Supplementary Information for

Robust Ionic Liquid/Ethanolamine-Superbase Solvents Enable Rapid, Efficient and Mild Dissolution of Lignocellulosic Biomass

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Kamlet-Taft LSER method

The linear relationship between lignin solubility and KT parameter was determined by fitting a linear solvation energy relationship (LSER) using multiple linear regression according to our previous work and other literature.[1,2] In this work, the maximum p-value used was 0.05, and multiple linear regression was expressed by the following equation:

$$\ln S = XYZ_0 + a\alpha + b\beta + c\pi^* \tag{1}$$

where a, b and c are coefficients of each parameter and XYZ_0 is intercept. Multiple linear regressions were performed on all the different variables [(α, β, π^*), (α, β), (α, π^*), (β, π^*), (α), (β), (π^*)] to determine the coefficients, and correlations were accepted if the variables all proved statistically significant ($p < 0.05$). Otherwise, there is no correlation.

Table S1 Solubilities (g/100 g solvent) of lignocellulose in various neat ILs and EA-superbase mixtures at 90 °C.

Solvent systems	Solubility[a]
EA-DBN	< 1.0
EA-DBU	< 1.0
EA-TMG	< 1.0
EmimOAc	1.5 (±0.15)
PmimOAc	1.0 (±0.15)
BmimOAc	< 1.0
AmimOAc	< 1.0
EmimCl	< 1.0
PmimCl	< 1.0
BmimCl	< 1.0
AmimCl	< 1.0

[a]Values of solubility were the average of twice measurements.

Table S2 Solubilities (g/100 g solvent) of lignocellulose in various IL/EA-superbase systems (1:1) at 90 °C.

Solvent systems	Solubility[a]	Solvent systems	Solubility[a]	Solvent systems	Solubility[a]
EmimOAc/EA-DBN	9.5 (±0.35)	EmimOAc/EA-DBU	8.6 (±0.30)	EmimOAc/EA-TMG	7.0 (±0.25)
PmimOAc/EA-DBN	9.0 (±0.32)	PmimOAc/EA-DBU	8.1 (±0.30)	PmimOAc/EA-TMG	6.6 (±0.22)
BmimOAc/EA-DBN	3.2 (±0.15)	BmimOAc/EA-DBU	2.8 (±0.12)	BmimOAc/EA-TMG	< 1.0
AmimOAc/EA-DBN	3.0 (±0.15)	AmimOAc/EA-DBU	2.2 (±0.10)	AmimOAc/EA-TMG	< 1.0
EmimCl/EA-DBN	8.0 (±0.28)	EmimCl/EA-DBN	–[b]	EmimCl/EA-TMG	–[b]
PmimCl/EA-DBN	7.3 (±0.25)	PmimCl/EA-DBU	–[b]	PmimCl/EA-TMG	1.2 (±0.12)
BmimCl/EA-DBN	4.0 (±0.18)	BmimCl/EA-DBU	3.2 (±0.15)	BmimCl/EA-TMG	< 1.0
AmimCl/EA-DBN	1.8 (±0.15)	AmimCl/EA-DBU	–[b]	AmimCl/EA-TMG	–[b]

[a]Values of solubility were the average of twice measurements.
[b]The solubility of lignocellulose was not detected because the IL and EA-superbase did not form a homogeneous solvent.

Table S3 Solubilities (g/100 g solvent) of lignocellulose in various IL/EA (1:1) and IL/superbase (1:1) systems at 90 °C.

Solvent systems	Solubility[a]	Solvent systems	Solubility[a]	Solvent systems	Solubility[a]	Solvent systems	Solubility[a]
EmimOAc/EA	6.5 (±0.22)	EmimOAc/DBN	4.3 (±0.18)	EmimOAc/DBU	-[b]	EmimOAc/TMG	-[b]
PmimOAc/EA	6.2 (±0.22)	PmimOAc/DBN	4.0 (±0.15)	PmimOAc/DBU	-[b]	PmimOAc/TMG	1.0 (±0.10)
BmimOAc/EA	< 1.0	BmimOAc/DBN	1.2 (±0.10)	BmimOAc/DBU	< 1	BmimOAc/TMG	-[b]
AmimOAc/EA	< 1.0	AmimOAc/DBN	1.0 (±0.10)	AmimOAc/DBU	-[b]	AmimOAc/TMG	-[b]
EmimCl/EA	2.0 (±0.10)	EmimCl/DBN	-[b]	EmimCl/DBU	-[b]	EmimCl/TMG	-[b]
PmimCl/EA	1.0 (±0.10)	PmimCl/DBN	-[b]	PmimCl/DBU	-[b]	PmimCl/TMG	-[b]
BmimCl/EA	< 1.0	BmimCl/DBN	3.0 (±0.18)	BmimCl/DBU	-[b]	BmimCl/TMG	-[b]
AmimCl/EA	1.0 (±0.10)	AmimCl/DBN	-[b]	AmimCl/DBU	-[b]	AmimCl/TMG	-[b]

[a]Values of solubility were the average of twice measurements.
[b]The solubility of lignocellulose was not detected because the IL and the superbase did not form a homogeneous solvent.

Table S4 Solubilities (g/100 g solvent) of lignocellulose in different IL/EA-superbase systems (1:1) at different temperatures.

Solvent systems	Solubility[a]		
	70 °C	80 °C	90 °C
EmimOAc/EA-DBN	4.5 (±0.16)	7.0 (±0.25)	9.5 (±0.35)
PmimOAc/EA-DBN	2.3 (±0.10)	5.5 (±0.2)	9.0 (±0.35)
EmimCl/EA-DBN	3.6 (±0.15)	6.0 (±0.22)	8.0 (±0.3)
PmimCl/EA-DBN	2.5 (±0.1)	5.0 (±0.2)	7.3 (±0.25)
EmimOAc/EA-DBU	4.0 (±0.18)	6.0 (±0.25)	8.6 (±0.35)
EmimOAc/EA-TMG	3.0 (±0.15)	4.8 (±0.2)	7.0 (±0.25)

[a]Values of solubility were the average of twice measurements.

Table S5 Solubilities (g/100 g solvent) of lignocellulose in EmimOAc/EA-DBN systems with varied molar ratios at 90 °C.

Molar ratio	Solubility[a]
1:0	1.5 (±0.15)
5:1	4.0 (±0.2)
4:1	6.0 (±0.28)
3:1	7.4 (±0.3)
2:1	8.5 (±0.32)
1:1	9.5 (±0.35)
1:2	9.0 (±0.35)
1:3	6.5 (±0.28)
1:4	3.6 (±0.2)
1:5	1.7 (±0.15)
0:1	< 1

[a]Values of solubility were the average of twice measurements.

Table S6 Chemical composition of sugarcane bagasse before and after pretreatment and the solubilities (g/100 g solvent) of treated lignocellulosic samples in EmimOAc/EA-DBN systems at different temperatures.

Samples	Residue yield (wt%)	Composition of samples (wt%)			Lignin removal (%)	Hemicellulose removal (%)	Solubility[a] (g/100 g solvent)		
		Cellulose	Hemicellulose	Lignin			70 °C	80 °C	90 °C
Raw	-	40.04	26.49	21.94	-	-	4.5 (±0.16)	7.0 (±0.25)	9.5 (±0.35)
HF-lignocellulose[b]	60.5	61.78	6.26	33.67	7.15	85.74	6.4 (±0.20)	8.2 (±0.2)	11.8 (±0.42)
LF-lignocellulose[c]	65.15	58.12	34.80	5.34	84.15	14.41	8.5 (±0.30)	11.2 (±0.38)	15.0 (±0.45)

[a]Values of solubility were the average of twice measurements.
[b]Sample was obtained by hydrothermal pretreatment at 190 °C for 20 min.
[c]Sample was obtained by sodium chlorite pretreatment.

Table S7 Solubilities (g/100 g solvent) of various lignocellulosic biomass in EmimOAc/EA-DBN system at 90 °C.

Lignocellulose	Solubility[a]
Miscanthus giganteus	20.0 (±1.2)
Sorghum straw	14.6 (±0.8)
Corncob	10.3 (±0.5)
Sugarcane bagasse	9.5 (±0.35)
Moso bamboo	9.2 (±0.4)
Wheat straw	5.5 (±0.5)
Rice straw	5 (±0.5)
Populus tomentosa	3.8 (±0.3)
Pinus radiata	3.2 (±0.3)

[a]Values of solubility were the average of twice measurements.

Table S8 The Kamlet-Taft parameters of IL/EA-DBN (1:1, mol/mol) systems and the parent solvent (neat ILs and EA-DBN).

Solvent systems	Kamlet-Taft parameters[a]		
	α	β	π^*
EmimOAc	0.49	1.09	1.06
PmimOAc	0.46	0.99	1.06
BmimOAc	0.47	1.01	1.01
AmimOAc	0.48	0.99	1.08
EmimCl	_[b]	_[b]	_[b]
PmimCl	_[b]	_[b]	_[b]
BmimCl	_[b]	_[b]	_[b]
AmimCl	0.46	0.83	1.17
EA-DBN	0.81	1.00	0.91
EmimOAc/EA-DBN	0.51	1.12	1.00
PmimOAc/EA-DBN	0.56	1.10	0.96
BmimOAc/EA-DBN	0.63	1.01	1.04
AmimOAc/EA-DBN	0.63	0.99	1.04
EmimCl/EA-DBN	0.52	0.97	1.06
PmimCl/EA-DBN	0.57	0.97	1.06
BmimCl/EA-DBN	0.62	0.97	1.02
AmimCl/EA-DBN	0.68	0.94	1.02

[a]The value of the corresponding Kamlet-Taft parameter was the average of twice measurements. [b]The ILs were solid at room temperature and cannot be tested.

Table S9 Result of K-T parameters LSER fits for the lignocellulose solubility in different of IL/EA-DBN systems.[a]

Solvent systems	Parameters	LSER equation	p-values
Acetate-based IL/EA-DBN	α	ln S=7.64-10.24α	XYZ_0=0.033, α=0.052
	β	ln S=-8.57+9.27β	XYZ_0=0.011, β=0.008
	β-α	ln S=-0.72+5.07(β-α)	XYZ_0=0.182, β-α=0.021
Chloride-based IL/EA-DBN	α	ln S=-7.29-9.67α	XYZ_0=0.024, α=0.036
	β	ln S=-37.95+41.00β	XYZ_0=0.113, β=0.105
	β-α	ln S=-1.52+8.32(β-α)	XYZ_0=0.075, β-α=0.020

[a]In this work, a maximum p value was 0.05, if values proved statistically significant ($p < 0.05$), the correlation was accepted.

Table S10 Density (ρ), viscosity (η), conductivity (σ) and molar conductivity (Λ) of IL/EA-DBN systems at different temperatures.

Solvent systems	ρ (g·cm⁻³)			η (mPa·s)			σ (mS·cm⁻¹)			Λ (S·cm²·mol⁻¹)		
	30 °C	50 °C	70 °C	30 °C	50 °C	70 °C	30 °C	50 °C	70 °C	30 °C	50 °C	70 °C
EmimOAc	1.098	1.087	1.074	120.52	52.95	24.50	2.970	4.978	7.776	0.460	0.779	1.232
EmimOAc/EA-DBN	1.063	1.050	1.038	54.03	30.50	18.80	4.401	5.894	7.490	0.491	0.665	0.855
PmimOAc	1.079	1.069	1.057	252.00	120.80	60.45	1.217	2.105	3.695	0.208	0.363	0.644
PmimOAc/EA-DBN	1.055	1.044	1.034	60.10	36.13	25.87	2.723	4.017	5.148	0.318	0.474	0.613
BmimOAc	1.091	1.080	1.068	509.87	266.60	113.00	0.515	0.921	1.712	0.094	0.169	0.318
BmimOAc/EA-DBN	1.062	1.050	1.037	302.90	144.10	77.87	1.118	1.960	3.208	0.142	0.239	0.395
AmimOAc	1.110	1.099	1.087	392.25	205.80	95.95	0.753	1.210	2.356	0.124	0.201	0.395
AmimOAc/EA-DBN	1.070	1.059	1.048	162.60	95.5	55.90	1.549	2.513	3.744	0.177	0.291	0.438
EmimCl	1.111	1.094	1.078	_ᵃ	_ᵃ	_ᵃ	_ᵃ	_ᵃ	_ᵃ	_ᵃ	_ᵃ	_ᵃ
EmimCl/EA-DBN	1.066	1.056	1.044	94.95	54.40	25.00	3.433	4.851	7.294	0.356	0.508	0.773
PmimCl	1.078	1.062	1.046	_ᵃ	_ᵃ	_ᵃ	_ᵃ	_ᵃ	_ᵃ	_ᵃ	_ᵃ	_ᵃ
PmimCl/EA-DBN	1.061	1.050	1.039	112.05	65.07	37.73	2.179	3.536	5.226	0.237	0.388	0.580
BmimCl	1.079	1.063	1.048	_ᵃ	_ᵃ	_ᵃ	_ᵃ	_ᵃ	_ᵃ	_ᵃ	_ᵃ	_ᵃ
BmimCl/EA-DBN	1.055	1.045	1.033	144.65	73.40	40.93	1.733	2.731	4.215	0.197	0.314	0.490
AmimCl	1.127	1.116	1.104	701.00	352.70	182.00	0.601	1.049	1.915	0.085	0.149	0.275
AmimCl/EA-DBN	1.074	1.063	1.051	223.95	131.60	75.77	1.827	2.821	4.553	0.195	0.304	0.497

ᵃThe ILs were solid at this temperature and cannot be tested.

Table S11 Ionicity of each investigated solvent systems depending on temperature.

Solvent systems	% Ionicity		
	30 °C	50 °C	70 °C
EmimOAc	55.4	41.2	30.2
EmimOAc/EA-DBN	26.5	20.3	16.1
PmimOAc	52.4	43.8	38.9
PmimOAc/EA-DBN	19.1	17.1	15.8
BmimOAc	47.7	45.1	35.9
BmimOAc/EA-DBN	43.0	34.4	30.7
AmimOAc	48.5	41.3	37.9
AmimOAc/EA-DBN	28.8	27.8	24.5
EmimCl	-[a]	-[a]	-[a]
EmimCl/EA-DBN	33.8	27.6	19.3
PmimCl	-[a]	-[a]	-[a]
PmimCl/EA-DBN	26.5	25.2	21.9
BmimCl	-[a]	-[a]	-[a]
BmimCl/EA-DBN	28.5	23.0	20.1
AmimCl	59.3	52.6	50.1
AmimCl/EA-DBN	43.6	40.0	37.6

[a]The ILs were solid at this temperature and cannot be tested.

Table S12 Assignments of ^{1}H-^{13}C overlapped signals in 2D-NMR spectra of Sugarcane bagasse and regenerated sugarcane bagasse.

| Lable	δ_C/δ_H (ppm)[a]	δ_C/δ_H (ppm)[b]	Assignments
OMe	55.25/3.77	55.41/3.64	C-H in methoxyls
A_α	71.85/5.02	72.69/5.35	C_α-H_α in β-O-4 substructures
A_β(S)	85.95/4.24	86.33/4.08	C_β-H_β in β-O-4 substructures linked to S unit
$S_{2,6}$	103.50/6.88	104.10/6.72	$C_{2,6}$-$H_{2,6}$ in syringyl units
G_2	110.81/7.14	111.40/7.00	C_2-H_2 in guaiacyl units
G_5	115.20/6.90	115.30/6.77	C_5-H_5 in guaiacyl units
G_6	119.09/6.92	119.17/6.81	C_6-H_6 in guaiacyl units
$H_{2,6}$	127.50/7.20	ND	$C_{2,6}$-$H_{2,6}$ in p-hydroxyphenyl units
$pCA_{2,6}$	129.82/7.56	129.42/7.41	$C_{2,6}$-$H_{2,6}$ in p-coumarate
pCA_α	144.45/7.67	144.93/7.57	C_α-H_α in p-coumarate
pCA_β+FA_β	114.25/6.51	114.75/6.49	C_β-H_β in p-coumarate and ferulate
FA_2	110.81/7.45	110.81/7.28	C_2-H_2 in ferulate
FA_6	123.48/7.08	123.33/7.00	C_6-H_6 in ferulate
C_1	ND	105.51/4.35	C_1-H_1 in cellulose internal unit
C_2	73.10/3.08	73.11/3.15	C_2-H_2 in cellulose internal unit
C_3	73.25/3.58	73.30/3.60	C_3-H_3 in cellulose internal unit
C_4	80.02/3.53	79.58/3.45	C_4-H_4 in cellulose internal unit
C_5	76.30/3.25	76.35/3.28	C_5-H_5 in cellulose internal unit
C_6	60.12/3.77	59.54/3.76	C_6-H_6 in cellulose internal unit
X_1	101.55/4.44	101.67/4.30	C_1-H_1 in β-D-xylopyranoside
X_2	73.28/3.41	72.70/3.13	C_2-H_2 in β-D-xylopyranoside
X_3	73.77/3.46	73.91/3.34	C_3-H_3 in β-D-xylopyranoside
X_4	74.74/3.67	75.13/3.56	C_4-H_4 in β-D-xylopyranoside
X_{5ax}	63.04/3.32	63.20/3.19	C_{5ax}-H_{5ax} in β-D-xylopyranoside
X_{5eq}	63.04/4.04	63.20/3.90	C_{5eq}-H_{5eq} in β-D-xylopyranoside
X_{NR5}	65.97/3.90	65.54/3.69	C_5-H_5 in β-D-xylopyranoside（non-reducing end）
Ara_1	ND	107.27/5.47	C_1-H_1 in arabinan
Ara_2	81.08/4.06	80.24/3.92	C_2-H_2 in arabinan
Ara_3	78.06/3.83	77.81/3.72	C_3-H_3 in arabinan
Ara_5	66.72/3.68	ND	C_5-H_5 in arabinan
U_1	ND	97.77/5.14	C_1-H_1 in 4-O-methyl-α-D-glucuronic acid (U)
U_4	ND	81.56/3.19	C_4-H_4 in 4-O-methyl-α-D-glucuronic acid (U)
$U_{:OCH3}$	60.01/3.50	59.55/3.41	C-H in methoxyls of 4-O-methyl-α-D-glucuronic acid
XU_1	98.14/4.86	98.54/4.54	C_1-H_1 in (1→4)-β-D-Xylp-2-O-(4-O-methyl-α-D-GlcpA)
2-O-Ac-β-D-Xylp (2)	73.28/4.72	ND	2-O-acetylated β-D-xylopyranosyl
3-O-Ac-β-D-Xylp (3)	74.74/5.02	ND	3-O-acetylated β-D-xylopyranosyl
2,3-O-Ac-β-D-Xylp (2)	72.50/4.90	71.75/4.95	2,3-O-acetylated β-D-xylopyranosyl

[a]Assignments of sugarcane bagasse
[b]Assignments of regenerated sugarcane bagasse
ND, Not detected
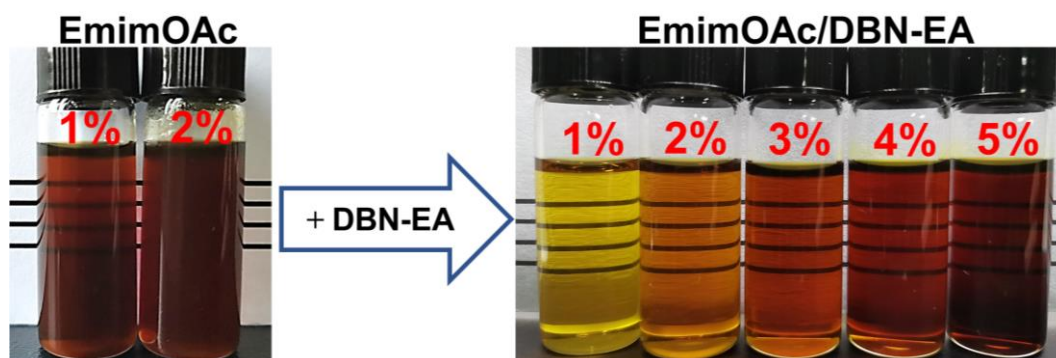
Fig. S1 Optical pictures of lignocellulose solution in EmimOAc and EmimOAc/EA-DBN system with different concentration (g/100 g solvent).
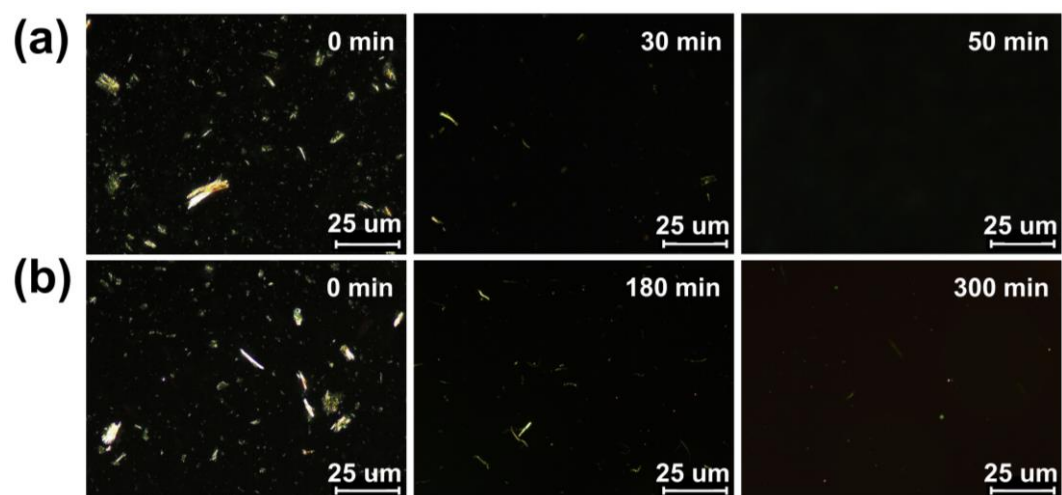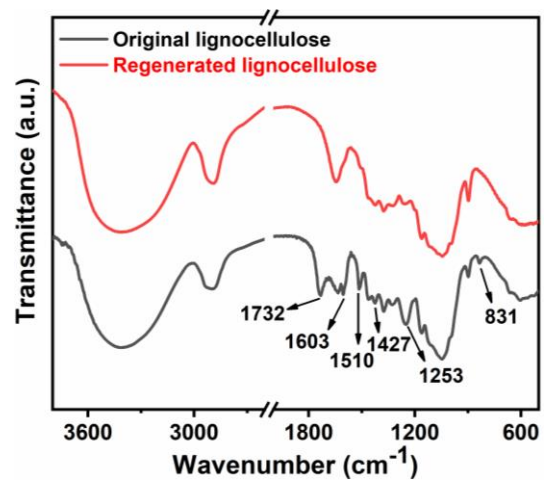
Fig. S2 Polarized optical microscopy pictures of the dissolution process of lignocellulose (1%, w/w) in (a) EmimOAc/EA-DBN system and (b) neat EmimOAc at 90 °C.
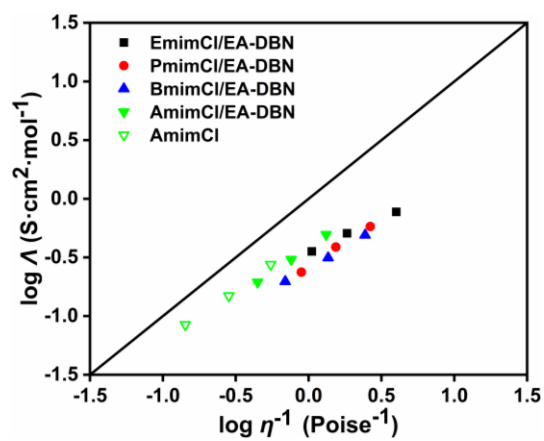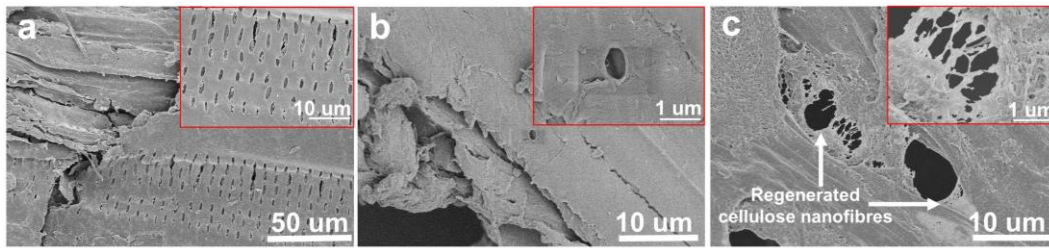
Fig. S3 Walden plot of neat chloride anion-based ILs and chloride anion-based IL/EA-DBN systems.

Fig. S4 FT-IR spectra of original lignocellulose and the regenerated lignocellulose sample from EmimOAc/EA-DBN system-EA system.

Fig. S5 Scanning electron microscopy (SEM) images of the sugarcane bagasse (a), and the corresponding ball milled sample (b) and regenerated sample (c).

References

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