Supplementary Information File for:

Sustainable Mesoporous carbon nanostructures derived from lignin for Early Detection Of Glucose.

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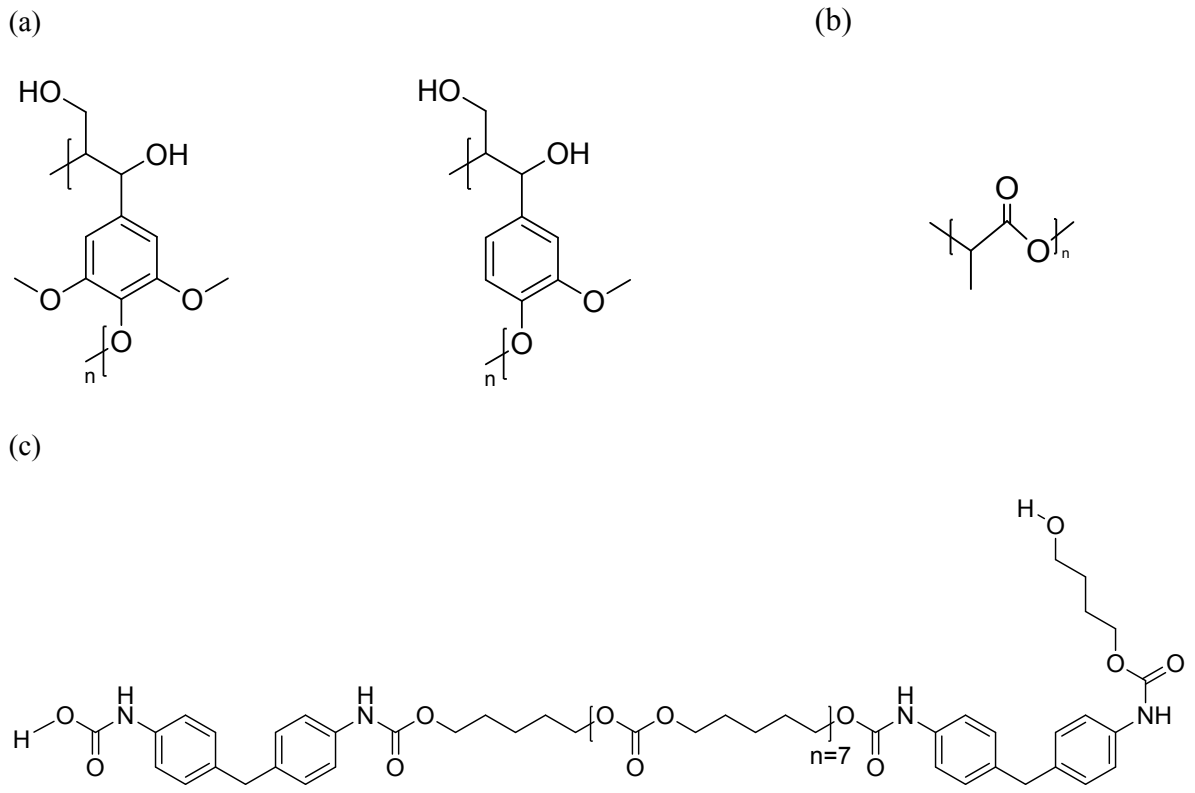


Figure S 1: Repeat Units of (a) AL, (b) PLA and (c) TPU (n=7)

Table S 1 : Calculation of the Group Molar Attraction Constant $\sum n_i F_i$ for AL, PLA and TPU repeat units

	F_i * ($(J.m^3)^{1/2}.mol^{-1}$)	AL		PLA		TPU	
		Number of groups n_i	$\sum n_i F_i$ ($(J.m^3)^{1/2}.mol^{-1}$)	Number of groups n_i	$\sum n_i F_i$ ($(J.m^3)^{1/2}.mol^{-1}$)	Number of groups n_i	$\sum n_i F_i$ ($(J.m^3)^{1/2}.mol^{-1}$)
$-CH_3$	0.3032	0	0	1	0.3032	0	0
$-CH_2-$	0.2689	2	0.5378	0	0	46	12.3694
>CH-	0.1758	4	0.7032	1	0.1758	0	0
=CH-	0.2485	0	0	0	0	0	0
$-O-CH_3$	0.236	3	0.708	0	0	0	0
>C=O	0.5376	0	0	0	0	0	0
-COO-	0.6677	0	0	1	0.6677	2	1.3354
-O-	0.2351	2	0.4702	0	0	1	0.2351
Aromatic CH	0.2395	5	1.1975	0	0	16	3.832
Aromatic C	0.2006	7	1.4042	0	0	8	1.6048
Aromatic Meta	0.0135	3	0.0405	0	0	0	0
Aromatic Para	0.0825	2	0.165	0	0	4	0.33
6-Membered Ring	-0.0479	2	-0.0958	0	0	4	-0.1916
-OH aromatic	0.3496	0	0	0	0	0	0
-OH aliphatic	0.4617	4	1.8468	0	0	0	0
-O-CO-O-	0.904	0	0	0	0	7	6.328
-O-CO-NH-	1.04	0	0	0	0	4	4.16
			6.9774		**1.14**		**30.00**

Table S2 : Solubility parameter and enthalpy of mixing for AL, PLA and TPU blends *: density was measured using a AccuPyc II 1340/ Gas Pycnometer working with Helium

Samples	Volumic Mass ρ ($kg.m^{-3}$)	Group Molar Constant $\sum n_i F_i$ ($(J.m^3)^{1/2}. mol^{-1}$)	Solubility Parameter δ ($MPa^{1/2}$)	Enthalpy of Mixing per unit of volume ($J.m^{-3}$)
AL	1325 *	6.9774	21.91	-
PLA	1250	1.14	19.91	-
TPU	1220	30.00	22.59	-
AL/PLA 50-50 (%vol)	-	-	-	1.00
AL/TPU 50-50 (%vol)	-	-	-	0.11

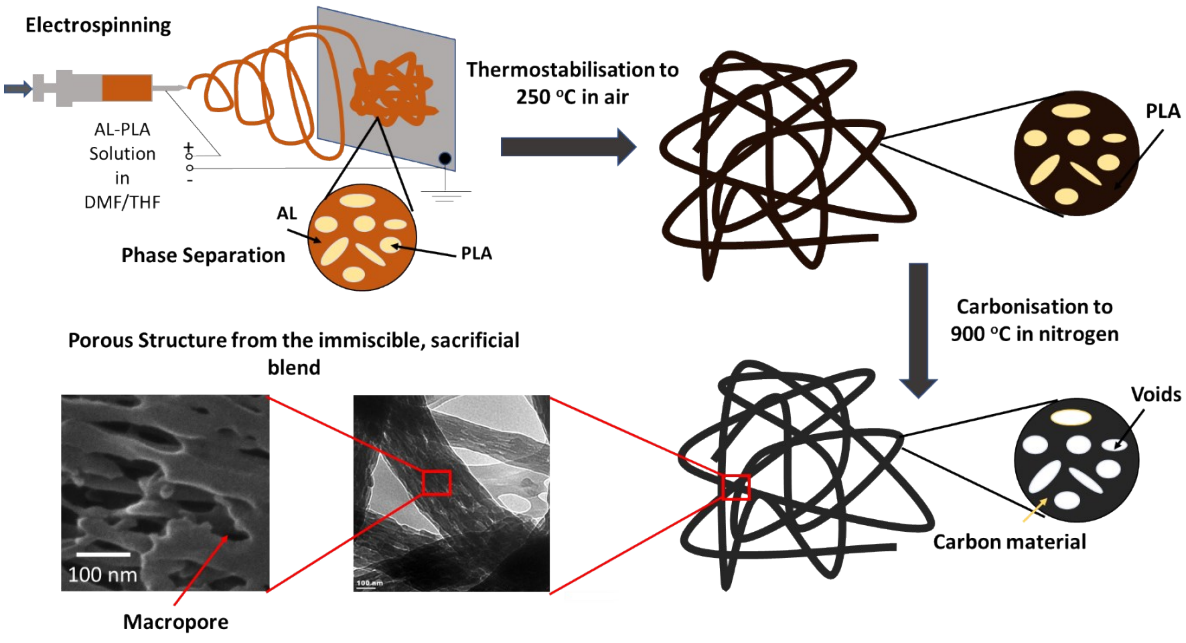
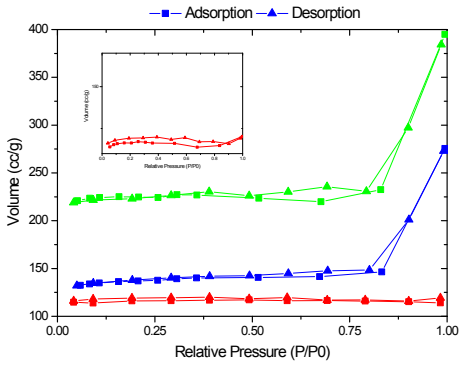


Figure S 2: Schematics of the synthesis of the AL-PLA CNF. The images were obtained by Helium Ion Microscopy (left) and TEM (right).

(a)



(b)

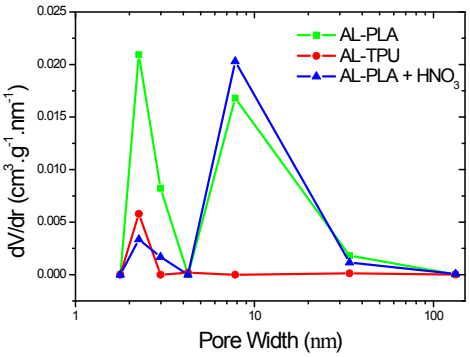
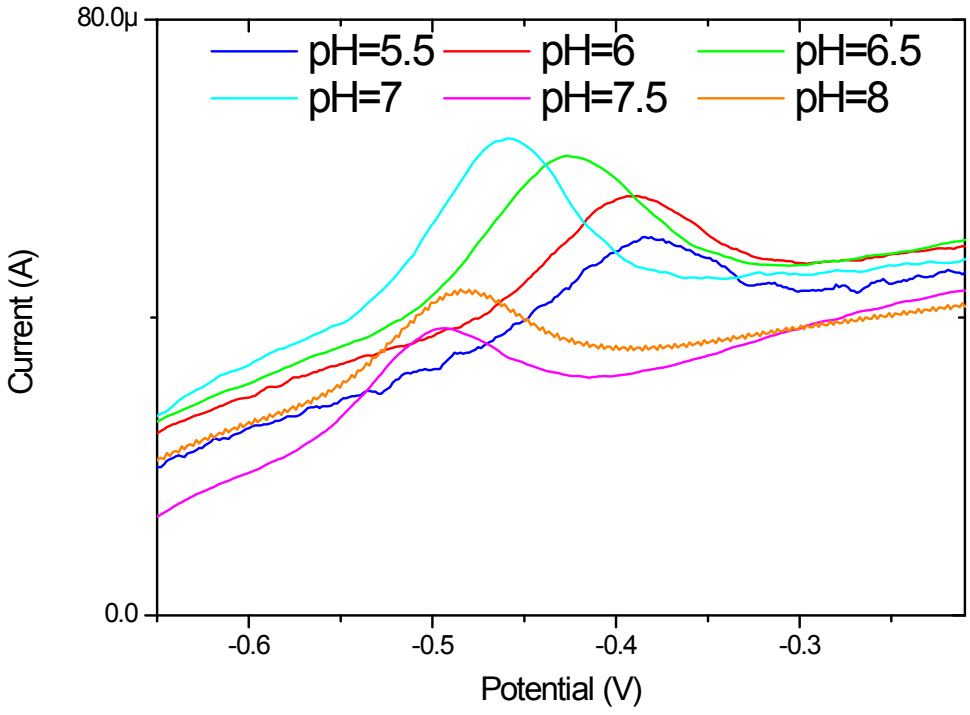


Figure S 3: N_2 adsorption-desorption isotherm (a) and Desorption pore width distribution (b) of (green) AL-PLA derived CnF; (red) AL-TPU derived CnF and (blue) AL-PLA derived CnF, treated subsequently with nitric acid



(a)

(b)

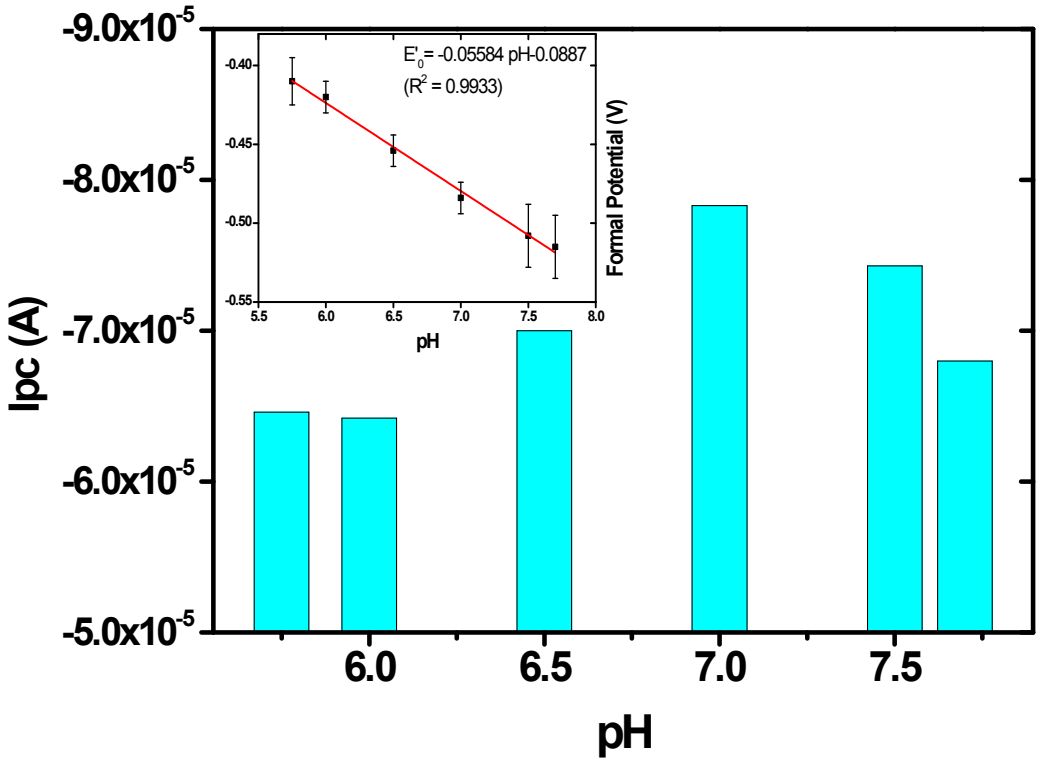


Figure S 4: a) CV of porous AL-PLA CnF at 50mV.s^{-1}, in 0.05 mol.L^{-1} N_2 saturated PBS at various pH values. b) Evolution of the cathodic peak intensity with varying pH. Inset of b) Plot of $E^{0'}$ vs pH.

Table S 3 : XPS Analysis Results on AL-PLA and AL-PLA with HNO3 treatment.

	Atomic Content			Species vs Carbon ratio			
	C	O	Au	C-C	C-O	C=O	O-C=O
AL-PLA	91.2	5.4	1.5	0.64	0.19	0.04	0.05
AL-PLA at 90 °C	92.2	5.8	0.1	0.66	0.20	0.03	0.05
AL-PLA with HNO_3 Treatment at 90 °C	66.2	25.9	0.5	0.55	0.21	0.09	0.10

Annexe 1 : Determination of the Miscibility of AL with PLA and TPU

Gibbs free energy can be determined to evaluate miscibility of AL with TPU and PLA, as we reported previously [1]. A negative Gibbs free energy of mixing is necessary for polymers to be miscible as follows:

$$\Delta G_m = \Delta H_m - T\Delta S_m; \Delta G_m < 0 \qquad (S1)$$

For a two components system ΔH_m can be expressed [2] as a function of the volume fraction φ_1 and φ_2 of the each components:

$$\Delta H_m = (\delta_1 - \delta_2)^2 \varphi_1 \varphi_2 V_S \qquad (S2)$$

With V_S, Volume of the system and δ_1 and δ_2 the respective solubility parameters of the polymers, expressed in in $(MJ.m^{-3})^{1/2}$ or $(MPa)^{1/2}$.

Given the second principle of thermodynamics, the entropy can only increased during mixing so $\Delta S_m > 0$. The magnitude of ΔS_m is governed by the specific interaction between the specific polymers and by their molecular weight. High molecular weight polymers tend to present a low mixing entropy. So $\Delta S_m \approx 0$. Therefore, the condition for polymer miscibility with $\Delta G_m < 0$ is $\Delta H_m \approx 0$. This condition is found to be true when the solubility parameters of the polymers are close in value.

Solubility parameters can be estimated using the group contribution method, which was introduced by Small. [3] Each functional group has a contribution F_i to the total molar attraction of the polymer. F_i is defined as a function of the cohesive energy E_i and the molar volume V_i of a functional group by the equation,

$$F_i = (E_i V_i)^{1/2} \qquad (S3)$$

With E_i in $J.mol^{-1}$, V_i in $m^3.mol^{-1}$ and F_i in $(J.m^3)^{1/2}.mol^{-1}$.

The solubility parameter δ of a polymer is calculated as follows:

$$\delta = \frac{\rho \sum n_i F_i}{M} \qquad (S4)$$

With ρ and M density of the polymer in $kg.m^{-3}$ and molar mass in $kg.mol^{-1}$ of a repeat unit, respectively and $\sum n_i F_i$ the sum of all the molar group contribution for a repeat unit, in $(J.m^3)^{1/2}.mol^{-1}$. [2]

The repeat units for AL, TPU and PLA can be found in Figure S1. The structure of AL repeat units is described in [1]. As a hardwood lignin, AL presents an equal distribution between Synapyl and Guaiacyl groups with a majority of β-O-4 linkages. Details of the group molar attraction constant calculation can be found in Table S1.

The solubility of AL, PLA and TPU and the mixing enthalpy were calculated using (S1) and (S2) and are displayed in Table S2. The respective enthalpy of mixing of PLA and TPU blends show strong miscibility between TPU and AL while PLA is immiscible with the lignin.

References:

1. A. Beaucamp, Y. Wang, M. Culebras and M. N. Collins, *Green Chemistry*, 2019, **21**, 5063-5072.
2. J. E. Mark, *Physical properties of polymers handbook*, Springer, 2007.
3. P. A. Small, *Journal of Applied Chemistry*, 1953, **3**, 71-80.