

Cellulose Nanocrystals in Sustainable Energy Systems

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The transition to low-carbon emitting technologies provokes an increasing demand in energy conversion and storage systems such as fuel cells, batteries, and supercapacitors, and consequently, the need for their raw materials. The use of new chemistries from earth-abundant precursors instead of scarce, toxic, and nondegradable components existing in current systems must be a priority in future years. Cellulose is the most abundant biopolymer on earth. Their crystalline constituents designated as cellulose nanocrystals (CNC) have been studied as functional materials due to their excellent structural and chemical properties. This review covers a recent collection of works on innocuous CNC-based materials with special attention to the fabrication methodologies of electrodes, electrolytes, membranes, and separators. The implementation of these CNC-derived materials in sustainable energy conversion and storage systems is also discussed.

Most of them do not contain costly and unfriendly metals and are profuse all over the earth. These characteristics are crucial for the scalability and world-wide implementation of battery systems around the world.

Because energy-providing processes occur at the electrode/electrolyte interface in these systems, the design and development of the electrode and electrolyte materials from biopolymers must favor the creation of adapted structural and textural properties on them. This fact will facilitate the molecular contact of the electrode surface and chemical species such as the solvent and the electrolyte's ions. Besides, it will enable facile electrochemical reactions

1. Introduction

Raw materials production is the main contributor to the energy cost and CO₂ generation during the manufacturing of energy conversion and storage systems, such as solar cells, fuel cells, batteries, and supercapacitors.^[1,2] To minimize the cost and the environmental impact, abundant materials and low-carbon emitting manufacturing routes must replace the conventional ones. For instance, electrode and electrolyte materials based on organic and polymeric compounds that might ultimately have been prepared or extracted from renewable biomass appear to be one sustainable solution.^[2,3]

and extend the life-term of the energy storage systems. Biopolymers such as polysaccharides (chitosan, cellulose, or starch) and polypeptides (collagen, keratin, and silk) are the ultimate source of organic-based materials from nature. Among these biopolymers, cellulose is the most abundant and one of the most versatile. Furthermore, their rich surface chemistry and high mechanical properties make it suitable for a wide range of applications including advanced electrodes and electrolytes.^[4] Cellulose is a hierarchical assembly of different structural components, where the CNCs are the smallest ordered units (Figure 1a).^[5] Because of their unique properties, nanocellulose-based materials have also been explored to build flexible, robust, and thin energy devices due to its nanosized nature.^[6]

Nanocellulose refers to cellulosic or cellulosic-derived materials with at least one nanoscale dimension (<100 nm). There are three main types of nanocellulose: i) cellulose nanocrystals (CNCs), also called cellulose nanowhiskers (CNWs) or nanocrystalline cellulose (NCN); ii) cellulose nanofibrils (CNFs), also known as nanofibrillated cellulose (NFC); and iii) bacterial cellulose (BC), also known as biocellulose.^[7] They fundamentally differ in form, method of production and index of crystallinity as it is shown in Table 1.

The following sections of this review show recent studies related to the use of neat, hybrid-based and carbonized derived CNCs as electrode materials in energy storage and conversion devices such as batteries or supercapacitors. Besides, most of the conversion and storage electrochemical systems consist of two electrodes in contact with an electrolyte solution and generally separated by a solid membrane or separator. So, we include in our discussion the implementation of CNC in solid electrolytes and in separator materials too.

2. CNC General Properties

CNC properties derive from their chemical composition, high aspect ratio, and large amount of surface hydroxyl functional

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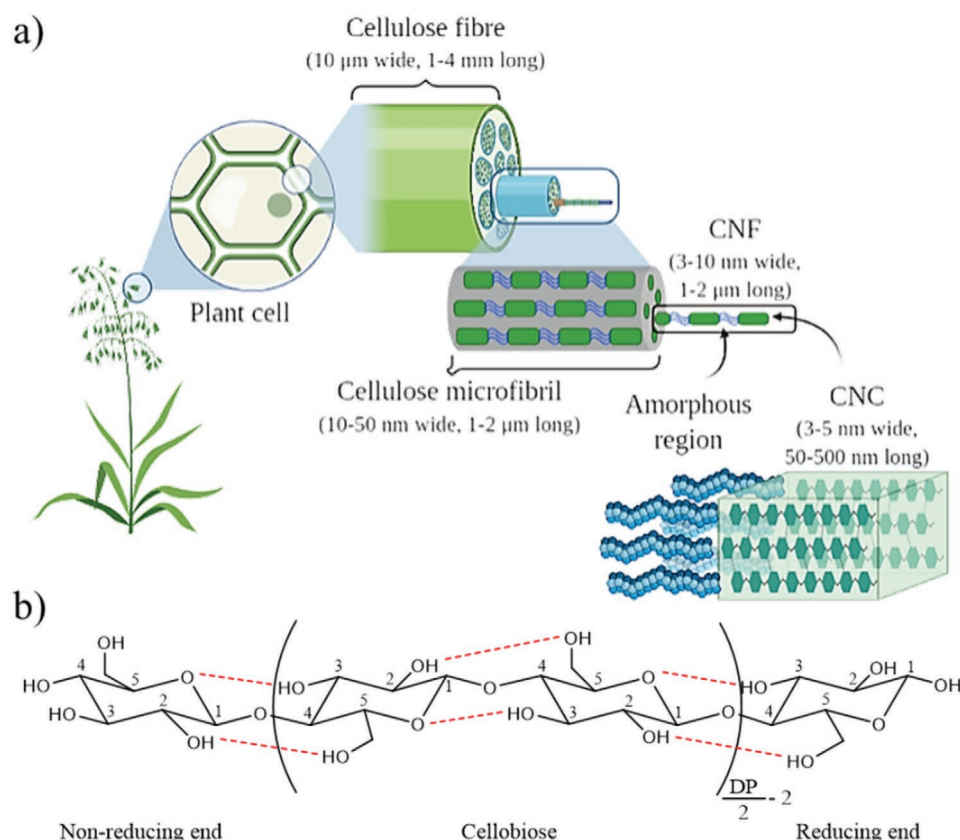


Figure 1. a) Schematic view of the hierarchical organization of cellulose in plants. b) Polymeric structure of cellulose chains showing intrachain hydrogen bonds (dashed line).

groups, which can establish intra and inter molecular interactions.

Some of the main properties of CNCs are

- High mechanical strength as a result of the strong intramolecular interactions.
- Aqueous assembling ability caused by intermolecular interactions that favors the creation of 3D ordered structures.
- Tunable surface chemistry because of the large amount of surface hydroxyl functional groups that can be chemically modified.

2.1. CNC Structure

CNCs are made of $\beta(1-4)$ connected chains of anhydro-glucopyranose units (AGU) in which every AGU unit is corkscrewed 180° with respect to its neighbors (Figure 1b). Due to the chair conformation adopted by the anhydro-glucopyranose units, all the hydroxyl groups are in the equatorial plane thus

the structure is stabilized by two intramolecular hydrogen bonds, which are responsible for their high mechanical strength.^[8,13] The aggregation of the chains into crystals and fibrils during the biosynthetic process occurs via intermolecular forces such as van der Waals interactions and hydrogen bonds. The different conformations of the AGU molecules give rise to the seven identified cellulose polymorphs, some found in algae, bacteria, and higher plants.^[8,13]

2.2. CNC Liquid Assembling Property

The presence of a large amount of hydroxyl groups grants CNCs with exceptional physical and chemical properties such as high mechanical strength, high surface area, and tunable surface chemistry.^[5,9,13] Chemical modifications of CNCs can be classified into covalent and noncovalent modifications. Covalent modifications include the characteristic reactivity of the hydroxyl group such as oxidation,^[14,15] cationization,^[16]

Table 1. Morphology, method of production and crystallinity index of cellulose nanoforms.

Cellulose nanoform	Morphology	Method of production	Index of crystallinity	Reference
CNC	Rod-like particles	Acid hydrolysis of wood cellulose	70–95%	[8–10]
CNF	Thread-like aggregates	Mechanical disaggregation of wood cellulose	—	[9–11]
BC	Thread-like aggregates forming hydrogels	Biosynthetic routes	70–80%	[10–12]

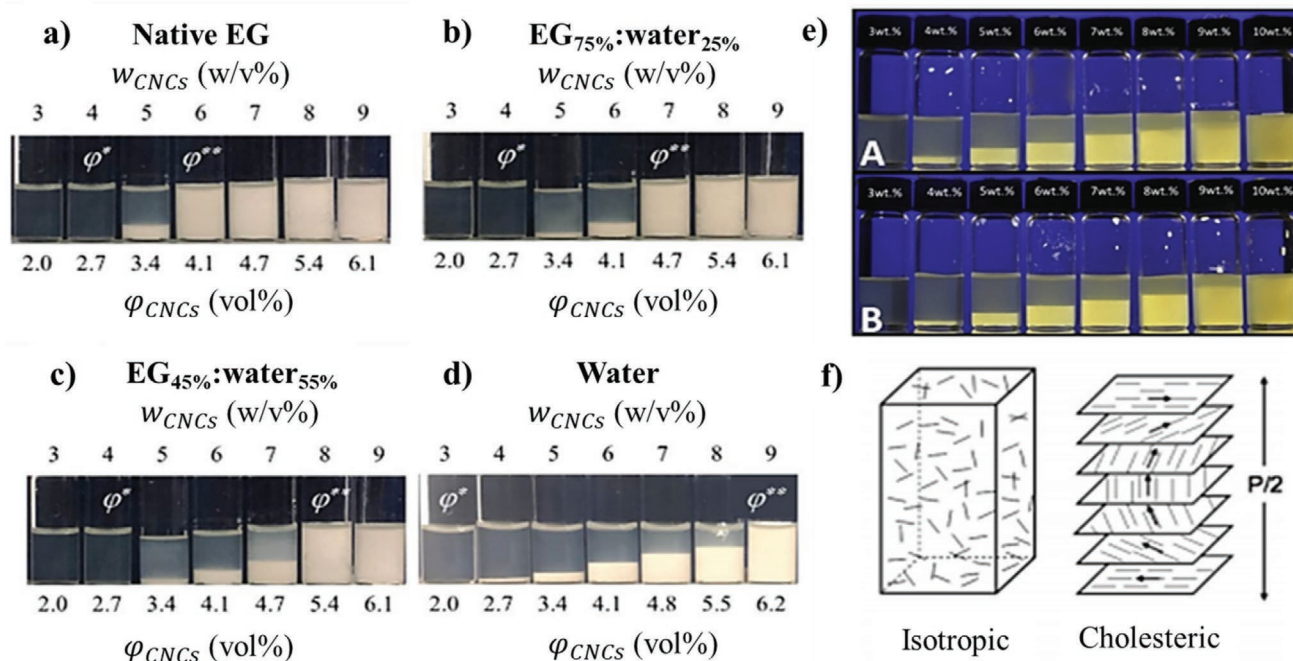


Figure 2. Images of CNCs suspensions in a) Native EG b) EG_{75%}:water_{25%} c) EG_{45%}:water_{55%} and d) water, at concentration range of $\phi_{CNCs} = 2.0$ – 6.2% . Adapted with permission.^[30] Copyright 2020, Royal Society of Chemistry. e) Phase separation in suspensions of cellulose nanocrystals A) Low surface charge-CNC; B) High surface charge-CNC in pure water at different CNC mass fractions w , as indicated on each vial cap. Reproduced under terms of the CC-BY license.^[31] Copyright 2016, The Authors, published by Frontiers in Materials. f) Schematic representation of CNC orientation in both the isotropic and anisotropic (chiral nematic) phases. Adapted with permission.^[8] Copyright 2010, American Chemical Society.

esterification,^[17] and silylation.^[18] On the other hand, noncovalent modifications are typically performed via adsorption of ionic^[19] and nonionic^[20,21] surfactants to control the dispersibility of the CNCs and to modify their surface properties.^[8,13] For instance, CNCs form isotropic suspensions in water at concentrations below 4 wt% due to the repulsive electrostatic interactions, and they aggregate at concentrations above 15 wt% due to the attractive intramolecular interactions.^[22–25] However, in the range 4–15 wt%, CNCs self-assemble into chiral nematic liquid crystals to minimize the repulsion caused by the electrostatic interactions without aggregation. Both, the pitch and the volume of the chiral nematic phase can be controlled as they depend on the interactions of the CNCs with the solvent, which can be modified by varying factors like the ionic strength of the suspension, or the CNC concentration (Figure 2).^[21,26] These chiral nematic structures can be freeze-dried to obtain hierarchical porous carbon structures with high surface area, after annealed in inert atmosphere. As it will be shown in the following sections, these porous structures are ideal for the development of electrode materials for energy conversion and storage applications.^[27–29] In fact, the hierarchical porous structures can accommodate large strain without pulverization, providing a good electronic contact and conduction during the reversible charge and discharge processes. Besides, the electrolyte ions will easily access the redox active centers inside the porous structures enabling capacity values close to the theoretical ones even at high cycling rates.

3. CNC Electrodes

CNC-based electrodes have been widely studied either via introducing conductive materials onto a CNC scaffold^[32–34] or have been carbonized to get a 3D carbon-based conductive material.^[35] In this review, we have classified the CNC-based electrodes in two main groups, which will be discussed below: CNC hybrid electrodes and carbonized CNC electrodes.

3.1. CNC-Based Hybrid Electrodes

In the last decades, many researchers have tackled the insulating character of the CNCs by combining them with conductive materials such as conducting polymers, metallic particles, or carbon-derived materials using different preparation methods (Figure 3). Two major strategies have been followed to prepare CNC-conductive composites: i) coating the conductive material layers onto the surface of CNC substrates and ii) mixing the conductive materials inside the CNC substrates via in situ polymerization or blending. The in situ polymerization consists on dispersing a monomer as a repetitive building-block precursor of the conducting polymer into the CNC matrix and then adding an initiator to build the CNC-conductive polymer composite.^[36–38] On the other hand, blending is a technique used to mix different materials to keep the properties of each of them individually in the hybrid composite or to enhance them through synergistic effect.^[39]

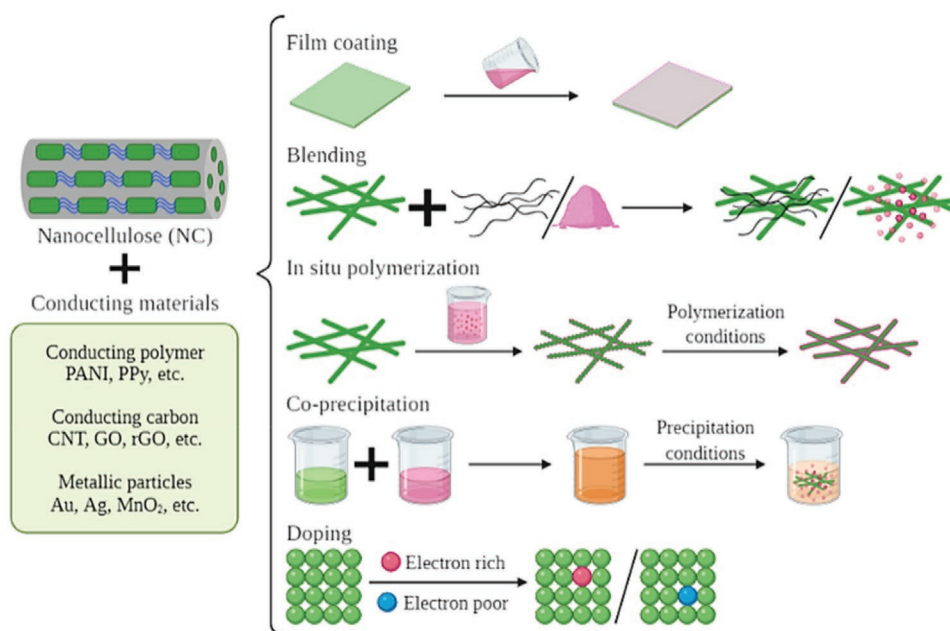


Figure 3. Fabrication routes to nanocellulose based conductive hybrid materials.

3.1.1. CNC-Conductive Polymer Hybrid Electrodes

Conjugated polymers, have been deeply studied for their applications in energy as electrochemical capacitors, sensors, solar cells, Organic light emitting diodes and fuel cell electrodes.^[7,40,41] Unfortunately, they suffer from low “solubility,” so recent studies have tried to overcome these problems by combining them with CNC due to its superior mechanical properties and improved dispersibility in aqueous solution. The most studied CNC-based composites include conducting polymers, such as polypyrrole (PPy, 0.3–100 S cm⁻¹), polyaniline (PANI, 0.01–5 S cm⁻¹), polyacetylene (PA, 3–1000 S cm⁻¹), polythiophene (PTh, 2–150 S cm⁻¹), poly(phenylenevinylene) (PPV, 0.001–100 S cm⁻¹) and their derivatives.^[41] In fact, several studies have managed to successfully combine CNC-based materials with conducting polymers via in situ polymerization. Tkalya et al.^[42] successfully lowered the percolation threshold for electronic conduction down to values of 0.4 wt%. PEDOT:PSS in poly(3,4-ethylenedioxythiophene)/poly(styrene-sulfonate)-based polystyrene (PEDOT:PSS-based PS) composites by adding CNCs, which act as a template. Moreover, the composite achieved higher electronic conductivity (7 S cm⁻¹) than the blend (6 S cm⁻¹), retaining 70% of the pure PEDOT:PSS conductivity (10 S cm⁻¹).

Some polymers, such as PPy tend to aggregate and grow localized onto the CNCs so they are hard to disperse. Wu et al.^[36] achieved an improved dispersion of the PPy on the TEMPO-oxidized CNC/PPy (TEMPO-CNC/PPy) composites with the addition of high molecular weight polyvinylpyrrolidone (PVP) prior to the polymerization. As a result of the better dispersion of PPy, the PPy/PVP/CNC composite showed higher electronic conductivity (37 S cm⁻¹ for PPy/PVP/CNC and 5 S cm⁻¹ for PPy/CNC) and capacitance (322 F g⁻¹ for PPy/PVP/CNC and 238 F g⁻¹ for PPy/CNC at 0.01 V s⁻¹).

3.1.2. CNC-Conductive Carbon Hybrid Electrodes

Since carbon nanomaterials such as carbon nanotubes (CNTs), graphene oxide (GO), or reduced GO (rGO) have excellent conductive properties (10⁸ and 10⁵ S cm⁻¹ for graphene^[43] and graphite, respectively^[44]) and are chemically stable in harsh environments thanks to their low reactivity,^[45] they have been studied in combination with CNCs. Although carbon nanomaterials can be coated onto CNC substrates, the interaction between the coated layer and the biopolymer is usually weak and the composites normally suffer from layer fall off. In contrast, the blending method let entrap the conductive materials inside the matrix, increasing the amount of carbon in the final composite and thus the electrical conductivity.^[39]

Most of the studies have focused on the understanding of the fundamental properties of the CNC-based composites so they can be implemented in advanced applications. Valentini et al.^[46] studied the effect of mixing CNC with GO on the surface on the electrical properties of pristine GO. The resulting composite showed enhanced electrical conductivity due to the excellent dispersion of the GO layers on the CNC matrix. In other studies, Tang et al.^[47] fabricated a ternary system including multiwalled carbon nanotubes (MWCNTs) and GO via blending, using CNCs as a binder for the GO/MWCNT nanocomposite. The resulting MWCNT/GO/CNC paper showed an excellent conductivity (9 S cm⁻¹) compared to a CNT/cellulose paper (6.7 S cm⁻¹)^[48] and to the MWCNT/CNC (6 S cm⁻¹) and GO/CNC (1 S cm⁻¹) coated papers.

Carbon/CNC composites have recently developed some important applications in sensors and flexible devices. Wu et al.^[33] studied the addition of CNC as a template to a carbon black (CB) 3D network on natural rubber (NR). The CB/CNC/NR material showed a decrease in the electrical conductivity percolation threshold with respect to the CB/NR traditional

composite (3 vol% CB for CB/CNC/NR and 7 vol% CB CB/NR) with a great enhancement of 12 orders of magnitude in electrical conductivity ($6.6 \times 10^{-14} \text{ S m}^{-1}$ for CB/NR and $2.4 \times 10^{-2} \text{ S m}^{-1}$ for CB/CNC/NR at 5 vol% CB). Furthermore, raising the CB loading up to 7.5 vol% CB, results in an electrical conductivity of 0.8 S m^{-1} . An increase in tensile strength (760%) was also observed due to the incorporation of the CNC template. Later, Wu et al.^[32] lowered the electrical conductivity percolation threshold of the CB/CNC/NR composite to 1.6 vol% CB and maintained the 12 orders of magnitude increase in conductivity at the lower load of carbon ($4.8 \times 10^{-13} \text{ S m}^{-1}$ for CB/NR and $3.5 \times 10^{-1} \text{ S m}^{-1}$ for CB/CNC/NR at 3.7 vol% CB). CNCs have thus shown their potential application with carbon nanomaterials to achieve cheaper materials (lower percolation thresholds and better dispersibility) with increased mechanical properties and flexibility.

3.1.3. CNC-Inorganic Particle Hybrid Electrodes

Metallic particles such as Cu usually exhibit higher conductivity values (10^5 S cm^{-1})^[49] than graphitic particles (10^4 S cm^{-1})^[50] what makes them interesting candidates for combining with nanocellulose matrixes to further prepare conductive paper-based electrode materials. Some of the preparation methods for the particles and the CNCs are coating, doping,^[51] and coprecipitation^[52] (Figure 3). In their studies, Hebeish et al.^[34] prepared a CNC-polyacrylamide copolymer and used it as a precursor for the synthesis of homogeneous Cu nanoparticle (CuNP)-doped CNC/polyacrylamide composite. The incorporation of a slight amount of CuNPs (0.8 wt%) meant an increase of 5 orders of magnitude in conductivity of the composite compared to the undoped copolymer ($1 \times 10^{-5} \text{ S m}^{-1}$ and $5.5 \times 10^{-10} \text{ S m}^{-1}$, respectively). The as-prepared composite was then proposed as a promising candidate material for conductive textiles. In other

studies, Lui et al.^[52] used CNC as templates to synthesize Fe_3O_4 nanoparticles (Fe_3O_4 -NPs) with increased stability in aqueous media via coprecipitation method. The prepared CNC/ Fe_3O_4 -NPs composite was then coated on a paper forming a conductive layer on its surface (27 mS m^{-1}).

3.2. Carbonized CNC Electrodes

High surface area porous carbon materials have traditionally been prepared from nonrenewable derivatives such as petroleum or coal using different methods^[53,54] like physical or chemical activation^[55–60] or templating.^[61,62] However, the fabrication routes involving these materials are nonsustainable and expensive.^[63] In the last decades, more sustainable materials with small particle size and high surface areas, such as CNC aerogels,^[64–68] have been carbonized to produce low cost 3D high surface area porous carbon structures. Yang et al.^[69] prepared lightweight hybrid electron conducting carbon aerogels by using via a sol–gel process. In Yang's work different chemically modified CNC led the formation of hybrid aerogels containing polypyrrole (PPy-NFs), polypyrrole-coated carbon nanotubes (PPy-CNTs), or spherical manganese dioxide nanoparticles (MnO_2 -NPs) within the 3D CNC framework (Figure 4). These aerogels were tested in symmetric supercapacitor cells with saturated Na_2SO_4 aqueous electrolyte. All the systems presented high areal capacitance values (3.3 , 2.4 , and 2.1 F cm^{-2} for PPy-NF, PPy-CNT, and MnO_2 -NP respectively at a scan rate of 2 mV s^{-1}) and high stability (84.2% for PPy-NF, 61.7% for PPy-CNT, and 92% for MnO_2 -NP after 2000 cycles) with coulombic efficiencies over 94% during cycling for all the devices. Zhuo et al.^[35] synthesized high surface area hierarchical porous carbon aerogels derived from cellulose via one step activation-carbonization. The aerogel showed high specific capacitance (328 F g^{-1} at 0.5 A g^{-1}) and cycling stability (specific capacitance

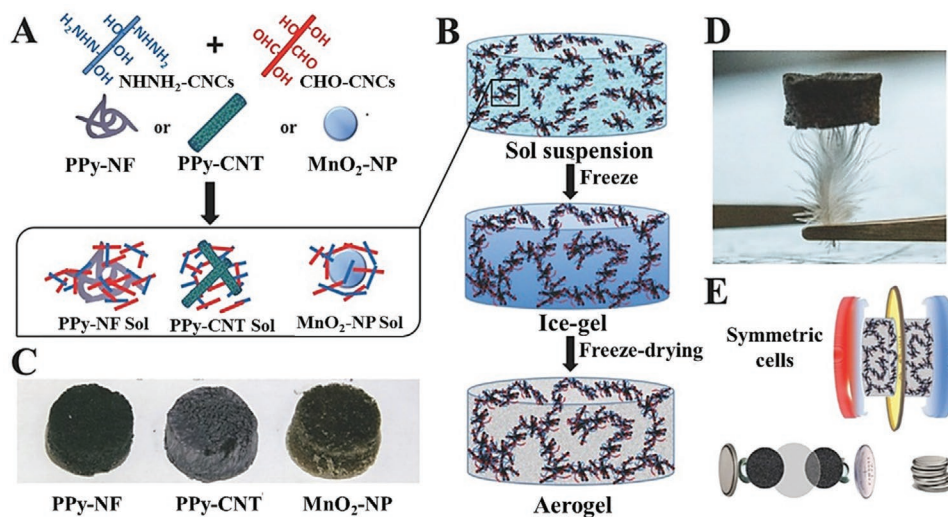


Figure 4. A) Schematic representation of the aerogel precursors, including functionalized CNCs and capacitive nanoparticles, which form the initial suspension of cross-linked clusters. B) The sol–gel process used to prepare aerogels. C) Photograph of the final hybrid aerogels with diameters of 1.5 cm. D) Photograph emphasizing the lightweight nature of a hybrid aerogel resting on top of a feather. E) Schematic showing the fabrication of symmetric supercapacitor cells in CR2032 type coin cell cases with two hybrid aerogels separated by a porous polyethylene membrane in saturated Na_2SO_4 aqueous electrolyte. Reproduced with permission.^[71] Copyright 2015, Wiley.

retention of 96% after 5000 cycles). In other studies, Nguyen et al.^[70] synthesized a mesoporous chiral TiC film by combining CNC with peroxotitanate and letting it order into a chiral nematic phase. Once carbonized, the as prepared composite showed excellent properties when tested as capacitor (210 F g^{-1} at 5 mV s^{-1}).

Recent studies have shown the possibility of tailoring the properties of carbon nanomaterials, such as their wettability or their conductivity, via substitution with heteroatoms like nitrogen, phosphorous, or sulfur, among others.^[72,73] In fact, nitrogen has lately gathered a lot of attention thanks to its ability to enhance the capacitance of the materials by increasing the redox pseudocapacitance.^[73] With CNC, Cheng et al.^[74] fabricated a N/O codoped carbonized CNC/PANi electrode (c-CNC/PANi). The electrode was tested in a Li-ion battery and showed excellent electrochemical properties. The c-CNC/PANi electrode exhibited low charge transfer resistance (76.3Ω) and almost double reversible capacity at 200 mA g^{-1} over 100 cycles (470 mA h g^{-1}) than pristine c-CNC (240 mA h g^{-1}). Besides, it presented a Coulombic efficiency of almost 100% after 2000 cycles.

4. CNC Electrolytes

Electrolytes are one of the key components of batteries.^[75] Different polymers have been used in solid or gel electrolytes.^[76–79] Solid polymer electrolyte (SPE) research in LIBs has focused on polyethylene oxide (PEO) and its derivatives due to their high stability voltage window during cycling,^[80] their high solvation properties, which facilitates the solubility of different metal-salts,^[75] and their high molecular chain mobility, which facilitates Li^+ conductivity.^[81] Nevertheless, some of these polymer electrolyte materials suffer from lack of mechanical strength due to the volumetric changes and cannot prevent metal dendrite growth occurring during the charge and discharge cycles, which provokes the failure of the battery. To enhance the mechanical properties of SPEs, nanocellulose has lately been investigated as building block for solid polymer and gel-like electrolytes. Samir et al.^[82] prepared a weakly cross-linked CNC/PEO electrolyte. The hybrid electrolyte presented similar ionic conductivity over a wide range of CNC loadings (up to 10 wt%) similar to highly cross-linked PEO electrolyte ($10^{-5} \text{ S cm}^{-1}$ at 20 and 40 °C, respectively). In addition, the mechanical strength of the electrolyte increased over 100 times when filled with CNCs.

5. CNC Separators

Separators (membranes) are one of the main components of electrochemical systems such as fuel cells and batteries. They prevent battery failures caused by short-circuit problems by keeping both electrodes separated from each other and act as bridges for the ion exchange between the electrolytes at both sides in fuel cells. The ionic conductivity has been proven to significantly affect the ohmic polarization (IR drop) of the cell. Due to their important role, separators must have excellent electrochemical and chemical stability, good electrolyte wettability, and good mechanical and thermal properties.^[83,84]

Traditionally, polyolefins such as polyethylene (PE) and polypropylene (PP) have been widely used as separators, especially for Lithium-ion batteries (LIBs), whereas Nafion is the most widely used membrane in fuel cells such as direct methanol fuel cell (DMFC) or polymer electrolyte membrane fuel cell (PEMFC). However, some drawbacks of traditional separators include hydrophobicity, low porosity, low electrolyte wettability, and weak mechanical and thermal properties. On top of that, most of the traditional separators derive from fossil fuels and are expensive. To improve the electrochemical response of the energy storage and conversion devices and to lower their cost, traditional separators must be replaced with materials with better intrinsic properties or ease of chemical tunability such as nanocellulose.^[85]

Nanocellulose offers high mechanical strength and rich functionality of hydroxyl groups, which are well known for strong hydrogen bonding and ease of chemical modification. The hydrogen bonding groups in nanocellulose can act as a path for proton hopping. The addition of dopant, cross-linker, or polymeric additives with functional groups to nanocellulose can further enhance its ionic conductivity.^[86] Nevertheless, nanocellulose separators suffer from two main drawbacks. First, their moisture content at room temperature. LIBs are very sensitive to water content (20–50 ppm) because it accelerates the degradation of lithium salts, such as LiPF_6 .^[87] and CNCs moisture content is far way above (21.4% at 95% relative humidity^[88]). For this reason, for their application in LIBs separators are subjected to thermal treatments in order to remove the water surplus.^[89] Second, nanocellulose papers are usually too densely packed and hinder the ionic conductivity lowering the performance of the LIBs.^[90] All considered, nanocellulose separators entail an improvement against traditional polyolefin separators, although they need to be tuned to get better porosity and reduce the water content in them. Wei et al.^[91] developed a flexible CNC-based membrane for a Li-metal battery. The membrane was composed of MnS/carbon nanofibers supported onto CNCs ($\text{MnS}@\text{CNC}/\text{carbon}$ nanofibers). It showed excellent electrochemical properties compared with the commercial PP membrane. The as-prepared membrane showed higher ionic conductivity ($1.533 \times 10^{-3} \text{ S cm}^{-1}$) than the PP membrane ($0.546 \times 10^{-3} \text{ S cm}^{-1}$) and the battery achieved higher capacities ($148.2 \text{ mA h g}^{-1}$ for the $\text{MnS}@\text{CNC}/\text{carbon}$ nanofiber membrane vs $129.4 \text{ mA h g}^{-1}$ for the PP membrane). Besides, the Li/Li symmetric batteries indicated that the flexible ordered $\text{MnS}@\text{CNC}/\text{carbon}$ nanofibers membrane could effectively inhibit the Li dendrite growth and enhance the cycling stability preserving 83% of the capacity after 600 cycles ($123.1 \text{ mA h g}^{-1}$) and high Coulombic efficiency (99%) (Figure 5).

Apart from this, nanocellulose is known to enhance the barrier properties and mechanical stability of the membranes, which are an essential requirement of the PEMs. Hasani-Sadrabadi et al.^[92] combined CNCs with Nafion altering its microstructure. This alteration enhanced the proton conductivity (0.2 S cm^{-1} of Nafion-CNC vs 0.15 S cm^{-1} of recast Nafion at 120 °C and 100% relative humidity) and suppressed the methanol permeability ($2.3 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ for Nafion-CNC vs $2.1 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for recast Nafion) with 5 wt% CNC. Besides, the Nafion-CNC composite membrane exhibited higher power density (91 mW cm^{-2}) compared to recast Nafion (47 mW cm^{-2}).

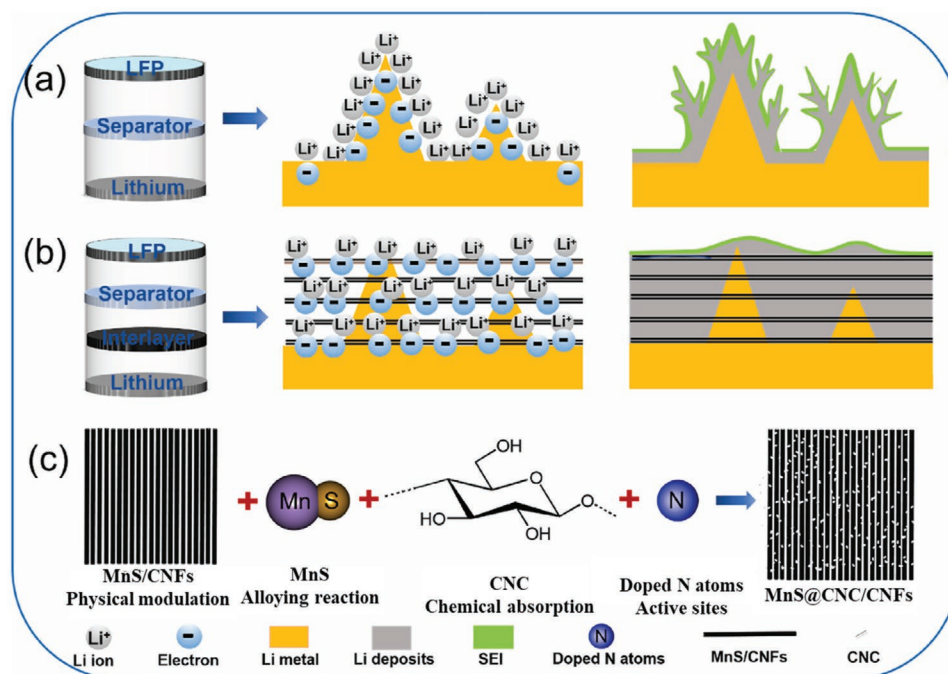


Figure 5. Schematic illustrations of a) The Li dendrite growth on the bare Li anode. b) The uniform Li deposition on the Li anode with the MnS@CNC/carbon nanofibers interlayer; and c) The synergistic effect of MnS@CNC/carbon nanofibers interlayer toward Li ions. Reproduced with permission.^[91] Copyright 2021, Elsevier B.V.

when tested in a methanol-air fuel cell with 5 M methanol. In other studies, Xu et al.^[93] synthesized an amino acid (AA) functionalized CNC composite (CNC-AA) using 5 different amino acids: glycine (Gly), 5-amino-valeric acid (Val), L-serine (Ser), L-leucine (Leu), and L-asparagine (Asp). The as-prepared CNC-AA composite was mixed with sulfonated poly(sulphone) (SPSF) resulting in a SPSF/CNC-AA PEM. Among these composites, SPSF/CNC-Ser (10 wt% Ser) showed the highest proton conductivity value (23 S m^{-1} at 80°C) which is significantly higher than commercial Nafion (3.5 S m^{-1} at 60°C and 70% relative humidity^[94] and 9 S m^{-1} at 95°C and 100% relative humidity^[95]). These composites also showed improved methanol barrier properties thanks to the hydrogen interactions between the $-\text{SO}_3\text{H}$ groups of the SPSF and the $-\text{OH}$ and $-\text{NH}_2$ groups of the CNC-AAs. The methanol permeability decreased as follows: SPSF ($11.8 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$) > SPSF/CNC-Ser > SPSF/CNC-Asp > SPSF/CNC-Leu > SPSF/CNC-Val > SPSF/CNC-Gly.

6. Summary and Prospects

Renewable and innocuous CNCs are suitable candidates for low-cost, advanced functional materials operating in sustainable batteries, supercapacitors, and fuel cells. Because of the specific chemical composition and intermolecular interactions, CNCs exhibit high crystallinity. These properties are crucial to fabricate CNC-based porous separators and reinforced solid electrolyte membranes exhibiting high mechanical strength. Besides, the transformation of CNCs into carbonaceous porous materials has allowed the creation of advanced electrode materials

for lithium-ion batteries and supercapacitors. The performance of these sustainable energy conversion and storage systems is assessed based on the physical and chemical properties of the CNC-derived materials.

Undoubtedly, there are still challenges to overcome that require research and a better understanding of CNCs properties. Among the main ones: i) the need to create hierarchical CNCs-carbon derived electrodes exhibiting millimeter thick and presenting a multiscale porosity. These CNC materials would have a great potential in electrochemical systems where an optimum balance between gravimetric power and energy densities is required; ii) the control of the final crystal structure in liquid CNC assemblies will be crucial to create novel mesoporous carbon structures with novel or enhanced electrochemical properties; iii) the creation of single-ion CNC electrolytes will also be most likely a promising strategy to enhance ion conductivity in free-standing solid polymer electrolytes and binders, along with their mechanical properties. For that, by applying the right surface chemistry, the anion might be covalently anchored to the polymer backbone of the nanocrystal. This new class of ionic CNCs conducting “salts” might evidence ion transport numbers close to the unity, excellent mechanical properties, and an electrochemical stability window stable at high voltage values; iv) biosynthetic alternatives will allow the creation of advanced multifunctional CNC materials. For instance, the biological incorporation of exogenous molecules before the growth of the nanocellulose fiber by BC, will allow to creation of novel or superior properties in CNC composites.

Nonetheless, CNCs have already demonstrated to be applicable in a wide range of low-cost devices with extraordinary impact in the energy field. As a result, we deem that on top of

the talked-of improvements of nanocellulose over conventional materials, the more organized structure of the CNCs and their chemical and structural versatility makes them suitable candidates to fabricate low-cost, advanced electrodes, and electrolyte materials with enhanced response.

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Conflict of Interest

The authors declare no conflict of interest.

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