Cellulose nanofiber: an advanced biomaterial soon to become ubiquitous

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Exactly 20 years have gone since Isogai and Kato in Japan reported a surprising discovery (1): regenerated and mercerized celluloses, despite being insoluble in water, when treated with the Anelli-Montanari reactants under the conditions identified by de Nooy for water-soluble polysaccharides in 1995 (2), namely aqueous hypochlorite buffered at pH 10-11 and a catalytic amount of TEMPO (2,2,6,6,-tetramethylpipelidine-1-oxyl radical) and sodium bromide, undergoes oxidation of the primary alcohol moiety at C-6 of the anhydroglucose unit giving place to a new water-soluble biomaterial: cellouronic acid.

Another 8 years, and in collaboration with Vignon's team in France and Nishiyama's in Japan, Isogai reported the discovery (3) of a new biomaterial simply obtained via the TEMPO-mediated oxidation of never-dried cellulose followed by disintegration into individual microfibrils by a simple mechanical treatment using a Waring Blendor: cellulose nanofiber (CNF).

The biomaterial has novel and unique properties. Aqueous dispersions of these cellulose nanofibers afford transparent films with high optical transparency and low haze called 'transparent nanopaper' which will be the key substrate for tomorrow's flexible electronics devices. Furthermore, CNF is mechanically very strong (five times stronger than steel) though being much lighter (one fifth lighter than steel) and resistant to heat. In principle, therefore, it could replace steel and even aluminum in several applications.

The first chemical plants producing the biomaterial in order of a few tens of tonnes per year are already operational, especially in Japan with several paper pulp companies in northern Europe and in northern America considering to enter its production. The paper pulp industry, indeed, is suffering from a dramatic fall of paper demand which forces it to diversify its business looking for new usages of wood cellulose.

The process, is often read, affords CNF at a cost of $90-100/kg. Said high cost is most likely due to the high cost of processing the hypochlorite dilute solution containing dissolved TEMPO and bromide after reaction. Separating the nitroxyl radicals in solution after the Anelli-Montanari oxidation, in fact, is an expensive, multi-step task (2).

Chemical companies, however, can now switch to heterogeneous catalysis. In 2017, indeed, chemists in Canada reported another surprising discovery: insoluble cellulose could be partly oxidized and defibrillated also using a silica-supported nitroxyl radical catalyst (5). In closer detail, the Karimi's catalyst (TEMPO@SiO_2@Fe_3O_4) was successfully applied to the green synthesis of CNF in water by oxidising part of the wood pulp C-6 surface hydroxyls on cellulose microfibril to carboxylates. The heterogeneous process smoothly led to 5 nm nanofibrils similar to those obtained in the oxidation mediated by TEMPO in solution (Figure 1). The catalyst, in addition, was easily recovered with a magnet and found reusable for 4 successive reaction cycles with no nitroxyl radical leaching.

The market of CNF, in the meanwhile, is booming. After the first applications in low value products such as toilet paper, the first sport shoes with a new CNF/foam polymer composite entered the marketplace in Japan earlier last June. The new composite foam enhances strength by approximately 20% and durability by approximately 7%, while still remaining lightweight (6) The shoes will be now commercialized across the world.

A major application, we argue, will be in electric vehicles where light and strong CNF-based composites will replace both metal and polymer parts, lowering the weight of the vehicle and further prolonging the autonomy of both battery electric vehicles (BEVs) and hydrogen-fuelled fuel cell electric vehicles (FCEVs). Indeed, last August Japanese researchers were reported to be at work (with major automotive company and its parts suppliers) on plastics with incorporated cellulose nanofibers for car and aircraft components (7).

Several high performance TEMPO-based solid catalysts are available to heterogeneously catalyze the reaction affording CNF (8). The first small chemical plants producing CNF will be rapidly scaled up and the old paper companies which for more than a century supplied paper and cardboard in all size and shapes will become manufacturers of cellulose nanofiber: a central biopolymer of the emerging solar economy.

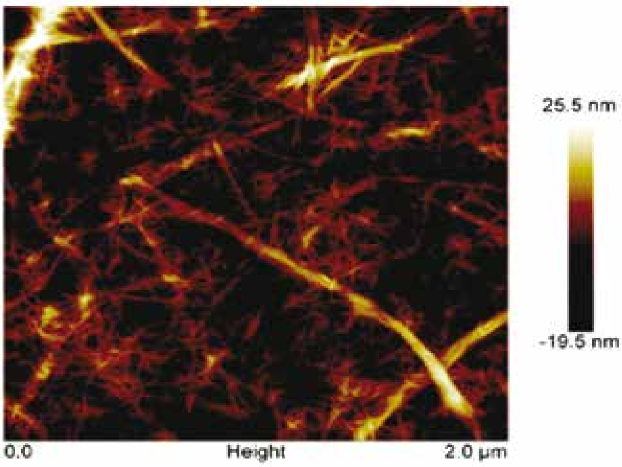

Figure 1. Atomic force microscopy picture of nanofibrillated cellulose obtained by cellulose oxidation over TEMPO@SiO_2@Fe_2O_3. (Reproduced from Ref.(5), with kind permission).

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