RECENT APPLICATIONS AND INNOVATIONS OF CELLULOSE BASED MATERIALS: A CRITICAL REVIEW

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This review presents recent research on cellulosic materials and its latest uses, as well as scientific possibilities for more applications. Cellulose continues to display its advantages over synthetic fibers and its potential to replace fossil-based materials, which are known to harm ecosystems. Common attractive applications of cellulose include packaging, healthcare materials, electronics and printing. Most applications seem to rotate around the equilibrium of hydrophilicity, its mechanical properties and optical properties. Details on industrial applications, knowledge gaps and green innovations in cellulose conductivity, as well as limitations of its thermal degradation, are thoroughly covered. Most innovations are motivated by industrial needs, because renewability and inexpensiveness are the latest additional values to most industries. All common and innovative pretreatments are well summarized in this review. Furthermore, the paper provides interesting details on cellulose polymer composites, their applications and some recommendations for further research.

Keywords: cellulose, applications, innovations, polymer composites

INTRODUCTION

Cellulose is the most abundant and renewable natural polymer on earth (with an annual production of 1.5 trillion tons).[1,2] It is the major constituent in all plants and is found entangled with hemicelluloses and lignin in a plant cell wall. As illustrated in Figure 1, the cellulose is found in all the parts of a plant, but its content differs from part to part. For instance, cellulose is known to be in higher concentration in a plant stem than in its leaves.[3-9] Moreover, cellulose is found in various sources, not limited to plants (wood, annual crops and residual agricultural waste), but also in marine animals (tunicates), algae, fungi, bacteria, invertebrates and even amoeba.[10]

The lignocellulose structure is bonded by covalent bonds and non-covalent bonds/forces.[3,4] There are also other materials found in lignocellulose: protein, waxes, sugars, salts and insoluble ash.[5-7] It is constantly replenished by photosynthesis and it is about one-third of a plant tissue. Cellulose functions as a structural component in plants, providing strength and stability in the plant cell walls and fibers.[8,9] Its structure is made up of anhydroglucose units, linked through a linear β-1,4-D glycosidic bond, and it has three hydroxyl groups in each glucose monomer, linked through acetal functions between the OH group of C4 and the C1 carbon atom (Figure 2).[1-5] It is a semicrystalline polymer, with a highly ordered structure (crystallites) and disordered regions (amorphous-like).[1,11] It is insoluble in water and most organic solvents due to the strong molecular bonding.[1] It has good mechanical properties, chemical stability, biocompatibility, hydrophilic and biodegradation properties.[12]

The structural and physical properties of cellulose have attracted much research attention for many applications, including in paper, films, building and coating materials, packaging, advanced materials, food, drugs and flexible electronics.[11,13]

GENERAL ASPECTS

Extraction of cellulose

Pretreatment processes are used to disrupt the complex structure of biomass and enable the extraction of each polymer.[14] There are several types of the pretreatment methods that are used for biomass dismantling and polymer extraction. These are grouped into physical, chemical, physicochemical and biological pretreatment methods (Figure 3).[3,15] Physical methods include milling, irradiation, hydrothermal pretreatment, pyrolysis and pulsed electric-field treatment.[15] Chemical and physicochemical methods comprise alkaline pretreatment, ionic liquids, bleaching, ammonia fiber explosion, organosolv processing, microwave pretreatment, acid hydrolysis, CO_2 explosion and supercritical fluid pretreatment. Biological methods use fungi to extract cellulose from biomass.[3,15]

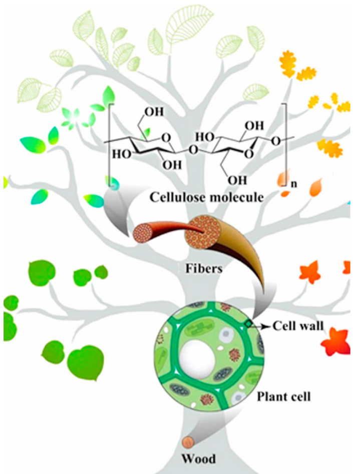

Figure 1: Cellulose from natural sources[2]

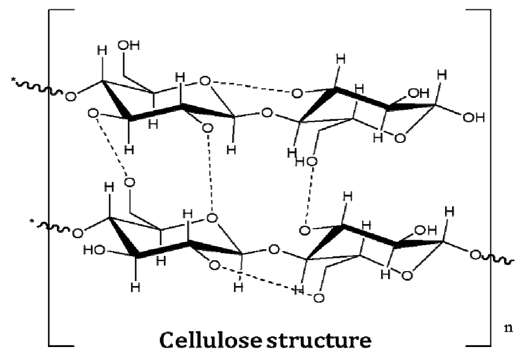

Figure 2: Structure of cellulose depicting inter- and intramolecular hydrogen bonds[5]

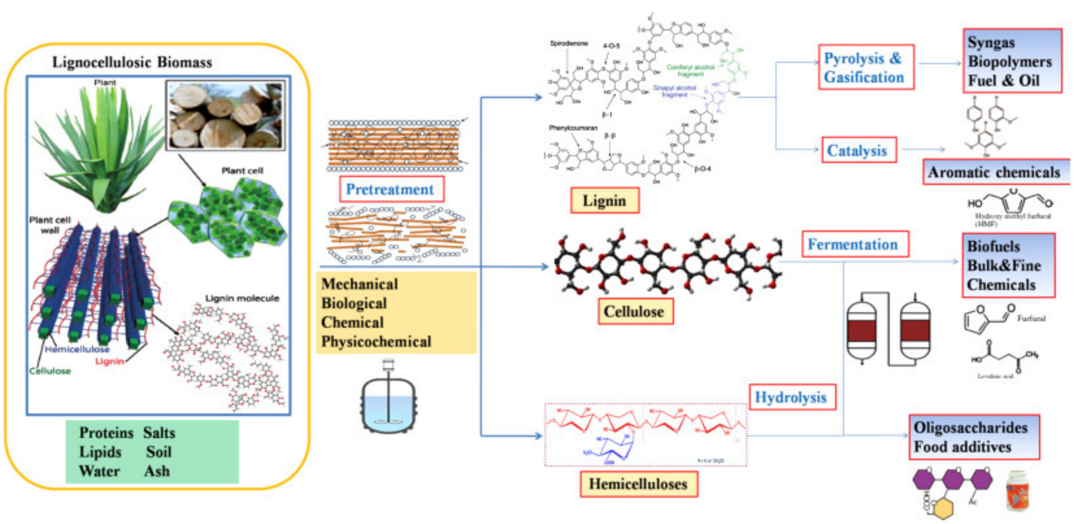

Figure 3: Pretreatment of biomass

Types of cellulose

There are four types of cellulose in the nano-range: nanocrystalline cellulose (NCC) or cellulose nanocrystals (CNCs), nanofibrillated cellulose (NFC) or cellulose nanofibrils (CNFs), bacterial cellulose (BC)[16,17] and cellulose nanobeads (CNBs)[24-29] (Figs. 4 and 5). Microcrystalline cellulose is a type of commercially available cellulose used for in pharmaceutical and food industry applications, as well as starting material to produce nanocellulose.[10,18-20] In terms of morphology, CNFs are soft, long chained aggregated nanofibrils, made of alternating crystalline and amorphous cellulose domains. The long cellulosic chains make it difficult to determine the length of CNF, while the width varies from 10 nm to 100 nm, depending on the source of cellulose, defibrillation process and pretreatment.[21] CNCs are rigid rod-like crystals with a diameter in the range of 10-20 nm (can also be in the range of 5-70 nm) and lengths of a few hundred nanometers.[22]

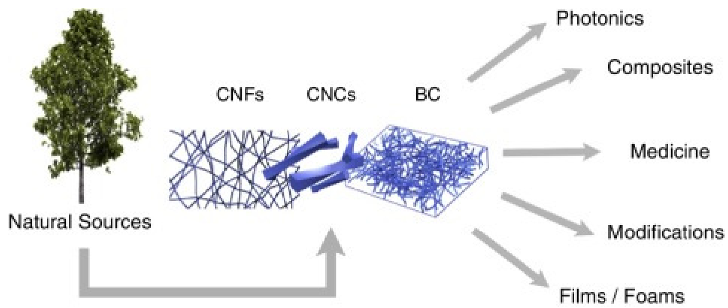

Figure 4: Types of nanocellulose and its applications[17]

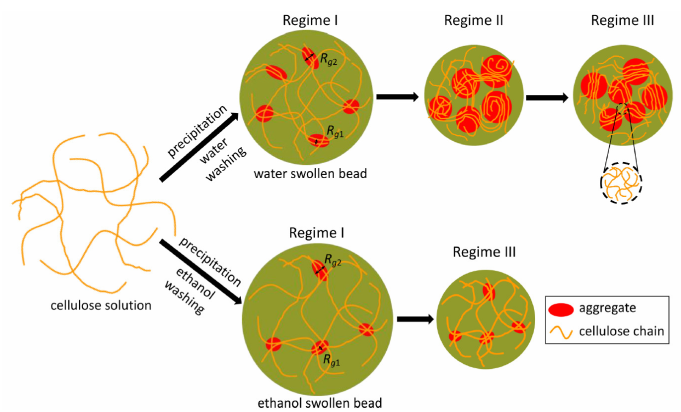

Figure 5: Schematic representation of structural evolution of water and ethanol swollen cellulose beads during solvent evaporation[27]

BC is an exopolysaccharide that consists of a homopolymer (D-glucose) of β-1,4-linkage synthesized by various bacterial species.[23] BC is similar to plant cellulose in terms of properties. Cellulose nanobeads (CNBs) are, in a nutshell, highly stable spherical nanoparticles. They have demonstrated good performance in medical applications. Specifically, in the development of lateral flow assays, their sensitivity has been shown to be greater than that of colloidal gold, and particle stability is excellent.[24-29]

Regenerated cellulose (RC) is a form of cellulose that is prepared by solvent dissolution and anti-solvent regeneration. It is designed in different forms for specific functions and with properties suitable for applications, such as oleogels, hydrogels/aerogels, beads, filaments, films/membrane and bioplastics.[24,25] Carboxyl methyl cellulose (CMC) is a derivatives of cellulose, which is anionic and water soluble.[26] CMC is formed by the introduction of –CH_2COOH groups into cellulose. The properties of CMC include high viscosity, transparency, biocompatibility, biodegradability, good gel and film forming properties, hydrophilicity and non-toxicity.[31] It is used in medical applications for drug delivery, tissue engineering, textile printing, paper industry, detergents and food.[31-33] CMC can also be used in additives due its ability to absorb large quantities of water, its ability to swell, its biocompatibility and low cost.[34,35]

INNOVATIVE APPLICATIONS OF CELLULOSE

In the modern era, environmental issues and the circulation flow of economy have become major concerns, while innovative applications using natural fibers may provide a solution.[36] Cellulose has shown a potential to be used as a basic material in several applications and inventions.

Cellulose from wastepaper

Considering that millions of tons of paper are produced annually on a global level, resulting in a large quantity of disposable municipal and industrial waste paper, it should be noted that wastepaper is a potential source of cellulose.[37,38] It is true, however, that recycling wastepaper shortens the fiber length, thus resulting in lower grade paper, of poorer quality, compared to non-recycled paper.[38] Nevertheless, recycling wastepaper is an alternative route to find innovative uses of cellulose. Recycling paper contributes positively to the environment and economy, since one ton of waste paper seemingly saves almost 17 trees and 7000 gallons of water.[38] Cellulose could be extracted from wastepaper using pretreatment techniques and applied in several applications.[36,38,39] Wastepaper is normally applied as reinforcement in composites and as a raw material to produce CNCs by acid hydrolysis with a crystallinity index of 74.1%.[36,40] Studies reported using the extracted CNCs to reinforce polyethylene terephthalate (PET) to form coated sheets. The composite showed improved water vapor barrier properties and PET transparency, thus making it suitable for food packaging applications.[39]

In another study, cotton wool, cotton textile and tissue paper were used in bioethanol synthesis, to convert cellulose to sorbitol, using ball-milling in catalysis.[42] Wastepaper was also used, but the yield obtained was poorer (7%) than those from other sources of cellulose: tissue paper, cotton wool and cotton textile (50% sorbitol yield).[42] The same study reported synthesizing xylitol and glycerol from the mentioned sources of cellulose, except wastepaper.

Cellulose in packaging

Cellulose-based materials are utilized in the packaging industry as wrapping materials and containers, primary and secondary packages, as well as in flexible and rigid packaging. The advantages of using cellulose in packaging include that it is lightweight, inexpensive, biodegradable and sustainable.[42] Cellophane is a regenerated cellulosic material used as film in the packaging industry. It has excellent gas barrier properties for dry conditions, however, the production of cellophane is not environmentally friendly.[43]

Nanocellulose has been utilized as films in the form of CNFs and CNCs. They are used in packaging as reinforcements to improve gas barrier properties in films.[42] However, nanocellulose absorbs moisture, thus it has poor water vapor barrier properties.[10] Cellulose fibers can be extracted from agricultural waste to produce biodegradable composites with good mechanical properties for packaging.[44] Oxidized CNF and polypyrrole were coated on paperboard to improve its mechanical properties and reduce gas permeability (Fig. 6).[45]

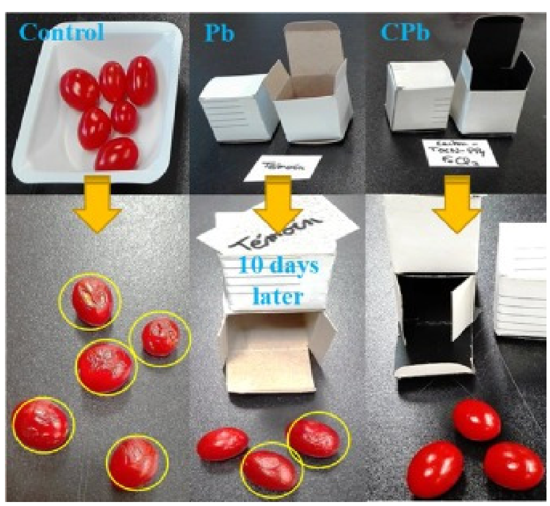

Figure 6: Simulation test for storing food for 10 days in developed packaging (Pb – paperboard and CPb – coated paperboard[45]

The coated paperboard exhibited a dense network, which made it suitable for multilayer paperboard packaging applications. These paperboards allow reducing packaging waste, since they are recyclable and biodegradable.

Nanocomposites prepared using CNCs/Ag nanohybrids and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) displayed good barrier properties, 99.9% antibacterial ratio and low migration levels in food simulants, which demonstrated their suitability for food packaging applications.[46] Nanocellulose–montmorillonite (MMT) composites were prepared and the obtained materials exhibited lower water vapor permeability and improved mechanical properties.[47] These composites are recyclable and compostable, thus, can be used in packaging applications. RC and MCC were used to form metallic hybrid nano-materials with the deposition of metal nanoparticles on their surface. The resulting nano-material hybrid had excellent antibacterial properties, suitable for usage in food packaging.[48]

Cellulose in biomedical applications

CMC beads have been successfully used for controlled drug release in nanocomposite applications.[49] The swelling properties of CMC beads allow incorporating drugs into the beads and then their release to the tissue of interest at a controlled pH. Sodium CMC has been investigated as a controlled delivery system in gastrointestinal drug delivery.[50] CMC is suitable for mucosal tissue and has been also used as scaffold in tissue engineering.[31] Injectable CMC hydrogels have been studied in soft tissue filler application and resulted in good mechanical and swelling properties.[51,52] Moreover, CMC hydrogels can be removed via enzymatic treatment since it is a cellulose derivative. Besides CMC, other cellulose derived materials present interest in similar applications. For example, CNCs can also be used in tissue engineering, namely in injectable tissue scaffolds, bone tissue regeneration, bone implants adhesion and drug release.[53] BC was used in tissue engineering for a bone regeneration process (Fig. 7).[54]

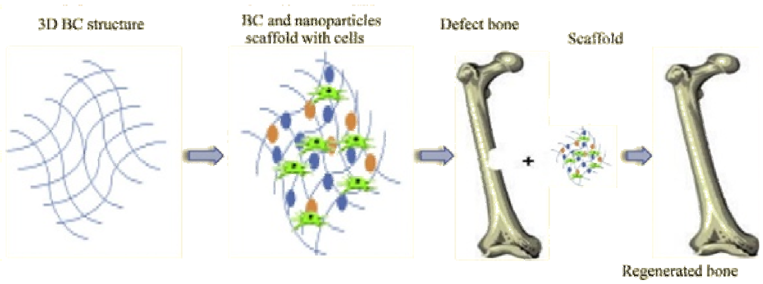

Figure 7: BC used in bone regeneration[54]

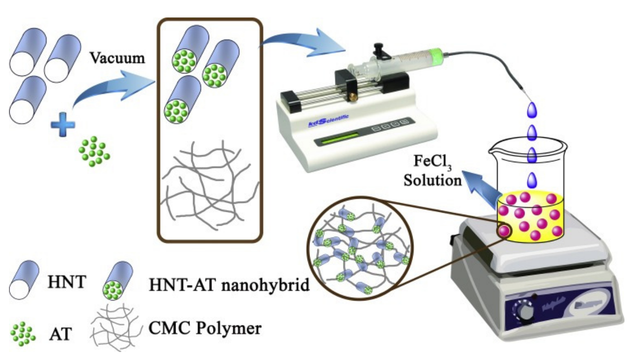

Figure 8: CMC/HNT-AT bionanocomposite preparation[56]

CMC was used as a stabilizer of Ag nanoparticles, which showed an improved antibacterial property. This study formulated a new type of antibacterial agent that can be applied in solving the problems of *in vitro* antibiotic resistance, combating pathogens that are disease resistant.[55]

In a study, pH sensitive bionanocomposite hydrogel beads were designed using CMC, halloysite nanotubes (HNT) and atenolol (AT)[56] (Fig. 8). The resulting bionanocomposite beads had improved pH sensitivity for swelling and good controlled drug releasing properties.Apart from CMC, bacterial nanofibers have been loaded with Ag nanoparticles and used as an antimicrobial wound dressing material to prevent bacterial growth.[33] The antimicrobial activity of Ag nanoparticles on the cellulose membrane was found to be more than 99.99% against *Escherichia coli* and *Staphylococcus aureus*. Furthermore, Shumilova *et al.*[57] proved that BC composites incorporating Ag nanoparticles and antibiotics could be used as wound dressings due to their effective antibacterial properties.

Niu *et al.*[58] reinforced polyacrylamide with CNF to improve mechanical properties for developing hydrogels with healing abilities. The strength was enhanced due to the strong hydrogen bonds among CNF and polyacrylamide after their cross-linking. Another similar study indicated that more modification of mechanical properties could be achieved through the alteration of CNF composition.[59] The preparation of CNCs, Ag and beeswax composites has been also reported; the composite material was used to coat the paper surface and exhibited good antibacterial properties and water resistance.[52] RC can be used to prepare cellulose-rich oleogels due to its good dispersion and stabilization emulsion ability.[60] Oleogels displayed good rheological properties, with good thixotropic recovery and high gel strength.

Cellulose in wastewater

Cellulose modified materials can be used as adsorbents for the removal of metal ions from water.[55,56] Abd El-Aziz *et al.*[62] chemically modified cellulose through graft copolymerization with hydrophilic vinyl monomers, such as acrylic acid, acryl amide and clay (montmorillonite), to improve its properties.[61] The monomers used in the graft copolymerization were selected due to their ability to form coordination bonds with heavy metals. They are called chelating polymers.[62] The grafted cellulose/clay composites efficiently adsorbed metal ions and removed them from aqueous solutions successfully. The addition of clay improved the biodegradability properties of the composites. Cellulose grafted copolymers were easy to separate from the aqueous medium, recover, regenerate and recycle after the bio-sorption process.[61] Tursi *et al.*[64] also showed the possibilities of using cellulose to extract hydrocarbons from polluted water. The cellulose fiber surface was chemically modified to hydrophobize cellulose to make it more suitable for adsorption of hydrocarbons from polluted water.[64] The extractant successfully removed hydrocarbons by adsorption. In another study, Salama *et al.*[65] successfully extracted methyl blue from wastewater by a CMC/metal oxide nanocomposite.

Of high interest is the study carried out by Chitpong *et al.*,[66] who developed cellulose nanofiber membranes prepared with cellulose acetate and modified with poly(glycidyl methacrylate). Poly(acrylic acid) was grafted on the nanofiber membranes for permeability and to transform them into ion-exchange membranes. The resultant composites showed a potential to remove heavy metal ions from wastewater (Fig. 9).[66]

Cellulose in electronics and printing

In the field of electronics, the optical properties of cellulose materials have also shown potential for applications in the form of conductive polymers and/or carbons and metallic particles (Fig. 10).[2] Nanocellulose materials are much more suitable for such applications, due to their better optical properties compared to those of regular cellulose. Additionally, they are also flexible, light in weight and environmentally friendly.

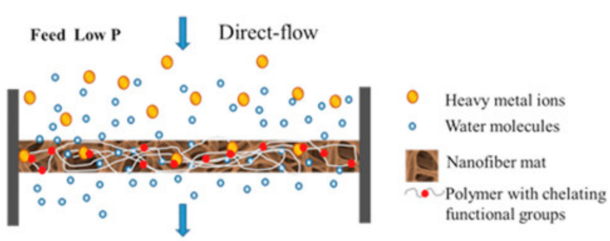

Figure 9: Ion-exchange cellulose nanofiber membrane for metal ion recovery from water[66]

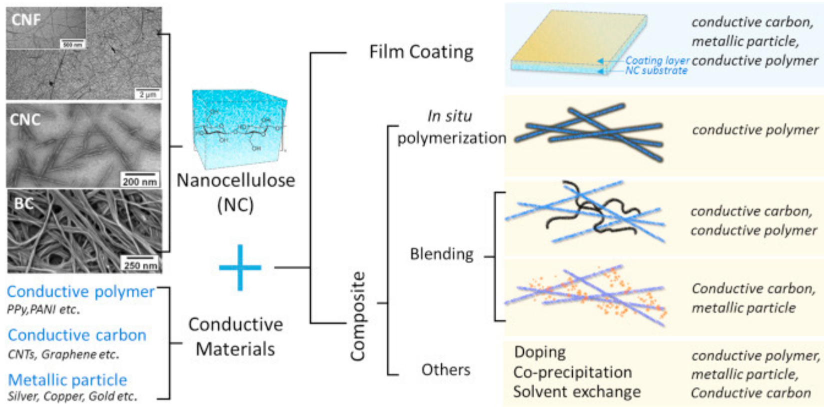

Figure 50: Nanocellulose fabrication routes for electronic applications[2]

Figure 11: Polypyrrole/CNC/PVP hybrid[69]

Nanocellulose has been modified both physically and chemically to produce power sources, energy storage devices, supercapacitors and rechargeable lithium batteries. Such devices are of interest in portable electronic devices, electronic automobiles, large energy storage systems, solar cells, sportswear, light armor in military wear.[2,67] Nanocellulose can be combined with many conductive materials to make it suitable for electronic applications, however, the conductivity level, the cost of the conductive material, its physical and chemical stability, toxicity, biodegradability and preparation technique are some of the limitations that have hindered its use in such applications.[2]

Nanocellulose can be used for reinforcing conductive polymers to result in composites or for coating a conductive material to produce conductive hybrids.[2] The resulting conductive cellulose based polymers are used in energy storage applications and electronic devices. Cellulose has been processed with copper nanowires to produce a transparent conductor, which is flexible and degradable.[68] Cellulose acted as a dielectric layer, improving the heat stability of the conductor due to the thermal properties of cellulose. Copper nanowires also contributed to improved heat stability due to the shell made of carbon and oxygen, thus, restricting the oxidation of the conductor. Polypyrrole was polymerized on poly(*N*-vinylpyrrolidone) (PVP)/CNCs composite to result in a one-dimensional fibril core-shell structure (Fig. 11).[69] PVP acted as a surface modifier, which improved the polypyrrole deposition on CNCs. The hybrid had high conductivity compared, to the one without PVP, thus, an improvement in electrochemical properties had been achieved.

The versatility of cellulose based materials turns out to be an additional advantage for possible inexpensive supercapacitors.[70] For instance, polypyrrole is a conducting polymer with poor mechanical properties and processability. The incorporation of CNCs with polypyrrole resulted in a light in weight, cheap and renewable hybrid with improved conductivity and mechanical properties.[71] This improved the chances of applicability of polypyrrole in supercapacitors, where the rigidity of CNCs provided support.[53,72] In another study, CNCs were incorporated in polyaniline for developing conductive films with improved strength and flexibility.[73] A similar study proved that CNCs can also be incorporated in graphene nanosheets (GNS) to produce electrical supercapacitors[74] (Fig. 12). The graphene nanosheets were used to coat cellulose fibers. This resulted in a flexible composite, which was then adhered to copper foil.

In addition to their usage in supercapacitors, CNCs can be used to produce flexible and lightweight substrates for usage in electronic devices.[53] Sadasivuni *et al.*[75] filled graphene oxide with CNCs and obtained a composite that can be used as a sensor. In a separate study, recycled wastepaper was incorporated with reduced graphene oxide (rGO) to result in a paper-based flexible supercapacitor electrode (Fig. 13).[36] The resulted green and flexible energy storage supercapacitor could be used in wearable electronics. The nanocomposite sensor was transparent and biodegradable, and was able to quantify the chemicals concentration, reproduce signals with a fast response and high sensitivity. Besides, Grishkewich *et al.*[53] revealed a potential usage of CNCs as separators in batteries and fuel cells.

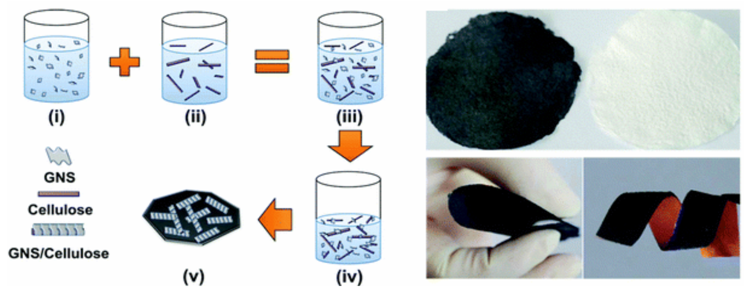

Figure 12: GNS/cellulose composite paper and a cellulose white paper (top); the bent composite paper; and a flexible supercapacitor with a copper foil (electrical conductor)[74]

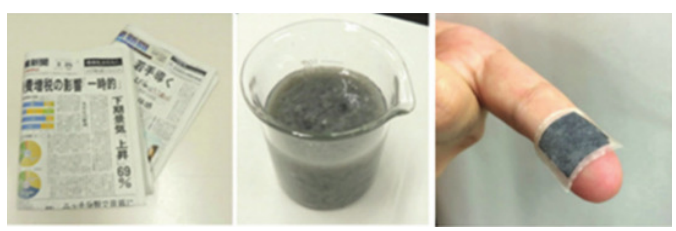

Figure 13: Wastepaper (left); recycled wastepaper/rGO aqueous suspension (middle); and paper-based flexible supercapacitor (right)[76]

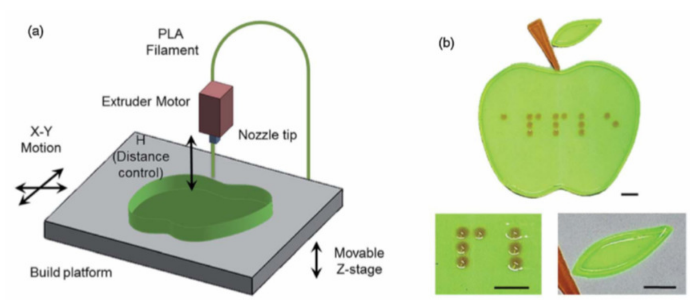

Figure 14: 3D printing system (a) and tactile Braille graphic pattern of an apple (b)[78]

In the paper industry, cellulose is mostly used as a non-conductive flexible material. However, it has been recently reported that it can also be modified to be used as a component in the design of conductive inks, since currently used conductive inks are metals.[76] Moreover, the modification of its surface can also improve its usage in the printing industry, turning it into a material that controls the surface, the drying of inks and the improvement of printing device performance.[76]

In three-dimensional (3-D) printing, cellulose and cellulosic materials are good candidates due to their bio-based properties.[76] Jo *et al.*[78] used a cellulose paper (A4, basis weight of 80 g^{-2}) as a building platform, while melted polylactic acid (PLA) was used as a filament in the 3-D printing of tactile Braille patterns. The composite had good interfacial adhesive strength, thus, the printed dots retained their original shape after printing (Fig. 14).[70,78]

Table 1
Classification of biofuels[83]

Generation	Feedstock	Examples
First-generation biofuels	Sugar, starch, vegetable oils, or animal fats	Bioalcohols, vegetable oil, biodiesel, biosyngas, biogas
Second-generation biofuels	Non-food crops, wheat straw, corn, wood, solid waste, energy crops	Bialcohols, bio-oil, bio-DMF, biohydrogen, bio-Fischer-Tropsch diesel
Third-generation biofuels	Algae	Vegetable oil, biodiesel
Fourth-generation biofuels	Vegetable oil, biodiesel	Biogasoline

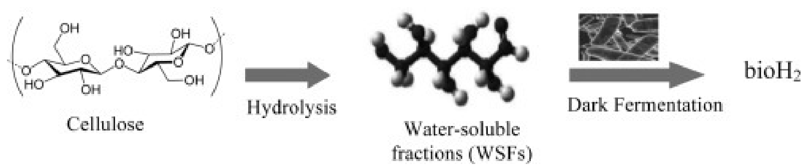

Figure 15: Conversion of cellulose into biohydrogen[81]

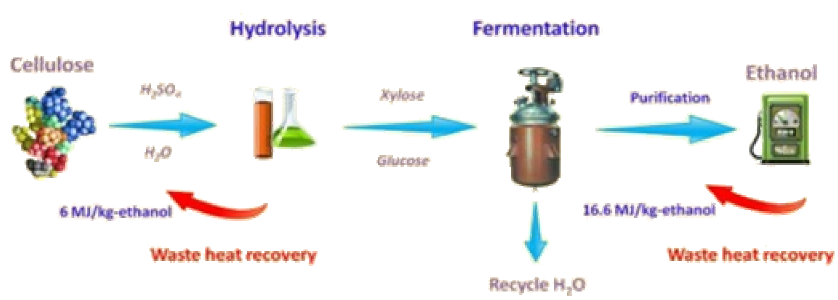

Figure 16: Bioethanol production by heat integration[85]

Biofuels

Cellulose in the form of sugar monomer (glucose) can be used in the production of biofuels by microorganisms through saccharification and fermentation processes.[79,80] Biofuels are products resulting from the chemical energy stored by biomass during photosynthesis, which are bio-converted into energy rich gases and liquids.[81] They are similar to fossil fuels based compounds, thus can be used as a renewable energy source.[82] The most important part in the conversion of sugars to biofuel is the separation of cellulose and hemicelluloses, followed by the hydrolysis of cellulose and hemicelluloses to their structural units.[81] The structural units are then converted into biofuels. Commercially, these stages need more development for efficiency. Biofuels are classified according to their generation (Table 1).[83] First-generation biofuels are less sustainable than the following generations.

Biohydrogen can be produced from structural sugars and more complex polymers, such as cellulose, by dark fermentation. Gupta *et al*.[84] co-fermented glucose, starch and cellulose to produce biohydrogen with improved hydrogen yields. Using mixed cultures under mesophilic conditions, they produced biohydrogen by a two-step system with a heterogeneous catalyst. The first step was the hydrolysis of cellulose with ZrO_2 catalyst, which resulted in water-soluble fractions (WSFs). WSFs include furfural, hydroxymethylfurfural (HMF) and acetic acid as by-products of cellulose hydrolysis. The second step was the dark fermentation of WSFs, in which different microorganisms were tested for their ability to produce bio-hydrogen (Fig. 15).[81]

Bioethanol is known as a biofuel that is a product of petrochemical synthesis. It is normally produced from biomass through cellulose hydrolysis, fermentation and purification (Fig. 16).[78,80] Balat *et al.*[86] indicated that sugar crops have the potential to yield 60% bioethanol production. In fact, it was also shown that sugarcane and corn produce more bioethanol compared to other crops. The bioethanol could apparently be utilized directly in automobiles or be blended with gasoline. Furthermore, it can also be used as an octane-boost, which is an additive used to reduce pollution in unleaded gasoline.[82] Globally, at present, bioethanol is produced by industrial fermentation, which is clearly more expensive than the petrochemical process.[86-88]

CONCLUSION

Cellulose based materials are widely studied and used in several applications due to the renewability, low cost and abundance of cellulose. Thus, they have high potential to replace fossil-based materials, which are currently a major environmental concern. The properties of cellulose based materials make them attractive for many applications, such as drug carriers, tissue engineering, packaging, electronics, emulsifiers, adhesives, fillers in composites and adsorbents.

Innovative uses of cellulose in industrial applications require retaining its biodegradability and non-toxicity. Unfortunately, many investigated applications still face a lot of challenges in implementation. For instance, recent use of ionic liquids to produce nanocellulose at a lab scale has been increasingly reported. However, ionic liquids are expensive and not applicable for industrial use. Cellulose based composites can be scaled up for industrial use, but processing parameters play a huge role in this. In composites, homogenous and uniform dispersion of nanocellulose in a matrix is still a challenge. Improvements in the methodology used in the preparation of cellulose composites for industrial applications are still needed. In the print industry, there is still a huge gap since cellulose as such is a non-conductive material. It requires modification to result in a biodegradable and environmentally friendly functional material. In electronics, the use of cellulose and cellulose based materials has not yet been applied in commercial applications. Unfortunately, this is true for most cellulose applications.

The need for pretreatment processes and cellulolytic enzymes currently hinders the application of bioethanol for commercial uses. Moreover, the biofuel production process, involving pretreatment stages to turn biomass to cellulose, followed by its hydrolysis to its structural sugars, is not commercially feasible. Further innovations are necessary to bridge this gap between research results at the laboratory level and their industrial implementation.

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