

**lignin nanoparticles**

Vasileios Tsampallas<sup>1,2</sup>, Maria Kaliva<sup>1,2</sup>, Anastaisa Tzerainidi<sup>1,2</sup>, Evangelia Vassilaki<sup>1,2,3</sup>, Min Ge<sup>3</sup>, Svitlana Filonenko<sup>3</sup>, George Petekidis<sup>1,2</sup>, Markus Antonietti<sup>3</sup>, Maria Vamvakaki<sup>1,2</sup>



<sup>1</sup>Institute of Electronic Structure and Laser, FORTH, Heraklion, Crete, Greece

<sup>2</sup>Department of Materials Science and Engineering, University of Crete, Heraklion, Crete, Greece

<sup>3</sup>Max-Planck Institute of Colloids and Interfaces, Department of Colloid Chemistry, Potsdam, Germany

### Lignin

New J. Chem. 2021, 45, 6986-7013.

p-Coumaryl alcohol    Coniferyl alcohol    Synapyl alcohol

### Applications of Lignin NPs

Int. J. Mol. Sci. 2022, 23, 7254

### Aim of the Work

Conventional methods: Lignin without treatment → Inhomogeneous interactions → Polydisperse LNPs

In this work: Lignin after solvent extraction → Homogeneous interactions → Monodisperse LNPs

Small 2022, 18, 2200671

**Preparation of monodisperse lignin nanoparticles (LNPs) by lignin fractionation**

+

**Molecular and chemical characterization of lignin Fractions**

+

**Size Tuning of LNPs**

### Step 1: Fractionation of Lignin

#### Solvent extraction

Enzymatic hydrolysis lignin (EHL) → EtOH → Ethanol Fraction F1 + Insoluble Fraction → Aceton → Aceton Fraction F2 + Insoluble Fraction (F<sub>insol</sub>)

### Molecular and Chemical Characterization of the EHL Fractions

EHL:  $M_n = 1400$  g/mol, PD = 2.09

$F_{ACETONE}$ :  $M_n = 1300$  g/mol, PD 1.71

$F_{EtOH}$ :  $M_n = 750$  g/mol, PD 1.41

Elution Time (min)

#### Functional groups content

	Phenolic-OH	Aliphatic-OH	COOH	Total OH+COOH
$F_{ACETONE}$	1.76	0.47	0.015	3.99
$F_{EtOH}$	2.28	0.68	0.012	6.04

$F_{ACETONE}$ : most hydrophobic fraction

#### <sup>31</sup>P NMR spectra

### Step 2: Formation of Lignin NPs

#### Solvent/Antisolvent Self Assembly

1. Lignin concentration    2. Addition rate

Remove the good solvent → LNPs

### Monodisperse NPs using $F_{ACETONE}$

Addition rate 0,62ml/min

$F_{EtOH}$  → Polydisperse LNPs

$F_{ACETONE}$  → Highly monodisperse LNPs

Concentration	Diameter (nm)	PDI
0,5 mg/ml	509 ± 213	0,17
1 mg/ml	551 ± 93	0.028
2 mg/ml	665 ± 62	0.09
4 mg/ml	780 ± 101	0.023
8 mg/ml	1364 ± 207	0.023

Tunable size by varying the Lignin Concentration

### Effect of $F_{ACETONE}$ Addition Rate on LNPs Size During Self-Assembly

Addition Rate	Diameter (nm)
0.2 ml/min	534 ± 54
3.75 ml/min	356 ± 39
8 ml/min	249 ± 34
20 ml/min	163 ± 29
instant	99 ± 20

Control Size via the Addition Rate

### Synthesis of Bamboo Lignin NPs

Diameter 40 ± 30 nm

Particles obtained without fractionation  
Small, yet polydisperse NPs

### Acknowledgments

The research project was financed by the EU HORIZON-WIDERA-2021-ACCESS-03-01-Twinning project "Advancing Research & Innovation of FORTH in Green Soft Matter" FORGREENSOFT, (GA No: 101078989).