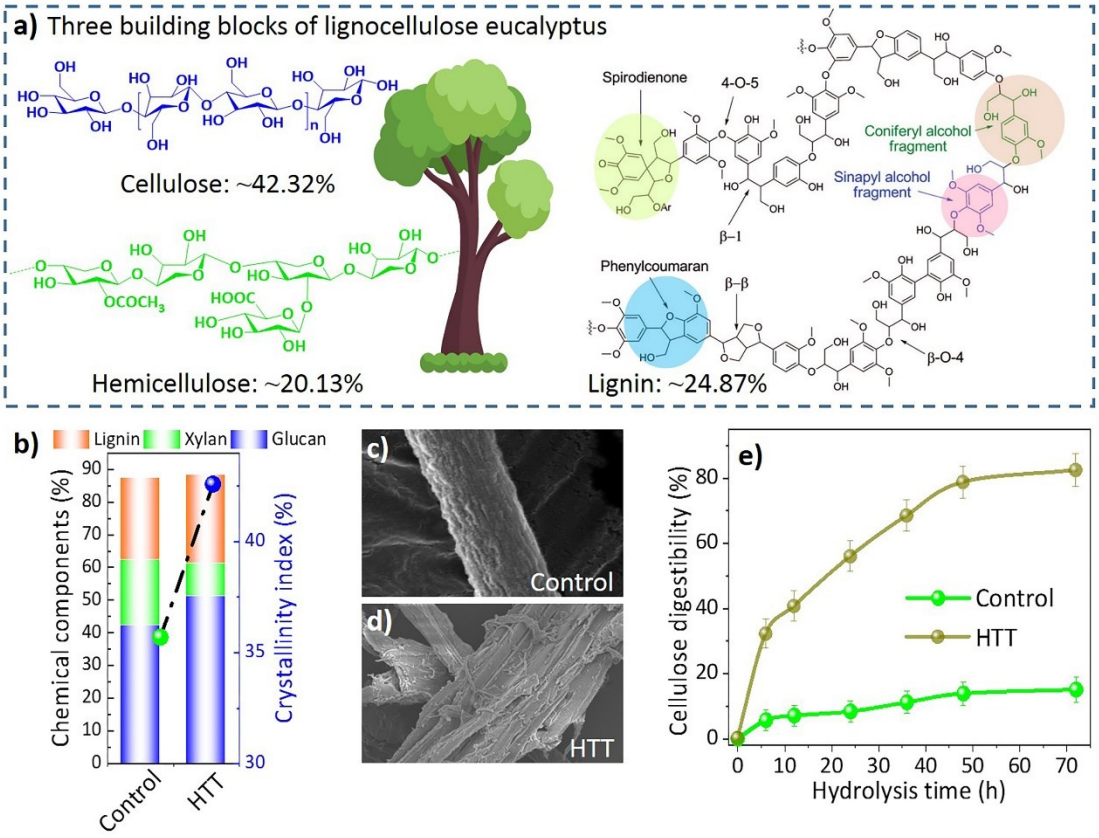

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Table S1. Assignments of ^{13}C-^{1}H cross signals in the HSQC spectra of lignin.

Label	δC/δH (ppm)	Assignments
Bβ	53.5/3.12	Cβ−Hβ in β-β′ (resinol) substructures (B)
−OCH_3	55.6/3.69	C−H in methoxyls
Aγ	59.8/3.21-3.84	Cγ−Hγ in β-*O*-4′ substructures (A)
Iγ	61.8/4.10	Cγ−Hγ in *p*-hydroxycinnamyl alcohol end groups (I)
Bγ	71.4/3.80-4.18	Cγ−Hγ in β-β′ resinol substructures (B)
Aα	71.8/4.82	Cα−Hα in β-*O*-4′ substructures linked to a S unit (A)
Aβ(G)	83.9/4.30	Cβ−Hβ in β-*O*-4′ substructures linked to a G unit (A)
Bα	84.9/4.58	Cα−Hα in β-β′ (resinol) substructures (B)
Aβ(S)	86.0/4.11	Cβ−Hβ in β-*O*-4′ substructures linked to S (A, erythro)
Aβ(S)	86.8/3.98	Cβ−Hβ in β-*O*-4′ substructures linked to S (A, threo)
Cα	86.6/5.48	Cα−Hα in phenylcoumaran substructures (C)
S2,6	104.2/6.71	C2,6−H2,6 in syringyl units (S)
S′2,6	106.7/7.25	C2,6−H2,6 in oxidized (Cα=O) syringyl units (S′)
G2	111.5/6.97	C2−H2 in guaiacyl units (G)
G5	114.8/6.71	C5−H5 in guaiacyl units (G)
G6	119.8/6.75	C6−H6 in guaiacyl units (G)