Supporting information

Combination of ball-milling and non thermal atmospheric plasma as physical treatments for the saccharification of microcrystalline cellulose

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Chemicals

Microcrystalline cellulose (MCC) PH AVICEL 105 was kindly provided by FMC Biopolymer. This cellulose has a DP of 200, a particle size lower than 38 μm and a water content of 5 wt%. pH (10g/L, 25°C) of this microcrystalline cellulose is 5.5.

Amberlyst 35 (wet) used in this work was kindly provided by Rohm & Hass. A35 has a macroreticular pore structure (surface area = 50 m^2/g) with an acid sulfonic content of 5.2 mmol/g.

Measurements of the degree of polymerization (DP) of cellulose

DP measurements were performed by viscosimetry analyses according to the NF G 06-037 norm. Typically, 0.061g of cellulose was dissolved in 12.5 mL of cupriethylenediamine and 12.5 mL of water. The solution was stirred for 2 hours at room temperature. Viscosity data were determined in a UBBELOHDE thermostated capillary tube viscosimeter (25°C). Relation between the viscosity and DP is given in the NF G 06-037 norm using normalized abacus.

For cello-oligomers soluble in DMSO, the DP can be also measured by ^{1}H NMR in d6-DMSO by measuring the ratio (integration) between signals of the anomeric positions ($\alpha + \beta$) and those of the cello-oligomer backbone.

Analytical methods:

Analysis of glucose was performed on a Shimadzu Prominence LC equipped with a degasser DGU-20A3, a pump system (LC-20AQ), a thermostated autosamplor SIL-20AC (samples were maintained at 15°C) and an oven CTO-20AC maintained at 40°C. Glucose was separated on a Shodex KS-802 column, using water as eluent, and quantified by a refractor indice detector

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 DPX. Chemical shift are expressed in ppm relative to Me_4Si and spectra were collected in d_6-DMSO. IR spectra were recorded on a FT-IR Perkin Elmer (spectrum one) using ATR technology. Thermogravimetric analysis (TGA) was carried out using a thermobalance Q600 DTA instrument. Measurements were collected by heating the sample from 25 to 600°C with a ramp of 5°C min^{-1} and an air flow of 100 mL min^{-1}. XRD patterns were recorded on a Bruker D5005 Bragg–Brentano (θ-θ) diffractometer operated with a copper tube powered at 40 kV and 40 mA ($Cu_{K\alpha1}$ = 1.54060 A° and $Cu_{K\alpha2}$ = 1.54443 A°). Scattering intensities were measured over an angular range of $10° < 2\theta < 50°$ with a step size (2θ) of 0.1° and a step time of 2 s.

Decrystallization of cellulose by ball-milling

Typically, 2 g of MCC was introduced into a 125 mm diameter zirconium bowl, and the milling was performed at 200 rpm with 25 zirconium balls (10 mm diameter) PM100 from RETSCH. In agreement with previous reports, 48 h of ball-milling were required to ensure the decrystallization of MCC.

Description of non thermal atmospheric plasma

A non thermal atmospheric plasma is a highly energetic ionized gas. The application of a high voltage between two electrodes leads to the formation of an electric field, in which electrons are accelerated and collides with molecules of the gas phase creating electronic filaments, also called streamers. It results in the formation of excited species, such as electrons, radicals, ions, excited molecules or atoms. When generated in air, the plasma produces firstly highly oxidative intermediates such as $O^\bullet$, $OH^\bullet$, $N^\bullet$ due to the collision of electrons and gas molecules and secondary products such as NO_x and O_3. These reactive intermediates are very convenient for the surface modification or functionalization.

The plasma reactor used for this study is a dielectric barrier discharge (DBD) type and is formed by a box made of glass plates (4mm thick) and is described elsewhere (ref 9 in the manuscript). One electrode is a copper film fixed outside on the top of the box. The other electrode is a copper grid placed inside the box and covered by a thin glass plate (1 mm thick) in order to avoid the direct contact of the mesh with the material. The dielectric barriers are then formed by the glass wall of the box and the thin glass plate. The gap between the glass wall and the thin glass plate is 2mm.

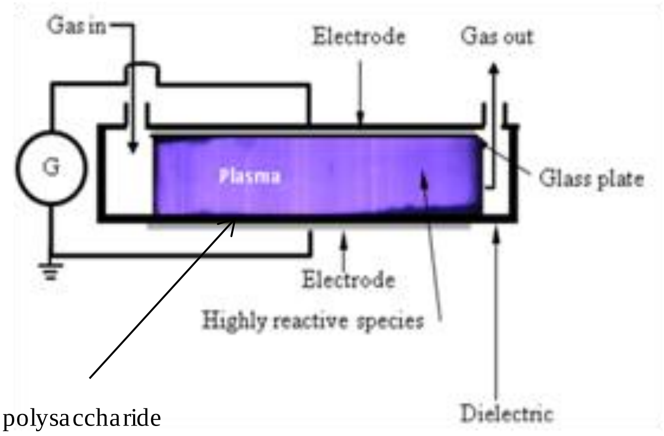

***Figure S1**: Schematic illustration of the NTAP reactor*

The electrodes are connected to a bi-polar pulse generator (A2E Technologies-Enertronic). The electrical parameters are measured via two high voltage probes (Lecroy, PPE20KV-CC) and one current probe (Stangenes Industry 60MHz) connected to a digital oscilloscope (Lecroy WaveSurfer 64Xs-A, 600MHz). The experiments were carried out under a humid air flow ($30 mL.min^{-1}$, 1.5% mol H_2O) at room temperature. The plasma treatment duration was comprised between 30 to 180 min. All the treatments were performed at a constant frequency of 2000 Hz. The discharge power P (in W) was kept constant (26W) and was calculated from the following equation:

$$P = f\int_{t=0}^{\frac{1}{f}} U_t \times I_t \times dt$$

Where U_t is the applied voltage (V), I_t the current (A), t the time (s) and f the frequency (Hz). Note that treating 1g of cellulose for 1h at 26W corresponds to an energy expense of 93.6 KJ

Dissolution of BM/NTAP cellulose in DMSO

Typically 150 mg of BM/NTAP treated cellulose were added to 30 ml of DMSO and stirred for 2 hours at 60 °C. Then the mixture was cooled to room temperature, centrifugated and the DMSO solution containing the cello-oligomers was removed. The remaining insoluble cellulose was washed two times with 2 ml of acetone and 2 ml of ethanol. After drying overnight at 60 °C, the recovered insoluble cellulose was weighted. The percent of cellulose dissolved in DMSO was thus obtained as follow:

% dissolution = (150 mg – quantity of remaining cellulose in DMSO) x100

The maximum of solubility of cello-oligomers in DMSO (27 g/L) was determined by saturating 2 mL of DMSO with cello-oligomers (DP=36).

Catalytic hydrolysis of BM/NTAP cellulose over A35 cation exchange resin

Hydrolysis of BM/NTAP cellulose was performed in an automated multimode microwave oven MicroSynth from Milestone s.r.l. (Italy). This oven operates at 2.45 GHz and temperature is controlled by a fiberoptic sensor. Temperature was monitored by insertion of a calibrated fiberoptic sensor in the reaction mixture while stirring properly. The maximum power input could be adjusted between 0 and 1000 Watt. Under microwave heating, the internal temperature of the reaction vessel reached the reaction set-points in 5 min, and was maintained at temperature ± 5°C using a power compensation feedback control.

In a typical procedure, BM/NTAP cellulose (0.2 g), A35 (0.080 g) and 3 mL of H_2O were introduced into a microwave reactor, sealed and heated with a magnetic stirring bar at the desired temperature. At the end of the reaction, the microwave heating was stopped and the reaction vessel was cooled down to room temperature. The reaction mixture was then centrifugated and the recovered aqueous solution was analyzed by HPLC.

Decrystallization of MCC in [BMIM]OAc

100g of ionic liquid ([BMIm]AcO) was first heated at 80 °C in a 250 mL glass reaction vessel with a magnetic stirring bar prior to add 5 g of MCC. After 3 h, MCC was completely dissolved. At this stage, the hot solution was poured into 500 mL of 95% ethanol with rapid agitation to induce the precipitation of dissolved cellulose. The resulting slurry was filtered and the recovered cellulose was redispersed in 500 mL of additional ethanol. Filtration and redispersion steps were repeated for three times and the filter cake was dried under vacuum at 40 °C to yield a free-flowing powder product (See Table 1 in the manuscript).

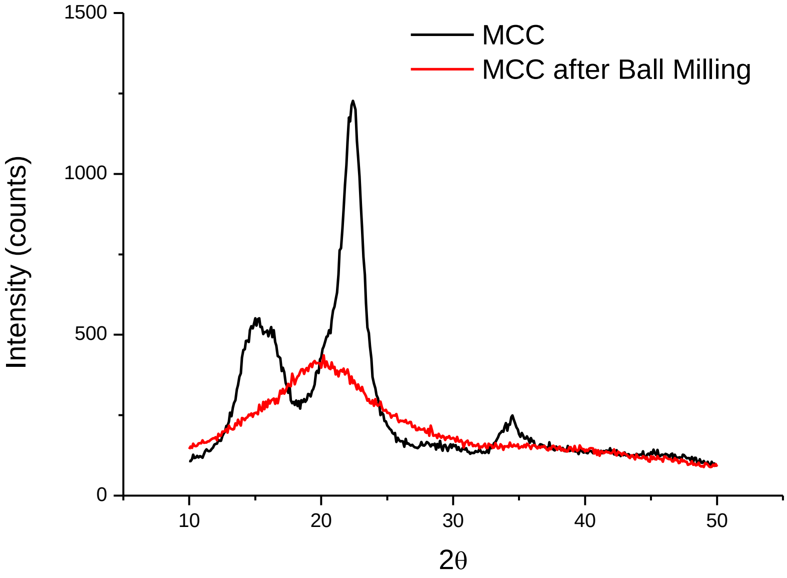

Fig. S2. XRD analysis of MCC and ball-milled cellulose

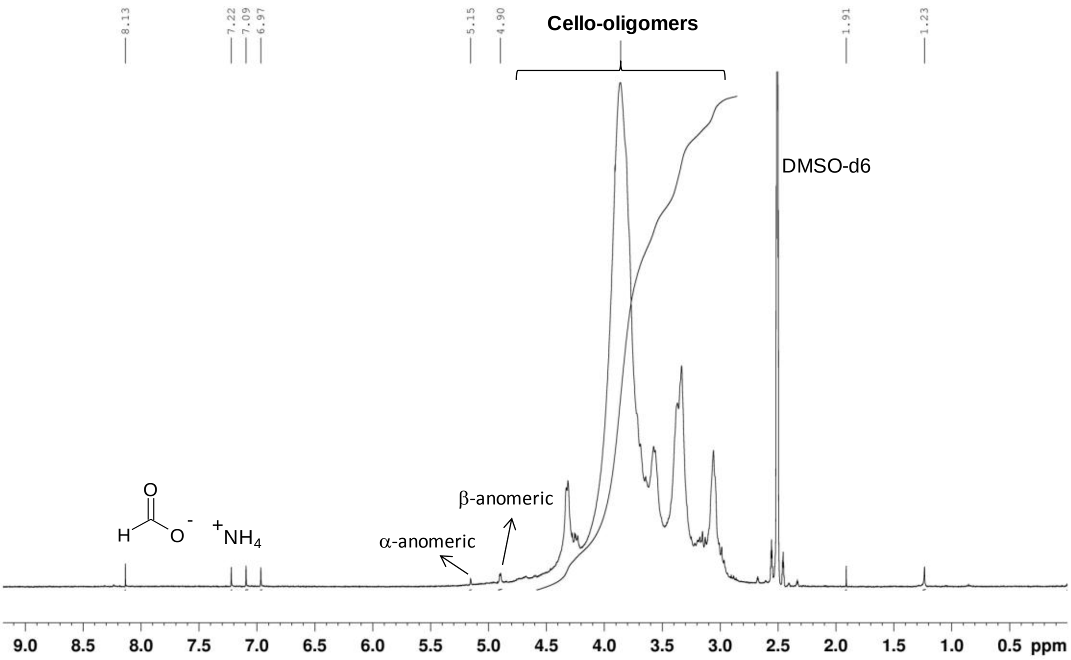

Fig. S3. ^{1}H NMR of cello-oligomers recovered after 60 min of NTAP treatment of ball-milled cellulose (recorded in d6-DMSO, 25°C)

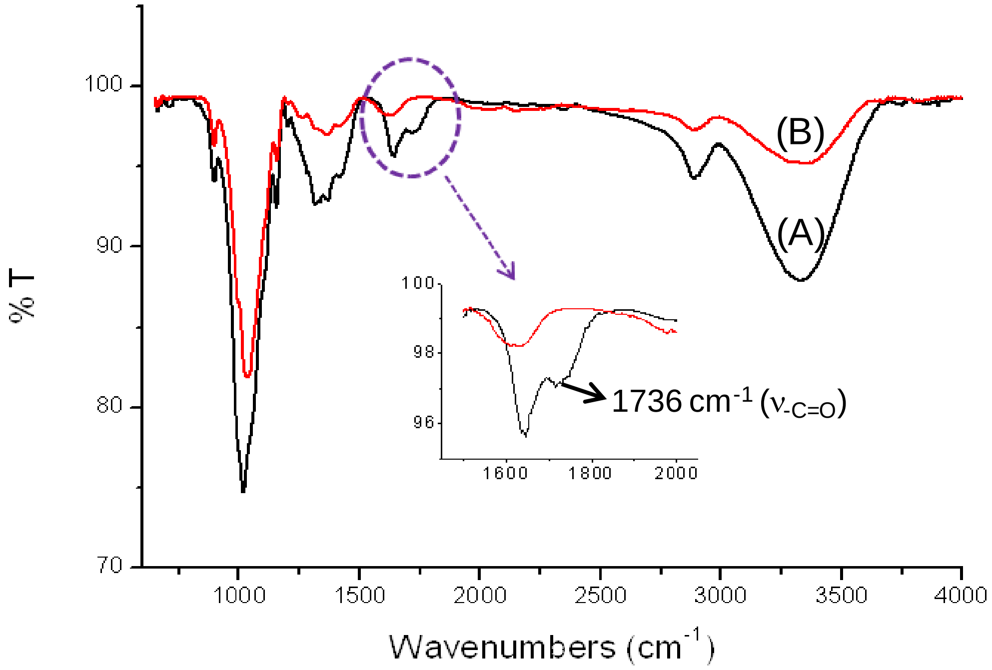

Fig. S4. IR spectra of ball-milled cellulose after 60 min of NTAP treatment (A) as collected and (B) after washing with cold water

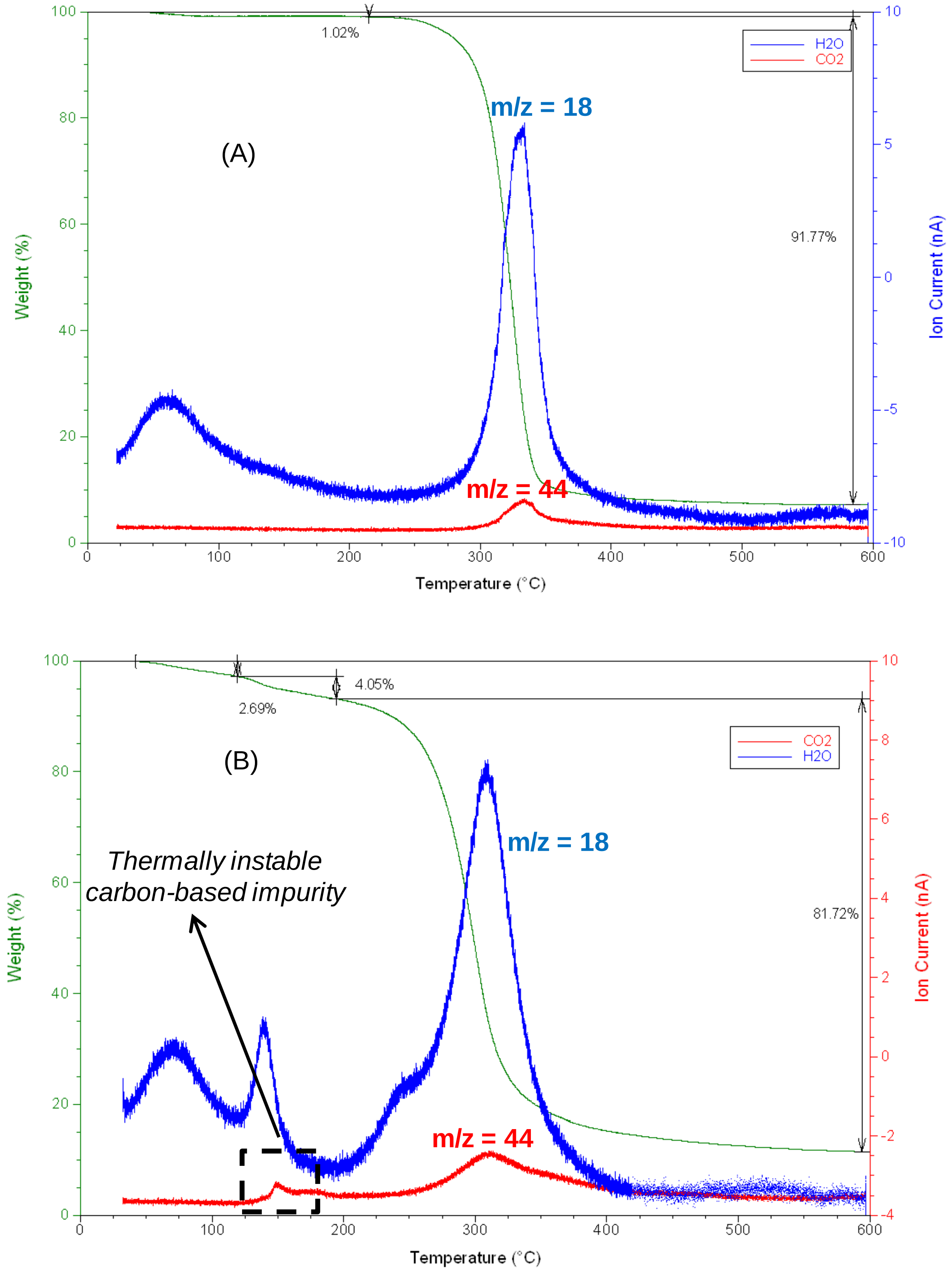

Fig S5 : TGA/MS analysis of (A) MCC and (B) ball-milled cellulose after 60 min of NTAP treatment