processes

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Article

Pd/Au based catalysts immobilization in polymeric nanofibrous membranes via electrospinning for the selective oxidation of 5-hydroxymethylfurfural

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Electrospinning for PAN-*based membrane preparation*

PAN-based electrospun membranes were produced by electrospinning polymeric solutions of PAN dissolved in DMF at a concentration of 8 % w/v and containing the proper amount of inorganic powders (either TiO_2 or TiO_2 supported metal nanoparticles). Each formulation was prepared as follows: first the proper amount of powder was suspended in DMF and vigorously stirred for about 30 minutes, then PAN powder was added to the suspension that was kept under stirring for about 1 hour to complete PAN dissolution. Table S1 reports the amounts of both PAN and inorganic component employed to prepare each formulation, together with the corresponding electrospinning processing conditions that were optimized to have a stable jet during the process. Electrospinning was carried out at ambient temperature (19-22°C) and relative humidity in the range 40-45%.

Table S1. Amounts of PAN and inorganic fraction used to prepare the suspension in DMF and electrospinning processing conditions.

Membrane	polymer (g)	Metal/TiO_2 (g)	Metal content (%)	Voltage (kV)	Flow rate (ml/h)	Needle-collector distance (cm)	Average fiber diameter (nm)	BET specific surface area (m^2/g)
PAN	0,8	-	0	19	1,2	20	260±60	11
PAN+TiO_2	0,8	1,6	0	23	1,2	20	220±60	48
PAN+Au/TiO_2	0,8	1,6	1	23	0,8	20	240±50	46
PAN+AuPd/TiO_2	0,8	1,6	1	23	1,2	20	270±60	46

Electrospinning for Nylon- based membrane preparation

The starting NP colloidal suspension used for Nylon 6,6 based membranes had a metal content of $9.2x10^{-2}$ wt% and had to be reduced in volume prior addressing either support onto titania or dispersion into polymeric solution for direct electrospinning.

Nylon 6,6 based electrospun membranes were prepared by adding a suitable amount (Table S2) of dried titania or dried AuPd/TiO_2 to Formic Acid (FA). Solids were dried in the oven before use in order to remove adsorbed water, making sure that no additional water was added to the system. Once the TiO_2 or AuPd/TiO_2 was suspended, Nylon was added (13 wt% polymer/[solvent+polymer]) and stirred until complete dissolution. Finally, $CHCl_3$ was added and the system gently stirred prior undergoing electrospinning. Solvent system was FA:$CHCl_3$=60:40, while Nyl:solvent=13:87.

Table S2. Amount of Nylon and inorganic fraction used to prepare FA/$CHCl_3$ suspensions.

Membrane	Nyl (g)	TiO_2 (g)	Metal content (%)	Colloidal suspension (g)	Concentrated FA suspension (g)	Additional FA (g)	$CHCl_3$ (g)
Nyl	1,30	-	0	-	-	5,22	3,48
Nyl+TiO_2	1,30	0,60	0	-	-	5,22	3,48
Nyl+AuPd/TiO_2	1,30	0,61	1	20,64[a)]	-	5,22	3,48
Nyl+AuPd	1,30	-	1	19,98[b)]	3,10	2,12	3,48
Nyl+AuPd+TiO_2	1,30	0,60	1	20,32 [b)]	2,30	2,92	3,48

a) Amount of colloidal suspension used for impregnating 0.06 g TiO_2.

b) Amount of colloidal suspension that, after volume reduction and solvent switching from water to FA, was used to dissolve Nylon.

When NP were suspended directly in the polymeric solutions without titania as a support, the colloidal suspension had to be concentrated (Table S2) and then washed with FA by centrifugation using 50 kDa Amicon Ultra filters (Millipore) in order to eliminate the maximum amount of water from the system. Water tolerance for avoiding Nyl precipitation was evaluated in 17%. The volume of colloidal suspension that would be concentrated was calculated to have total metal loading in the membranes at 1 wt% related to the total mass, assuming complete solvent evaporation.

The centrifugation process was carried out using 6 filters for an amount of approximately 28 mL of colloidal suspension, and centrifugation for 20 minutes at 1500 rpm was carried out after each step. The wash of the solution was attained by adding 4 g of FA per filter.

The evolution of the hydrodynamic diameter at every centrifugation step was follow by DLS analysis (Figure S1) and at the end of the process the real size of the nanoparticles was checked by XRD measurement (Figure S2).

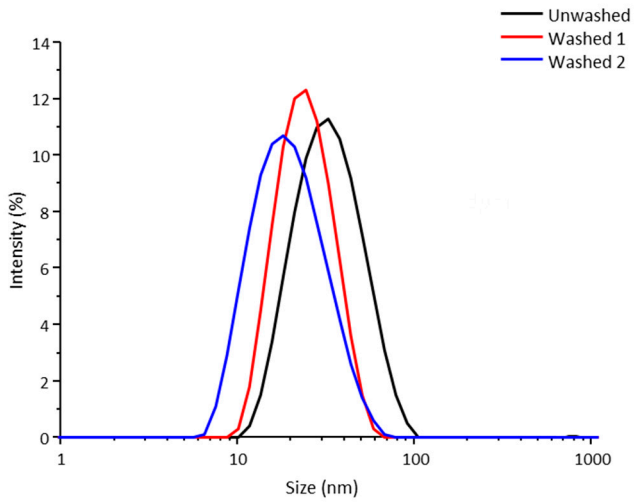

Figure S1. DLS analyses of NPs suspensions: as synthesized (black line), after 1 washing step (red line), after 2 washing steps (blue line).

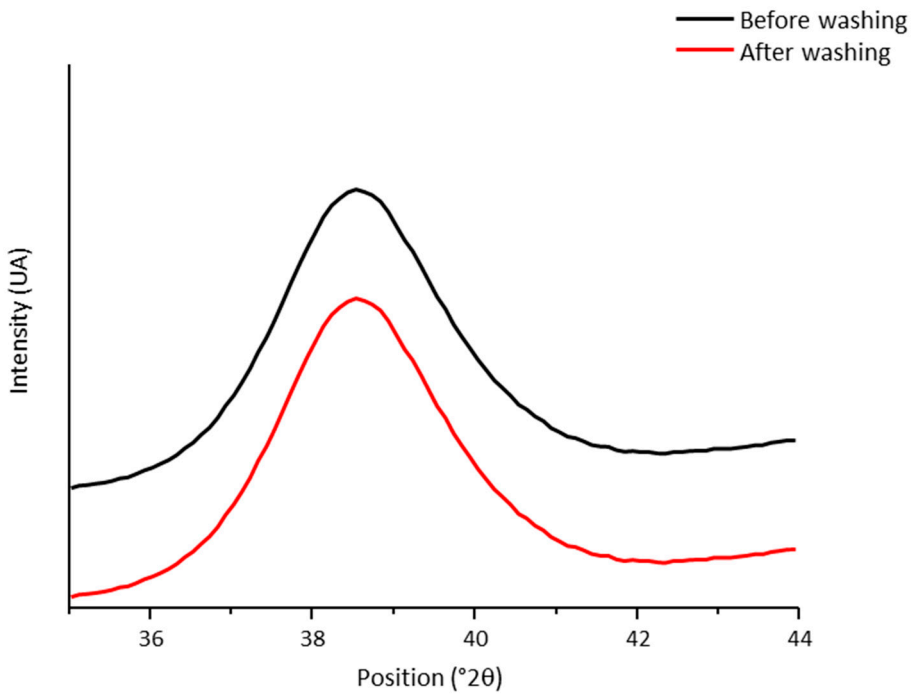

Figure S2. XRD analyses of dried NPs suspensions: before and after washing with formic acid (black and red line, respectively).

The right amount of formic acid was then added to reach the volume of solution needed to have the ratio of solvent expected (FA:$CHCl_3$=60:40). When the case, TiO_2 was added to the concentrated solution of nanoparticles and stirred to be suspended. Once TiO_2 was suspended, the Nyl was added and stirred until complete dissolution. Finally, the $CHCl_3$ was added.

Table S3. Electrospinning processing conditions and average diameter obtained.

Membrane	**Voltage (kV)**	**Flow rate (ml/h)**	**Needle-collector distance (cm)**
Nyl	19	0,20	15
Nyl+TiO_2	19	0,25	15
Nyl+AuPd/TiO_2	19	0,25	15
Nyl+AuPd	18	0,20	15
Nyl+AuPd+TiO_2	19	0,25	15

Nanoparticle preparation and characterization

Table S4. Characteristic of prepared catalysts and average diameters of metallic dimension estimated from XRD and TEM analysis. .

Sample	**NPs ∅ XRD (nm)**	**NPs ∅ TEM (nm)**	**Surface Area (m^2/g)**	**Notes**
Au NPs	4.0	5.0	-	Water suspension

AuPd NPs	4.5	4.0	-	Water suspension
AuPd NPs-FA	4.5	4.0	-	Suspended in formic acid
TiO_2	-	-	82	Commercial powder
Au/TiO_2	5.5	5.3	80	Supported catalyst
$AuPd/TiO_2$	6.5	6.0	79	Supported catalyst

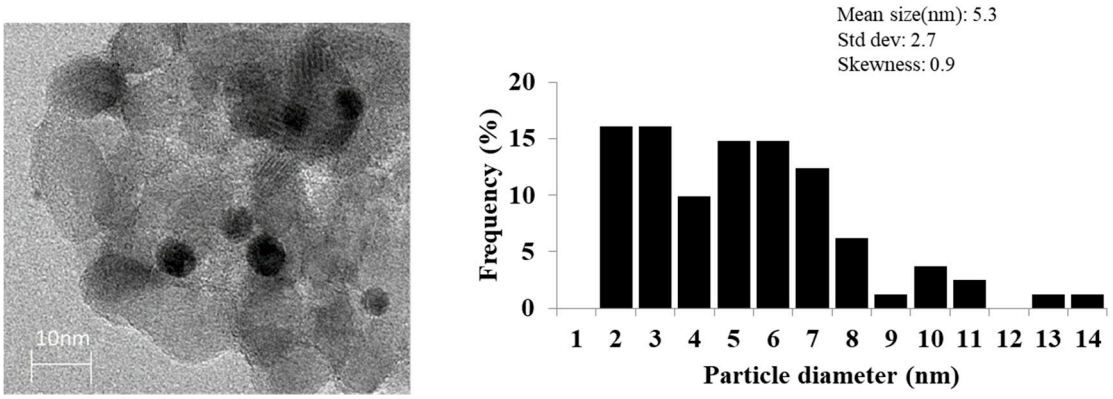

Figure S3. Representative TEM images of Au/TiO_2 supported on TiO_2 and their size distribution histograms.

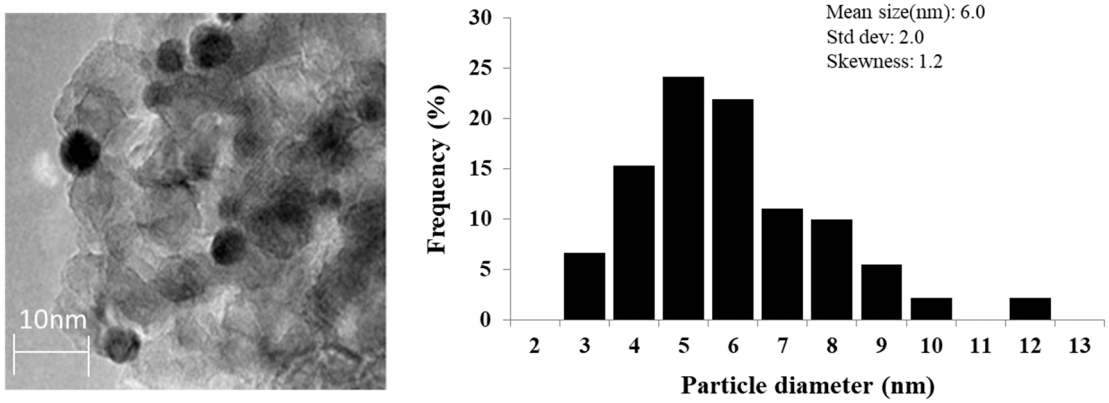

Figure S4. Representative TEM images of $AuPd/TiO_2$ supported on TiO_2 and their size distribution histograms.

PAN-based membranes

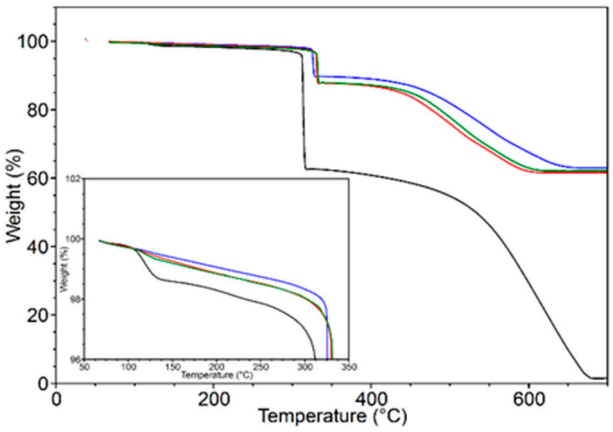

Figure S5. TGA curves of PAN-based membranes: PAN (black), PAN+TiO_2 (blue), PAN+Au/TiO_2 (green) and PAN+AuPd/TiO_2 (red).

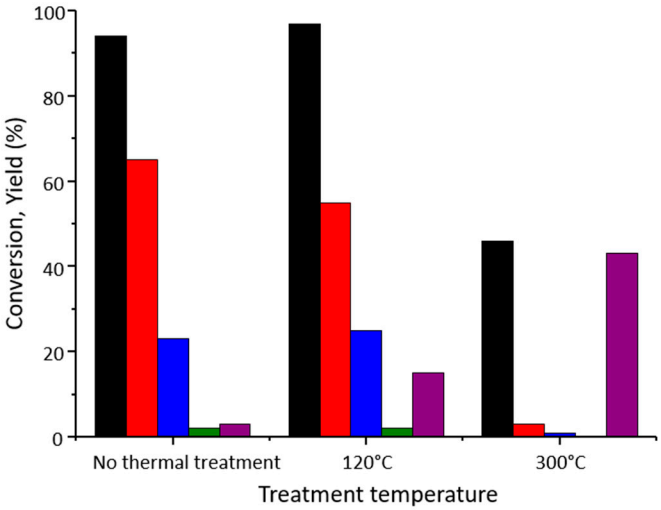

Figure S6. Effect of thermal treatments on PAN+AuPd/TiO_2 membranes catalytic activity. Operative conditions: 70°C, O_2 pressure 10bar, 25mL water, HMF concentration 18mM, HMF:NaOH molar ratio 1:2, HMF:(Au+Pd) molar ratio 100:1. Legend: ▪ HMF Conversion, ▪ HMFCA yield, ▪ FFCA yield, ▪ FDCA yield, ▪ C-LOSS.

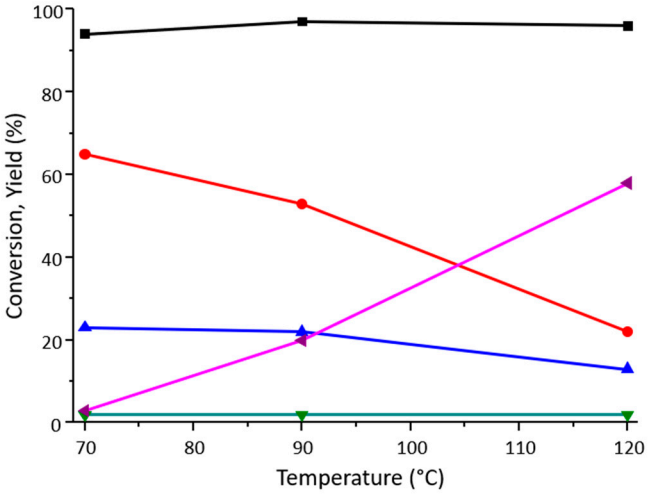

Figure S7. Reaction temperature effect on the catalytic performance of PAN+AuPd/TiO_2 sample. Operative conditions: O_2 pressure 10bar, 25mL water, HMF concentration 18mM, HMF:NaOH molar ratio 1:2, HMF:(Au+Pd) molar ratio 100:1. Legend: ▪ HMF Conversion, • HMFCA yield, ▲ FFCA yield, ▼ FDCA yield, ◂ C-LOSS.

Nylon-based membranes

Figure 8. reports the first DSC heating scans of PAN and Nylon membranes while Figure S8B reports the second DSC heating scans after quench. In the first heating scan PAN displays at 108 °C a step change of thermal capacity ascribable to the glass transition temperature, possibly overlapped with the endothermal wide peak of residual solvent evaporation. The presence of residual DMF in the electrospun fibers was also confirmed by TGA analysis. The same value of glass transition can be measured in the second heating scan.

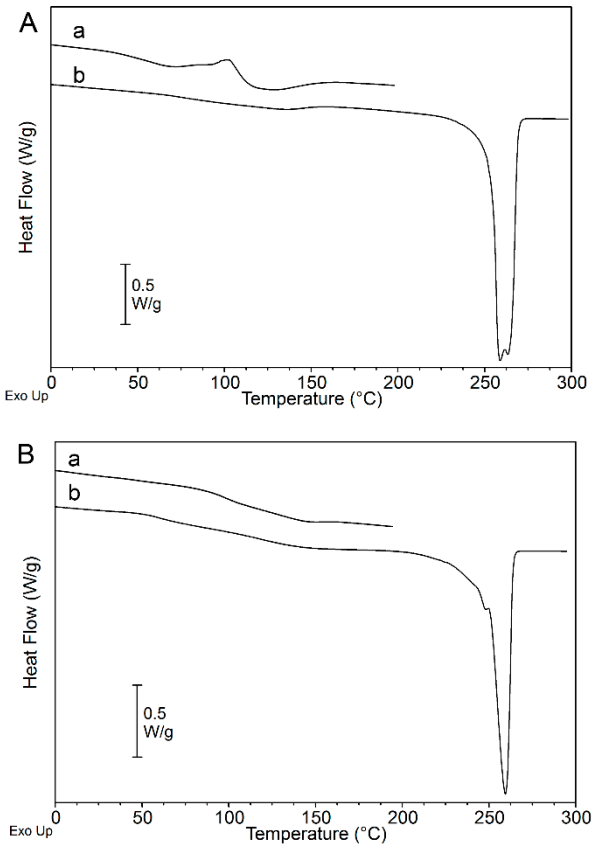

Figure S8. A) DSC first heating scan and B) second heating scan scan after quench of PAN (a) and Nylon (b).

All Nyl membranes were characterized by TGA to obtain an evaluation of the actual inorganic content. In Table S5 the evaluation of the residual inorganic fraction recovered at the end of TGA run is reported, showing that the fibers composition well compares with the initial feeding. This means that the solution/suspension stability is enough to provide a homogenous composition of the fluid reaching the needle throughout the whole process, with no precipitation of Titania from the liquid phase.

As far as DSC measurements are concerned, the present data demonstrate the nucleation ability of the inorganic particles added to the polymer, irrespective of the particles dimension and amount: indeed, the fibers production induce an increase in the crystal content. Another important observation is the unusually high glass transition, that might stem for the higher crystal content, but also from the interaction of the macromolecules with the inorganic particles, even in content as low as 1 %wt, that are able to hamper molecular chain mobility thus increasing the T_g.

Table S5. Thermal characterization results for Nyl based nanofibers.

Membrane	Expected solid residue (%)	TGA residue (%)	T_g (°C)	T_m [a)] (°C)	H_m (J/g)	H_m* [b)] (J/g_{NYL})
Nyl	0	n.d.	66	264	81,6	81,6
Nyl+TiO_2	31,5	29,1	77	268	58,9	85,9
Nyl+AuPd/TiO_2	31,9	32,2	66	267 (262)	59.0	86.6
Nyl+AuPd	1	1,1	77	264 (254)	89,7	90,6
Nyl+AuPd+TiO_2	32,2	30,7	77	266	60,3	89,3

[a)] Figure in brackets represent the shoulder peak position, when present.

[b)] ΔH_m* represent the melting enthalpy normalized with respect to the actual NYL content in the fibers.

Catalytic activity of Nyl-based membranes

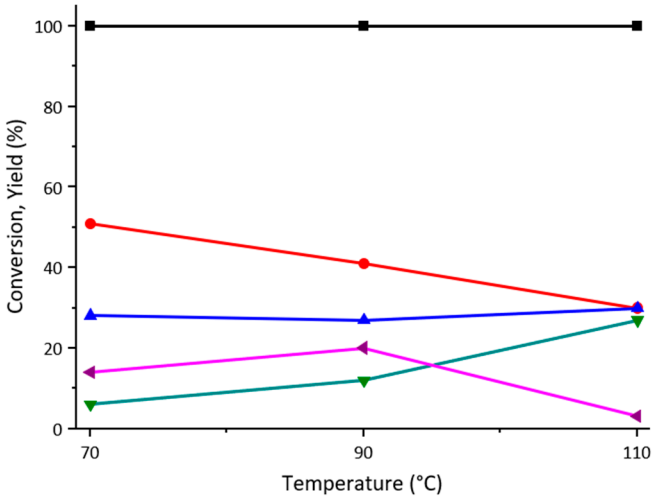

Figure S9. Effect of reaction temperature on NYL+AuPd/TiO_2 membranes catalytic activity. Operative conditions: 70°C, O_2 pressure 10bar, 25mL water, HMF concentration 18mM, HMF:NaOH molar ratio 1:2, HMF:(Au+Pd) molar ratio 100:1. Legend: ▪ HMF Conversion, • HMFCA yield, ▲ FFCA yield, ▼ FDCA yield, ◂ C-LOSS.