DESIGN OF BIO-BASED CARBONACEOUS FIBROUS STRUCTURES AS CATALYSTS IN FUEL CELLS

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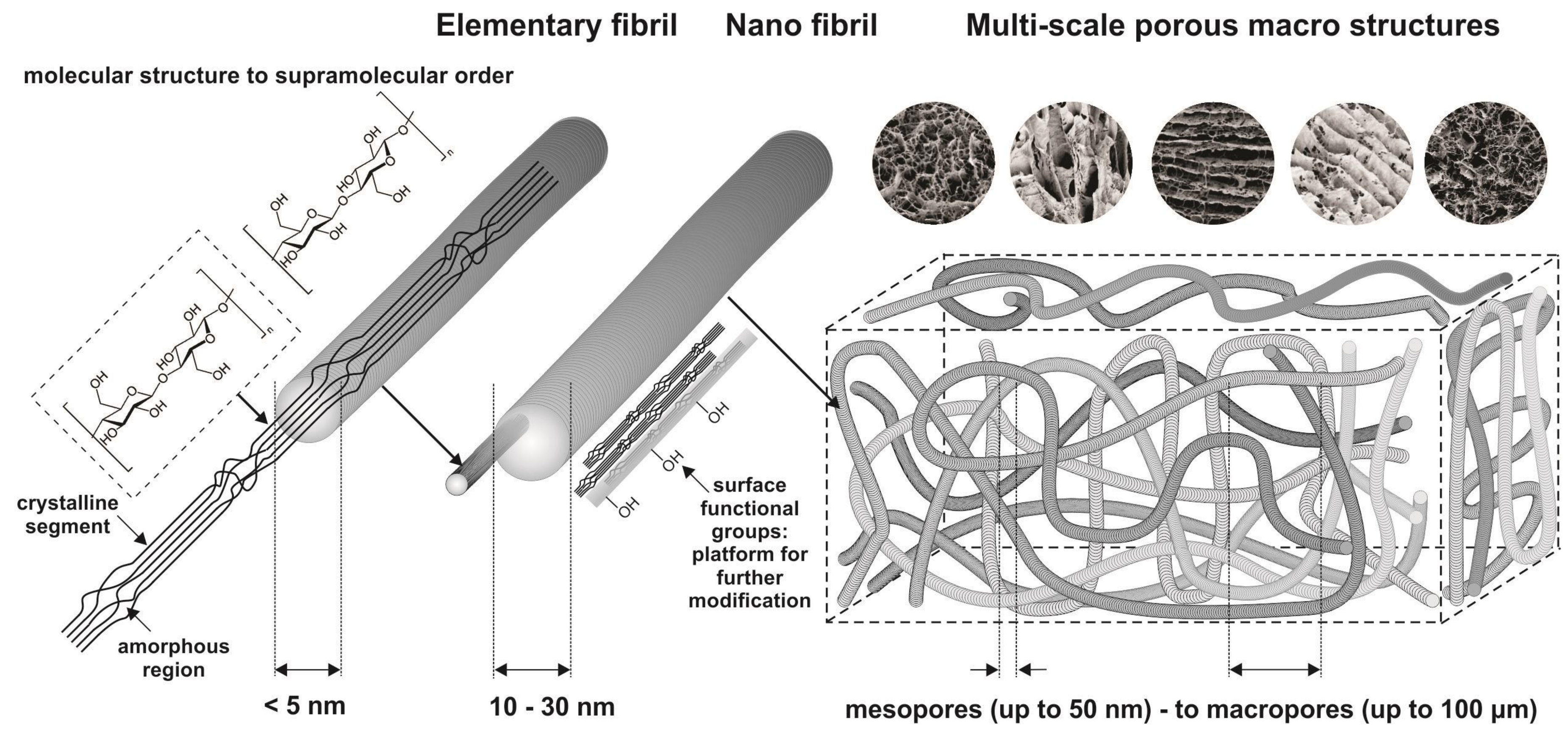
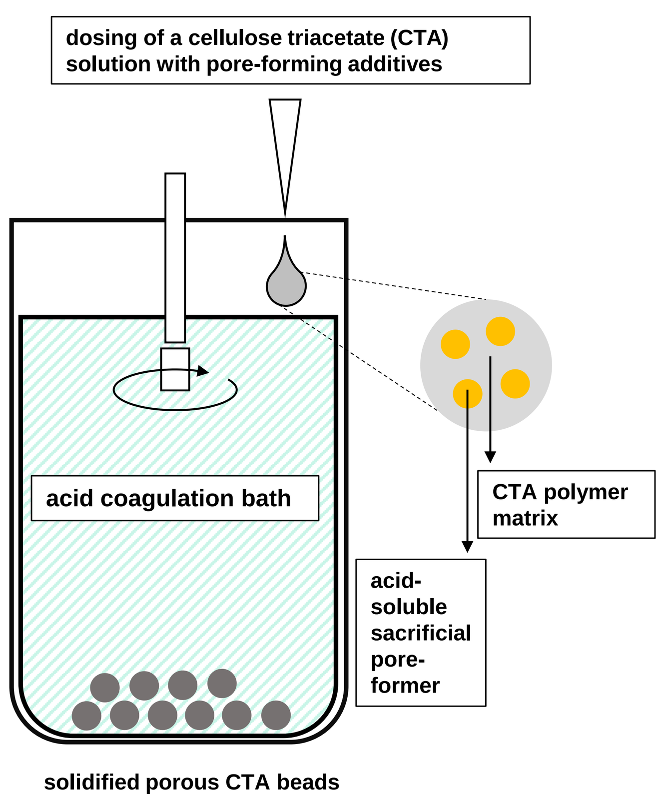
Abundance of cellulose in various plant species and a wide array of techniques, allowing for the processing of cellulose into various forms, make this ubiquitous renewable material a prime candidate for the large scale production of carbon fibrous matrices. Implementation of cellulose substrates as the starting building blocks for 3D carbonaceous structures can harness their **existing structural organization for the fabrication of controlled carbon porous materials**, **act as a platform for further functionalization**, while at the same time offer an inexpensive and environmentally-friendly alternative to the usage of synthetic oil-based carbon precursors. These renewable, wood-based materials present themselves as a viable green alternative, since they already possess an **intrinsically highly-ordered supermolecular arrangement in their natural state** (Figure 1) and a carbon-rich aromatic structure, as present in micro- and nano-fibrillar cellulose and lignin, respectively.

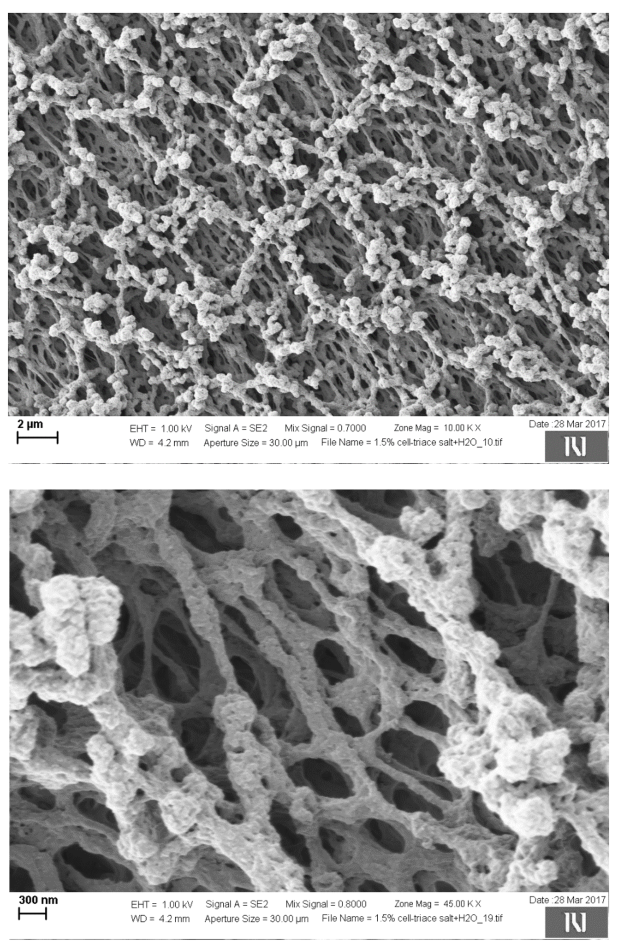
Different porous cellulose matrices were prepared using (i) nanofibrillar cellulose for fabrication of fibrillar aerogels and (ii) solutions of cellulose derivatives for preparation of porous beads. In addition, micron-sized regenerated cellulose fibres were employed as substrates for design of highly porous fibrillar building blocks.

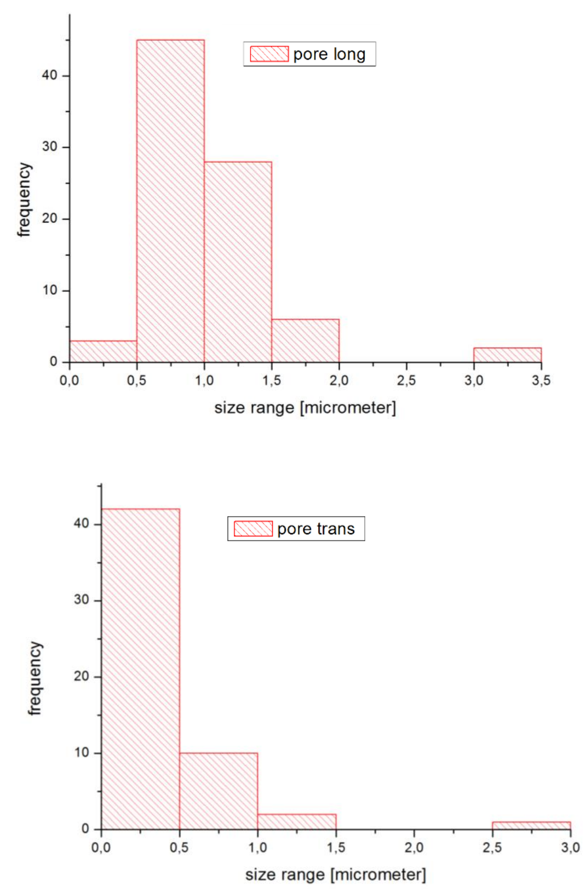


Structural levels of nano-fibrillated cellulose and schematic of its assembly into fibrous aerogel with multi-scale porosity; inset: circular images present scanning electron images of NFC aerogels with different morphology

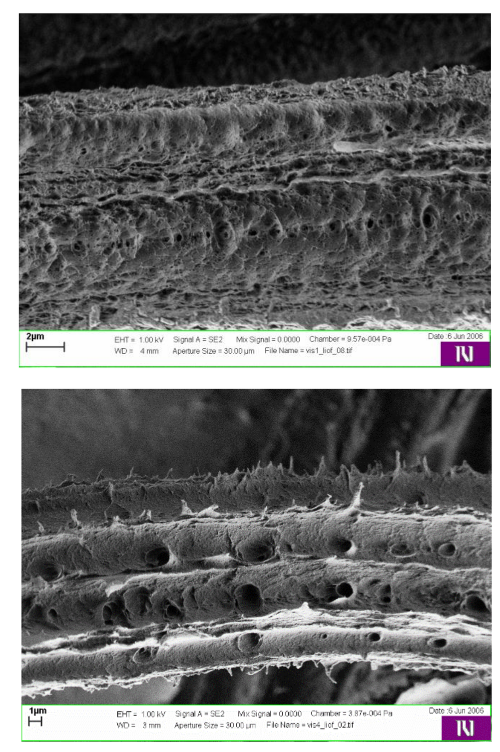
Fabrication of porous cellulose triacetate spheres

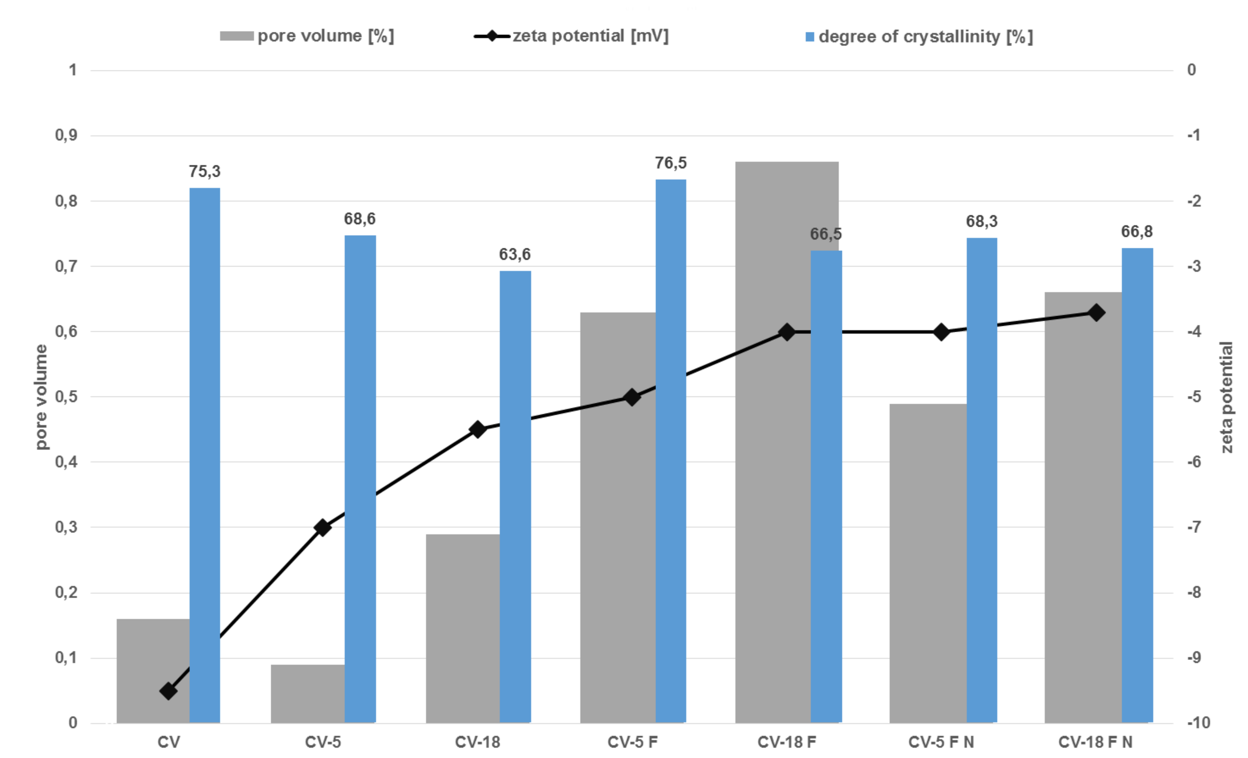




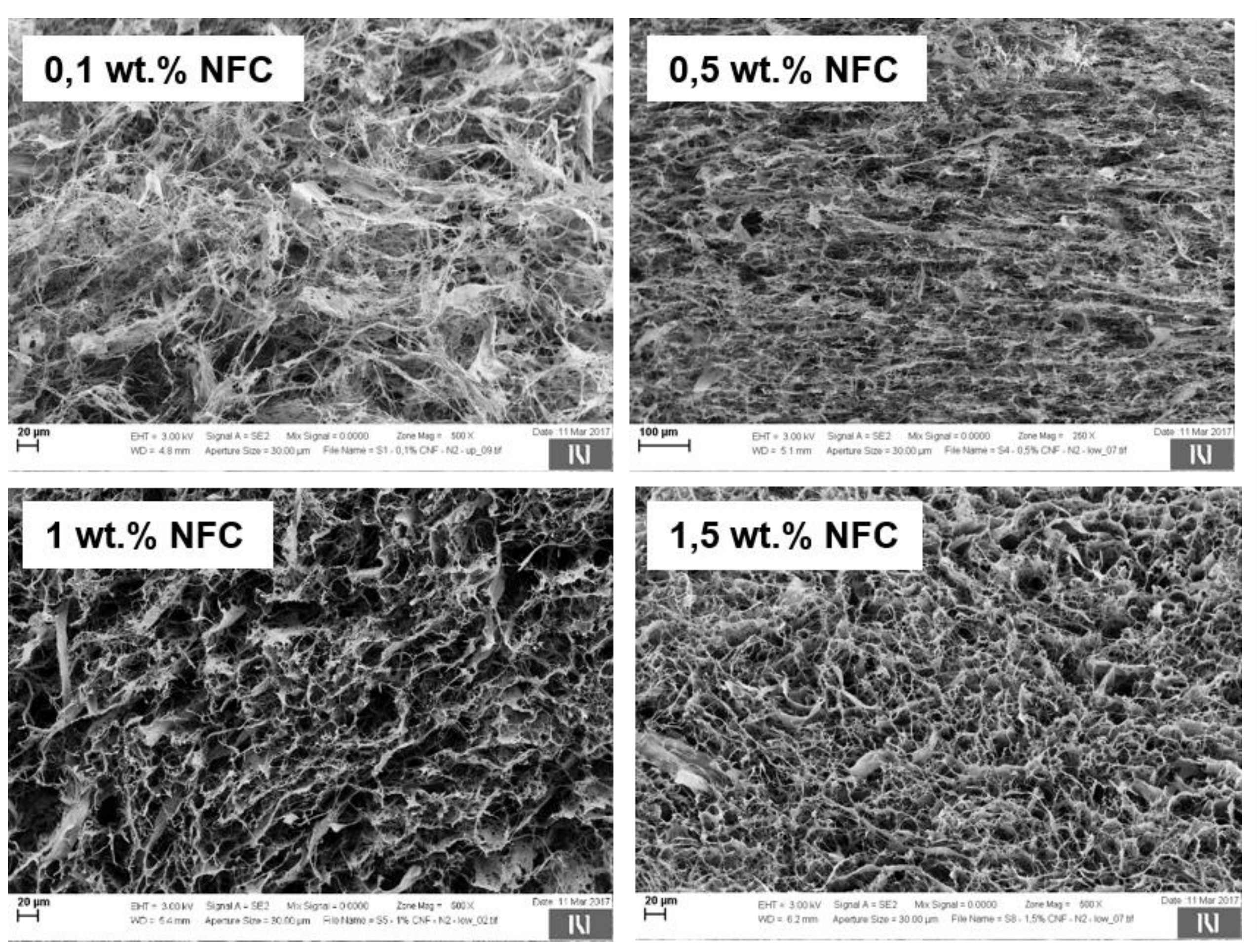


Micron-sized regenerated cellulose fibres with enhanced porosity

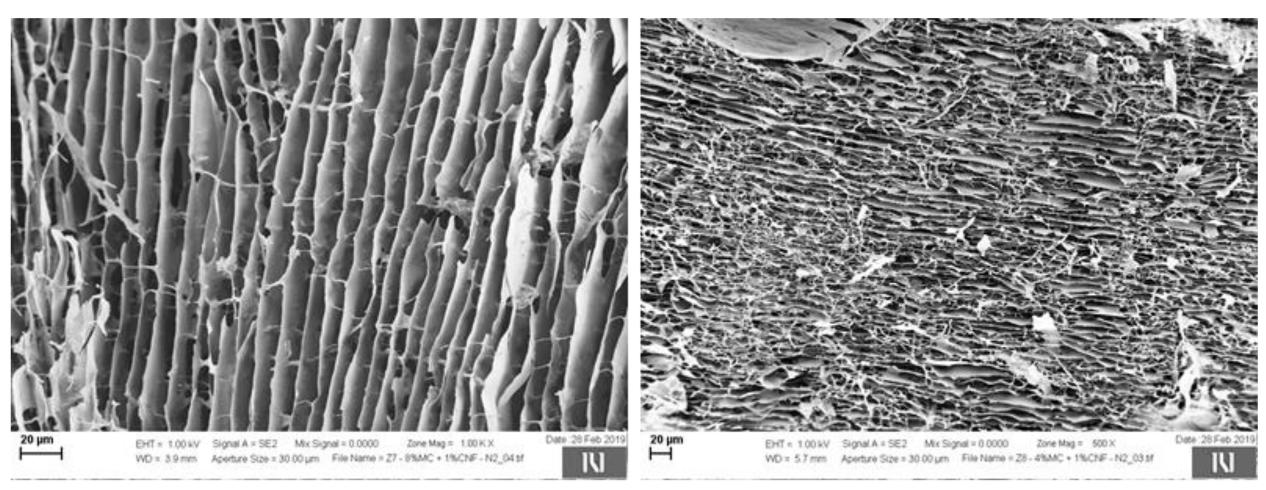




Nanofibrillar cellulose (NFC) aerogels with controlled porosity via ice templating



Influence of NFC concentration on aerogel morphology



Influence of methylcellulose on aerogel morphology

Growth of ice crystals during freezing of colloids or, in present case fibre suspensions, acts as porosity templating tool. Foregoing removal of the water in its liquid state, which would inevitably result in densely packed, non-porous structure and instead sublimate water in its solid state directly into water vapour, enables retention of structure where air occupies the spaces formerly filled with ice crystals. SEM images clearly confirm above statements, since the resultant aerogels exhibit a highly porous structure, with pore dimensions dependent on the concentration of nanofibrillar cellulose used. Influence of an addition of water-soluble polymer, i.e. methylcellulose into the fibrous slurry, is also shown; an evident, large-scale structuring of the aerogel is achieved, where somewhat random pore ordering of the CNF slurries alone is rendered into gallery-like sheets.

Catalyst requirements	Process conditions leading to proposed NFC-based carbon porous matrix and its properties
high catalytic activity towards ORR	(i) presence of non-noble metal particles and (ii) hetero-atom doped carbon matrix
high electrical conductivity	well-wired carbon fibrillar structure, in addition to presence of carbonized conductive polymer layers
high specific surface area and high porosity	multi-scale porosity, resulting from controlled assembly of nano-sized cellulose fibrils
uniform distribution of catalyst particles on the support	cellulose material can evenly uptake particle precursor solutions, resulting in subsequent uniform and discreet placement of particles
high interaction between catalyst particles and support surface	particles will nucleate and grow within cellulose structure, resulting in well embedded inorganic species within subsequent carbon matrix
high catalytic stability	highly ordered cellulose structure results in materials with high structural and mechanical integrity
high mass transport	precise engineering of cellulose fibril morphology offers control of high mass transport of reactants (e.g., oxygen) to active sites and at the same time effective removal of products (e.g., water)

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