

Nanocellulose-Enabled Electronics, Energy Harvesting Devices, Smart Materials and Sensors: A Review

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ABSTRACT: Cellulose nanomaterials have a number of interesting and unique properties that make them well-suited for use in electronics applications such as energy harvesting devices, actuators and sensors. Cellulose nanofibrils and nanocrystals have good mechanical properties, high transparency, and low coefficient of thermal expansion, among other properties that facilitate both active and inactive roles in electronics and related devices. For example, these nanomaterials have been demonstrated to operate as substrates for flexible electronics and displays, to improve the efficiency of photovoltaics, to work as a component of magnetostrictive composites and to act as a suitable lithium ion battery separator membrane. A discussion and overview of additional potential applications and of previously published research using cellulose nanomaterials for these advanced applications is provided in this article. The concept of using cellulose nanofibrils in stimuli-responsive materials is illustrated with highlights of preliminary results from magnetostrictive nanocellulose membranes actuated using magnetic fields.

KEYWORDS: Cellulose nanofibrils, cellulose nanocrystals, flexible electronics, photovoltaics, batteries, magnetostrictive composites

1 INTRODUCTION

The sustainability, excellent mechanical properties and interesting physical properties of cellulose nanomaterials have recently received a great deal of attention for modifying polymers and acting as both active and passive components in a wide range of potential products. The applications for which cellulose nanomaterials have been investigated include medical and pharmaceutical applications [1–7], paper and paper-board additives [8–12], paints and coatings [13–17], security papers [18–20], food packaging [21–27], electronic devices and displays [28–32], energy harvesting and storage devices [33–36], and many more. In this article, the properties of cellulose nanomaterials that lend them to implementation in electronics, sensors, energy harvesting devices, etc., will be highlighted, and a discussion and overview of examples for these advanced applications will be provided.

Cellulose nanomaterials are a renewable resource typically created from plants, and although their inclusion in electronics, energy storage devices and sensors is certainly not a panacea for the negative environmental impact of a growing electronic waste stream, they may provide the opportunity to mitigate the problem. According to the U.S. Environmental Protection Agency, 384,000,000 electronic devices were disposed of in 2010, and 152,000,000 of those were mobile devices [37]. Few of these devices contain biodegradable or compostable components, and recovering individual constituents is costly. A number of efforts have been made to incorporate bio-derived and biodegradable materials, including cellulose nanomaterials and biopolymers, into electronic applications. Some of those efforts are included here, and one can envision a future in which sustainable materials compose a large portion of electronic devices and in which the devices can be readily recycled or possibly composted to leave recoverable metal constituents. In many cases, though, cellulose nanomaterials offer additional attributes and performance features over conventional materials that drive the research into their inclusion in electronics.

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As cellulose is broken down into nanometer-scaled particles and fibers, the materials begin to exhibit some interesting and unique properties depending on their size, morphology, charge and other characteristics. Since these properties are important to their application, a brief primer into their categorization and properties is warranted here. Typically, cellulose nanomaterials, especially from plant sources, can be categorized as either cellulose nanocrystals (CNCs) or cellulose nanofibrils (CNFs). CNCs are discrete, rod-shaped cellulose particles (Figure 1) typically with high crystallinity and are primarily produced through acid hydrolysis of native cellulose. Typically, CNCs have nanometer-scaled diameters with lengths of hundreds to thousands of nanometers, and they often contain surface charge groups and can thus be colloidally stable. Conversely, CNFs are typically network structured nanoscaled fibers (Figure 2) that can be produced from countless methods usually involving some kind of chemical treatment followed by mechanical refining. The morphology of CNFs widely varies from process to process, and they can often have a wide distribution of diameters and lengths. Another type of cellulose nanomaterial is often called bacterial cellulose as it is produced by a species of bacteria generally called *Acetobacter xylinum* [38]. The fibers produced by these bacteria have cellulose I crystallinity with diameters of tens to hundreds of nanometers [2, 39]. A number of reports have been made on using bacterial cellulose as a substrate in electronic devices [40, 41]. Most of these findings are likely transferrable to CNFs from plant-based materials. In addition, nanofibers of regenerated cellulose can be created using the gel spinning process, and such cellulose nanofibers have also been employed in electronic applications [42]. CNCs and

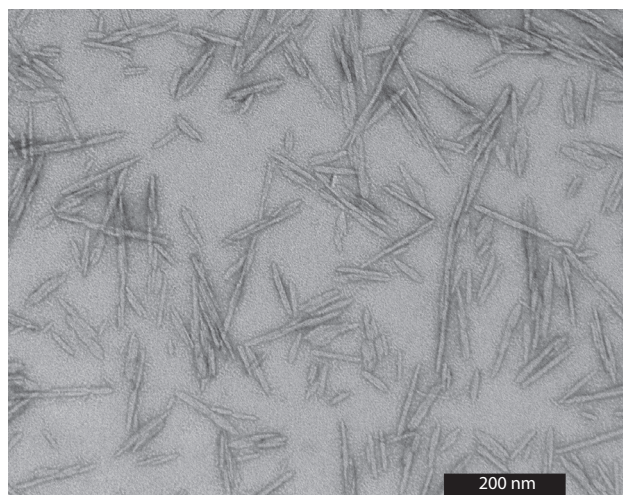


Figure 1 Transmission electron micrograph of cellulose nanocrystals from wood; scale bar is 200 nm.

CNFs each bring unique properties and applications, and both have been explored for use in electronics and functional devices.

Cellulose nanomaterials are often touted as potential polymer reinforcements because of their high strength and stiffness, and these good mechanical properties also lend these materials for use in functional devices such as electronics. The cellulose crystal has been measured to have extremely high strength and stiffness with values of about 10 GPa and up to about 200 GPa, respectively, but bulk materials, such as films, made from nanocellulose have considerably lower mechanical properties [43–47]. Nonetheless, cellulose nanomaterial films and composites have mechanical properties that rival or exceed many polymers. The tensile strength and modulus of randomly oriented CNF films, for example, are commonly as high as 200 MPa and 20 GPa, respectively [47–49]. As a comparison, polyethylene terephthalate (PET), which has been used as a substrate for flexible electronics, has tensile strength and modulus of approximately 55 MPa and 3 GPa, respectively [50–52]. Typically, only the tensile properties of CNF or CNC films are measured or reported, but their tear and bending behaviors are also important. The incorporation of polymers and other modifiers can aid in improving flexibility and improving durability, but little data is available, especially pertaining to their application in electronics and functional materials. Nonetheless, the mechanical properties of cellulose nanomaterials lend them to be employed as components in a variety of devices.

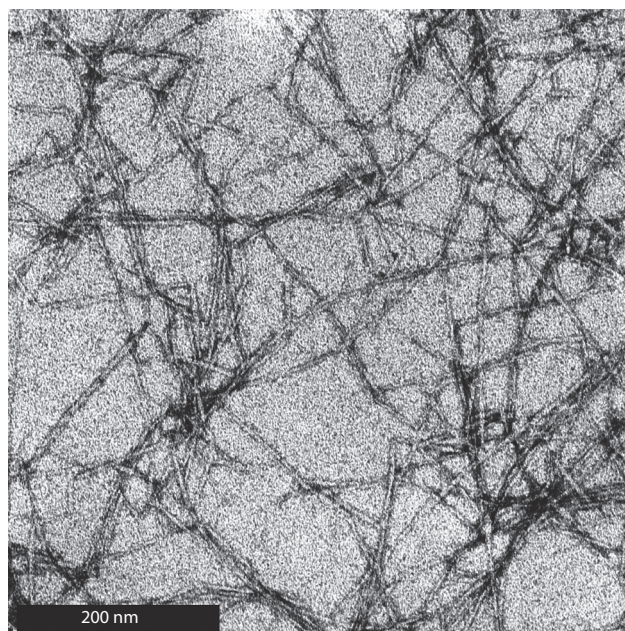


Figure 2 Transmission electron micrograph of cellulose nanofibrils from wood; scale bar is 200 nm.

The optical properties of cellulose nanomaterials are also distinctive from bulk cellulose and can be favorable for electronic applications. Films and composites made from cellulose nanomaterials, including CNCs, CNFs and bacterial cellulose, can be highly transparent (Figure 3), depending on how they are produced [41, 49, 53–58]. Fukuzumi *et al.* measured the light transmittance through a CNF film made from softwood pulp to be up to 90% but only 78% when made from hardwoods [53], and Nakagaito *et al.* compared the transparency of films made from a variety of materials, including bacterial cellulose [54]. The CNF films have also been measured to have high optical haze and strong scattering, which can potentially be exploited for photovoltaic applications [33, 34, 59]. Interestingly, CNC suspensions are also birefringent and optically active and can be assembled in films such that they exhibit tailorable and even switchable optical and color characteristics [18, 20, 46, 60]. These optical properties of cellulose nanomaterials offer enormous potential for use as electronic substrates, sensors, liquid crystal devices and more.

Cellulosic materials have low thermal expansion, which is desirable in electronic components that generate heat, and the coefficient of thermal expansion (CTE) for cellulose nanomaterials and their composites has been measured and reported for various CNF films. The thermal expansion of cellulose has been measured to be as low 0.1 ppm/K [61], and the CTE for films and composites containing cellulose nanomaterials has been reported to be as low as 1 ppm/K [62]. Bacterial cellulose typically has a lower CTE than plant-derived CNFs [54], and modification of bacterial

cellulose nanofibers was shown to be able to reduce the thermal expansion down to 1 ppm/K [62]. Nogi and Yano demonstrated that by adding only 5% of bacterial cellulose nanofibers to an acrylic resin, thermal expansion of the film from 20 to 150 °C could be reduced by more than a factor of 60 resulting in an in-plane thermal expansion of 4 ppm/K [41]. Nogi *et al.* measured the thermal expansion of “optically transparent nanofiber paper” from Douglas fir to be 8.5 ppm/K over the range of 20 to 150 °C [55], and Yagyu *et al.* measured the CTE of CNF films from wood to be 7–13 ppm/K [63]. These values are favorable compared to existing polymeric materials, which can have CTE values up to hundreds of ppm/K [43, 56]. Because low thermal expansion is important for electronics printed or deposited onto flexible substrates, cellulose nanomaterials may offer favorable properties and potentially improved performance over other polymer films.

Because of all these properties, including sustainability, high strength, flexibility, transparency and low thermal expansion, cellulose nanomaterials have been explored for their use in electronics and functional devices. In some cases, cellulose nanomaterials can provide advantages over traditional materials. For example, cellulose-based nanocomposites can overcome issues with piezoceramics such as brittleness [64], high toxicity in lead zirconate titanate (PZT) [64, 65], low energy conversion efficiency [66, 67], inability to operate under long life cycles without the issues of depolarization [68–70], and the lack of flexibility to operate under strong ambient vibrations [71, 72]. An overview of many of these applications is provided here, but this account is not intended to be comprehensive. Instead, this work aims to provide a broad perspective of how cellulose nanomaterials may play a role in electronics such as sensors, actuators, displays and energy harvesting devices.

2 SUBSTRATE MODIFICATION

Substrate quality is critical for the fabrication and performance of electronics on cellulose substrates, and methods for improving CNF substrates electronics have been explored and continue to be the focus of both research and commercialization efforts [30, 73–75]. Low surface roughness, strong water resistance and robust mechanical properties are all desirable properties for electronic substrates, and in many cases, cellulose nanomaterials may require modification or improvements to meet those needs. Torvinen *et al.* evaluated the effects of composition and processing on the properties of composite films containing CNF inorganic filler [75]. They found that



Figure 3 Cellulose nanofibril film overlaid on Forest Service logo.

calendering produced mechanically stable and flexible sheets with smooth surfaces on which silver nanoparticle ink could be printed. The films had similar surface roughness and sheet resistance as those from reference materials, including polyethylene terephthalate (PET), and they concluded that these CNF composite substrates would be suitable for use in electronic applications, such as RFID sensors and tags. For the case of transferring silicon nanomembrane (Si NM) devices to cellulose substrates, both the substrate coating and adhesive layers were found to affect the transferability to the substrate [30]. Thin, smooth epoxy layers resulted in better transfer to the substrate and also provided enough protection to limit swelling during subsequent wet cleaning steps. Couderc *et al.* coated CNF sheets with thin polyimide layer, which improved the dielectric properties, reduced the moisture uptake and decreased surface roughness [76]. Chinga-Carrasco *et al.* created CNF films modified with hexamethyldisilazane to improve water resistance and printability [73], and Shimaoka *et al.* reported a proprietary modification process producing films with substantially reduced moisture uptake and with low brittleness, such that they could be bent and rolled tightly without cracking [74]. Therefore, despite some of the drawbacks of pure CNF films, such as large moisture absorption, modifications and processing techniques have been demonstrated to yield CNF films suitable for electronic applications.

3 FLEXIBLE ELECTRONICS

Because cellulose nanofibril films can be transparent, have low CTE, are flexible and have good mechanical properties, they are excellent candidates for substrates for flexible electronics. A number of methods for creating electronics on cellulose nanomaterial substrates have been demonstrated and include printing circuits directly onto the substrates, using coating and thermal

deposition techniques and transferring prefabricated devices onto CNF substrates. The results from some of these electronic devices on nanocellulose substrates are described below.

Researchers at the University of Wisconsin and the USDA Forest Service Forest Products Laboratory recently demonstrated that high-speed transistors on silicon nanomembranes can be fabricated onto CNF films, as shown in Figures 4 and 5 [28, 30]. These flexible electronics were built by first fabricating the device on a special silicon wafer that allows thin silicon nanomembranes (Si NMs) to be released and then by transferring the Si NM to a CNF substrate. In the first step (Figure 5i), the n+ wells for the source and drain regions were formed using a spin-on-dopant diffusion process carried out in a nitrogen and oxygen ambient furnace at 850 °C for 20 minutes. Next, the thin silicon layer was released by wet etching with hydrofluoric acid (Figure 5ii), then the electrodes were

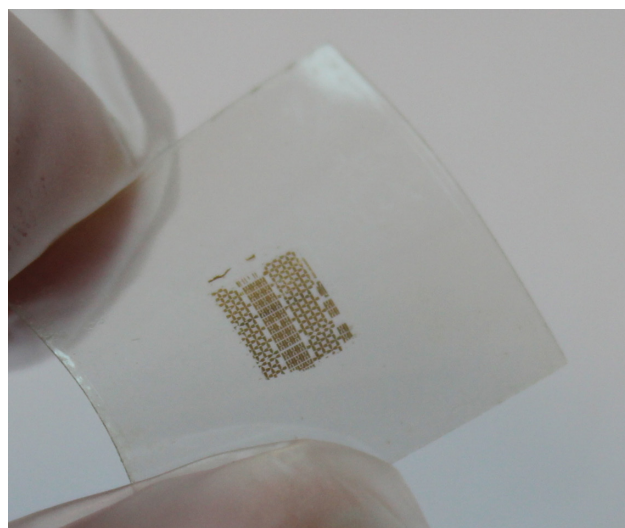


Figure 4 Flexible electronics on cellulose nanofibril substrate.

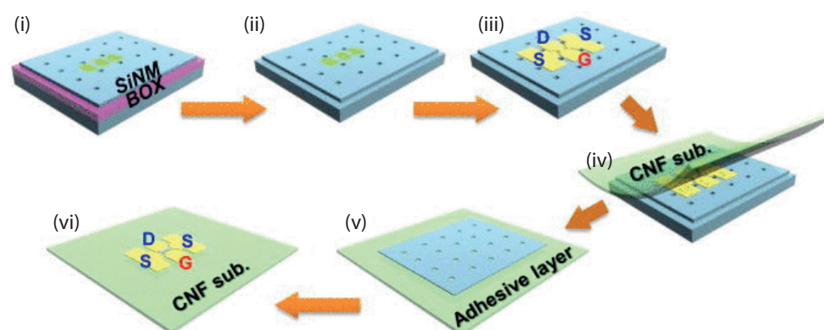


Figure 5 Schematic of production process for flexible electronics on CNF substrate. (Reprinted with permission from [28]; Copyright 2015 AIP Publishing LLC)

created (Figure 5iii). Next the Si NM was transferred to a CNF substrate with an adhesive layer (Figure 5iv–v), and finally the device was completed by photoresist patterning and dry etching steps (Figure 5vi). This thin-film transistor (TFT) built on the CNF substrates was demonstrated to operate in the microwave range with a transition frequency of 4.9 GHz while flat and 3.8 GHz while bent [28]. The substrate was found to have low gate leakage and field effect mobility values consistent with other Si NM transistors. The substrate was also shown to exhibit biodegradability, which could potentially offer opportunities to recover rare metals used in electronics. Such high speed electronics have numerous potential applications for communication and computation devices, and preliminary investigations show that cellulose nanomaterials perform satisfactorily.

In a more recent report from this group, various working electronic devices were fabricated on CNF substrates [31]. They reported an environmentally friendly method for creating gallium arsenide microwave devices on CNF substrates with performances comparable to those made on rigid devices. They also created Si-based complementary metal–oxide–semiconductor (CMOS) devices, including logic gates and a full adder, which worked at frequencies up to 5 kHz, as shown in Figure 6. The working characteristics of these devices were clearly shown, indicating that full circuits and working electronics can be created on CNF substrates.

In another example, flexible organic field-effect transistors (OFETs) were fabricated on flexible, transparent cellulose “nanopaper,” which was created by oxidation and mechanical refining of bleached softwood Kraft pulp [29]. They created CNF films with surface roughness of about 5 nm, transparency of 90% and coefficient of thermal expansion as low as 12 ppm/K. A transparent, conductive carbon nanotube layer was then coated onto the CNF substrate, followed by spin-coating of a poly(methyl methacrylate) (PMMA) dielectric layer. Next, they vacuum deposited an n-type organic semiconductor NTCDI-F15, a naphthalenetetracarboxylic diimide derivative. Finally, they evaporated silver electrodes through shadow masks onto the semiconductor. The device was reported to “exhibit good n-type transistor characteristics” and had effective carrier mobility of $4.3 \times 10^{-3} \text{ cm}^2/(\text{Vs})$ and $I_{\text{on}}/I_{\text{off}}$ ratio up to 200. The mobility only decreased by about 10% when the device was bent either parallel or perpendicular to the conduction channel direction. They also noted that, unlike other organic semiconductor devices, the good bonding between CNF and carbon nanotubes (CNTs) diminished the problem of protruding CNTs, which can cause an electrical short circuit. The highly transparent, flexible CNF substrate

exhibited excellent properties as a field-effect transistor substrate.

Printed electronics are another application in which cellulose nanomaterials have been demonstrated to be suitable as substrates [32, 63, 77, 78]. Printed electronics often employ inks consisting of nanometer-scale silver particles in suspension, but carbon nanotube (CNT)-CNF mixtures have also been suggested as potential conductive inks with the CNFs acting as the dispersing agent [78]. Nge *et al.* demonstrated that silver nanoparticle tracks printed on CNF substrates show lower electrical resistance than those printed on commonly used plastics such as polyimide and poly(ethylene naphthalate) (PEN) [77]. Those conductive tracks on CNF substrates showed better electrical performance during and after folding than those on plastic substrates. In another example, flexible silver antennas were printed on crosslinked CNF films using gravure printing techniques [32]. The devices were demonstrated to have good radio frequency performance for application in radio frequency identification (RFID) antenna tags. Although printed electronics do not typically match the performance of typical silicon-based electronics, there are a wide range of applications, including light-emitting diodes, sensors, medical devices, and radio frequency identification (RFID) antennas, for which CNF substrates can potentially be employed [79].

4 DISPLAYS AND LIGHT-EMITTING DIODES

Using CNFs as substrates for light-emitting diodes and displays has received a great deal of attention, including from electronics manufacturers, over the last several years. Okahisa *et al.* reported successful fabrication of an organic light-emitting diode (OLED) device on wood-based cellulose nanofibril composites [56] (Figure 7). They acetylated the CNFs, impregnated them with different acrylic resins and found the composite fabrication and formulation critical to the ability to fabricate a working device. The fabrication of the device involved multiple steps adopted from a device created on polymer substrates [80]. First, a smoothing layer was spin-coated on a CNF composite film, then a silicone oxynitride (SiON) barrier film was sputter deposited. The anodes were created by sputter deposition and patterning; the organic layers were vacuum deposited, and the cathode was fabricated by vacuum deposition. Finally, a passivation film layer was created by chemical vapor deposition. The device was able to illuminate lettering expressing the researcher’s affiliations. Legnani *et al.* produced OLEDs on bacterial cellulose membranes by depositing indium tin oxide thin films using radio frequency

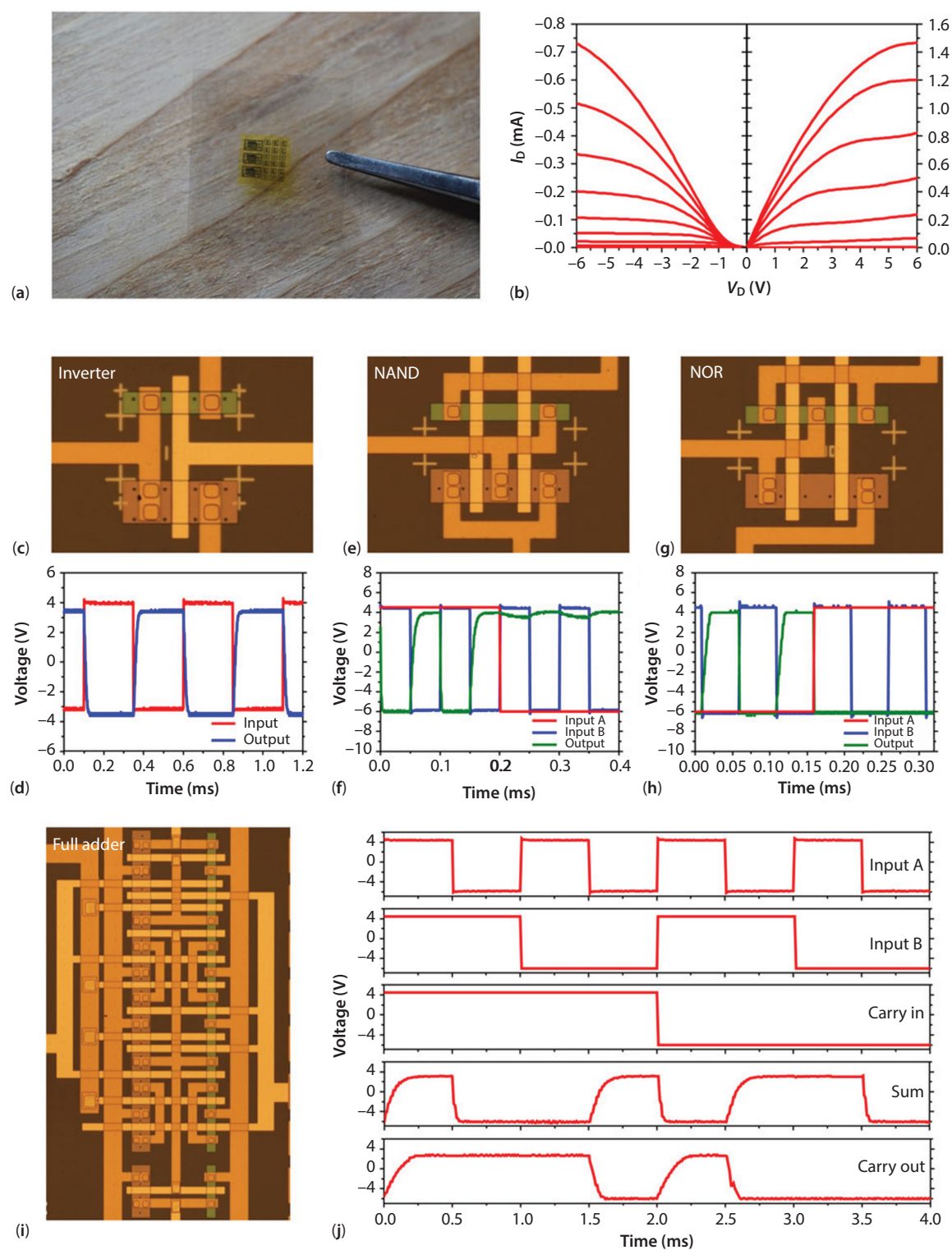


Figure 6 Digital electronics on CNF. (Reprinted under Creative Commons license from [31])



Figure 7 Flexible display on CNF substrate. (Reprinted with permission from [56]; Copyright 2009 Elsevier)

sputtering at room temperature [40]. Although their membranes had less than ideal optical transmittance, they achieved promising results with luminance levels up to 1200 cd/m². In another example, Yagyu *et al.* illuminated light-emitting diodes on CNF substrates by printing silver nanoparticles on the substrate followed by heat curing at up to 160 °C [63]. They found that the type and treatment of CNF used was important in reducing discoloration of the device and that heat treatment at temperatures above 150 °C was necessary to achieve good electrical conduction. The advancement of light-emitting diodes on cellulose nanofibril substrates could lead to devices with curved or bendable displays made on transparent, renewable substrates.

5 OPTO-ELECTRONICS

Another exciting application for cellulose nanomaterials is liquid crystal displays (LCDs) and other electro-optical devices. Cellulose nanocrystal suspensions display liquid crystal behavior, and the CNCs can be aligned under an electric field, making them potentially suitable for optical devices or displays [81–83]. By altering the electrical signal through the CNC suspensions, the orientation of the CNCs and thus transmittance of light can be controlled [82, 83]. Limited research for the use of CNCs in this manner is available, so it's difficult to know whether CNCs offer advantages over other materials for LCDs, but the opto-electric effect is a property that could potentially have a number of interesting applications.

6 ENERGY HARVESTING AND STORAGE

A number of energy harvesting and storage applications have been successfully fabricated using cellulose

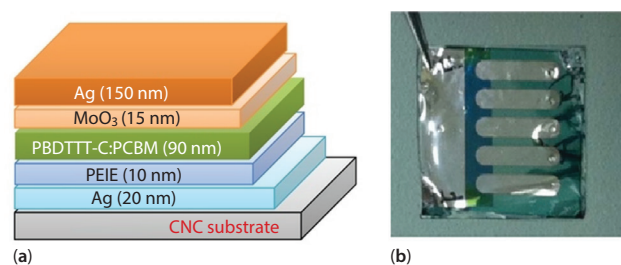


Figure 8 Schematic (a) and photograph (b) of organic solar cell on cellulose nanocrystal substrate. (Reprinted in part with permission from [93]; Copyright 2013 Macmillan Publishers Ltd.)

nanocrystals and nanofibrils. Cellulose nanomaterials have been used for energy harvesting in solar cells [33, 34, 36] and for energy storage in battery electrodes, as solid ion-conducting electrolytes and as separator membranes for Li-ion batteries, and a few examples of these applications are provided here [84–92]. In some cases, the cellulose nanomaterials were shown to offer unique improvements or perform as well or better than conventional materials.

Cellulose nanomaterials have been successfully incorporated as components of photovoltaics as evidenced by multiple reports [33, 34, 36]. Hu *et al.* demonstrated a working organic photovoltaic on cellulose nanofibril substrate [34]. In this example, the cellulose nanofibril substrates were made conducting by deposition of a tin-doped indium oxide layer. The organic layers were spin-coated and heat treated in multiple steps onto the substrate, and then metal electrodes were thermally evaporated onto the film. This organic solar cell on cellulose nanofibrils substrate was measured to have a power conversion efficiency lower than the control but which could likely be improved through processing improvements. Using a similar approach for constructing solar cells, Fang *et al.* demonstrated that the high transparency and optical haze of CNF films can be advantageously exploited to improve the power conversion efficiency of an organic solar cell by 10% simply by laminating it with a CNF film [33]. They measured the transparency and optical haze of the CNF film to be 96% and 60%, respectively, and the device had a power conversion efficiency of 5.88%. Zhou *et al.* produced a recyclable organic solar cell on a cellulose nanocrystal substrate, as shown in Figure 8, and they demonstrated the device could be readily deconstructed into its constituent components using a low energy process [93]. The device was fabricated by first depositing a semitransparent silver layer on the CNC film, which had nanometer-level roughness that eliminated the need for planarization. Organic photoactive layers were spin-coated onto the silver layer, and metal contacts were evaporated onto

the photoactive layers. The device reached a power conversion efficiency of 2.7% and demonstrated a potential approach for using sustainable cellulose nanomaterials as a component in recyclable electronic components.

Cellulose-based materials have been widely explored for use in batteries, and using cellulose nanomaterials is a natural extension for battery applications [85, 94]. Flexible electrodes for batteries and other applications have been created using cellulose nanomaterials as binders, templates, etc., in conjunction with conductive materials [84, 87, 88, 90]. For example, Jabbour *et al.* used graphite and cellulose nanofibrils, which they referred to as microfibrillated cellulose, to create flexible electrodes for batteries [84]. They found the electrodes had a conductivity of about 0.3 S/cm even as they were rolled around hoses with radii ranging from 3 to 32 mm, but this conductivity was significantly lower than reference electrodes. The electrode had specific discharge capacity close to the theoretical specific capacity of graphite and good cycling performances, and they expressed high optimism for cellulose nanomaterials to play a role as electrodes in electronic devices. In another example, flexible silicon-conductive cellulose nanopaper was demonstrated as a functional Li-ion battery electrode [87]. This electrode was fabricated by first creating a CNF-carbon nanotube (CNT) aerogel, followed by plasma-enhanced chemical vapor deposition (PECVD) of a thin silicon layer in the porous aerogel channels. The electrode performance was evaluated in coin-type Li-ion battery for up to 100 charge/discharge cycles, and they concluded that the electrode performed quite well with the discharge capacity remaining above 1200 mA h/g, which is more than three times the theoretical capacity of conventional graphite anodes. Such examples demonstrate the role that cellulose nanomaterials can play in electrodes for batteries and other applications and how they can be incorporated with other nanotechnology for advanced applications.

Cellulose nanofibrils also have the potential to replace thermoplastic polymer films as membrane separators for Li-ion batteries [85, 88, 91]. For example, Chun *et al.* compared the performance of separators made from CNFs created by high-pressure homogenization to a commercially available tri-layer polypropylene/polyethylene/polypropylene (PP/PE/PP) separator and found that the CNF separator showed comparable electrochemical performance to the commercial one. Furthermore, they concluded that the CNF separator offered some potential advantages over the PP/PE/PP separator, including improved ionic conductivity, electrolyte wettability, and thermal shrinkage. The thermal shrinkage of the CNF separator was judged to be negligible as compared to 36% for the PP/PE/PP one, which could lead to improved electrode isolation and safety of Li-ion batteries. Leijonmarck *et al.* reported a process in which the electrodes and separator were created from cellulose nanofibrils in a sequential filtration process as shown in Figure 9 [88]. The result of the sequential filtration process was a flexible, single-paper Li-ion battery cell, as shown in Figure 10. The anode consisted of CNFs, graphite and Super-P carbon; the cathode consisted of CNFs, LiFePO_4 , and Super-P carbon; and the separator contained CNFs and SiO_2 . The paper batter was soaked in electrolyte, then copper and aluminum foil charge collector were placed on the negative and positive sides of the battery, respectively, and the battery cells were sealed in a pouch. They tested the electrochemical performance of the battery cells and found that they could be used for hundreds of charge cycles while maintaining a large part of their capacity. They also found that the battery could work while being bent, indicating their applicability in flexible devices. Therefore, in addition to potentially improving the sustainability and environmental impact of battery components, cellulose nanomaterials could offer improvements over conventional Li-ion battery separator properties.

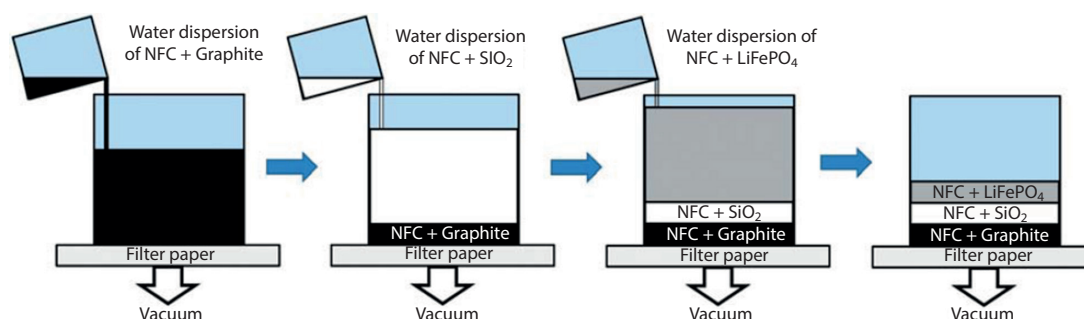


Figure 9 An illustration of the sequential filtration steps during the production of a paper battery cell. (Reproduced with permission from [88]; The Royal Society of Chemistry)

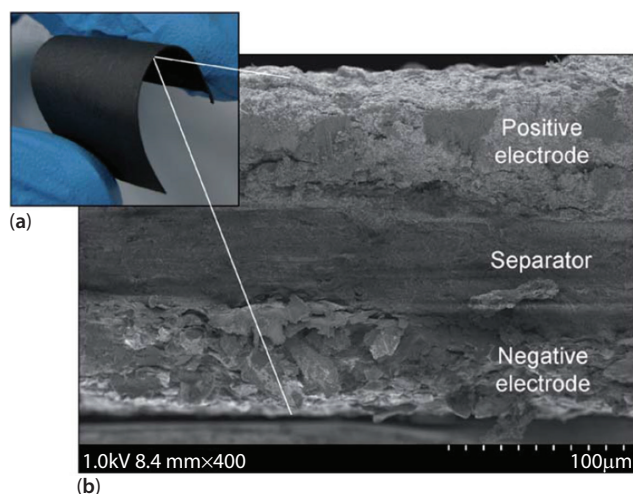


Figure 10 (a) Photograph illustrating the flexibility of a paper battery. (b) SEM image of a paper battery cross-section. (Reproduced with permission from [88]; The Royal Society of Chemistry)

Cellulose nanomaterials have also been demonstrated to play a role as a component in supercapacitor devices [42, 95–99]. Electrochemical capacitors are energy storage devices that operate by rapid charging/discharging at the interface between an electrode and electrolyte, and various studies have employed CNFs or CNCs as components of the electrodes [95–99]. In some cases, cellulose nanofibers were used as sacrificial precursors to produce carbonized fibers through high-temperature treatments and activation [42, 96]. In the case of carbonized nanofibers, working electrodes were essentially prepared by mixing the carbonized fibers with binders (polyvinylidene fluoride or polytetrafluoroethylene) and carbon or acetylene black and pressed into a flat electrode [42, 96]. In other cases, the cellulose nanomaterials were used as a component of composite electrodes [97–99]. These composite electrodes were fabricated by using cellulose nanomaterials and conducting polymers such as polyaniline [97, 98] or polypyrrole [99]. For example, Zhang *et al.* started with a CNF aerogel, coated silver onto the aerogel, then electrodeposited polyaniline (PANI) onto the aerogel [98]. The supercapacitor was fabricated by soaking aerogels in polyvinyl alcohol/phosphoric acid electrolyte gel, sandwiching a glass filter paper separator between two of these electrodes, then allowing the assembly to dry. They found the specific capacitance of these supercapacitors to be as high as 176 mF cm^{-2} and that there was almost no change under bending. In another example, Liew *et al.* used cellulose nanocrystals coated with a thin film of polypyrrole to create a highly porous electrode structure [99]. They found the cellulose nanocomposite to

have a high capacitance (256 F/g) and rapid charge/discharge, which they attributed to the porous 3-dimensional structure of the composite. They compared the cellulose composite supercapacitor to one made with carbon nanotubes (CNTs) and found that the cellulose nanocomposite was more durable than the CNT one with comparable performance. Cellulose nanomaterials have successfully been demonstrated to work in capacitor devices, which can complement or replace batteries in devices needing rapid charge/discharge properties and may play a role in both rigid and flexible electronic devices.

Cellulose nanocomposites containing CNCs and polydimethylsiloxane (PDMS) were shown to be capable of harvesting energy by exploiting the triboelectric effect, which converts mechanical energy to electricity [100, 101]. The initial CNC suspension was wet ball-milled, freeze-dried and ground to produce CNC flakes. The CNC flakes were mixed with PDMS and spin-coated into films. Aluminum electrodes were used, and the separation distance was adjusted by a programmed solenoid. Period compressions were applied to the film assemblies, and the output voltages were measured using an oscilloscope. The cellulose nanocomposites showed three times the voltage output and over ten times the maximum power value compared to pure PDMS films. Cellulose nanocomposites have the potential to be incorporated in energy harvesting devices, exploiting energy from ocean waves, human movement, air flow and more.

7 SENSORS

Cellulose nanomaterials have also been exploited as sensors and stimuli-sensitive functional materials, including for use in biomedical applications [102–106]. For example, Nielsen *et al.* modified CNCs with dual fluorescent labeling to create ratiometric pH-sensing nanoparticles [103]. The emission spectra of the CNC suspension varied with pH, and the ratio of intensity at multiple wavelengths showed clear transitions as a function of pH. Edwards *et al.* demonstrated that peptide modified CNCs in tandem with a cellulose membrane could be used as a biosensor wound dressing to detect a destructive protease [104]. In another example, pyrene-modified CNCs were demonstrated to be highly selective to sensing Fe^{3+} with good discrimination between Fe^{2+} and Fe^{3+} , demonstrating that cellulose nanomaterials have potential application as chemical sensors [105]. Modified cellulose nanomaterials have been shown to be responsive to the presence of specific chemicals and conditions, and one can imagine combining this sensing capability with cellulose-based electronic devices to create

fully functional electronic sensing devices for use in biomedical or chemical analysis applications.

8 PIEZOELECTRIC AND ELECTROACTIVE EFFECTS IN CELLULOSE NANOMATERIALS

Cellulose nanomaterials have also been demonstrated to display piezoelectric and electroactive effects, which potentially can be exploited for use as actuators and sensors in a wide range of devices, including microelectromechanical systems, robotics, speakers, micropumps and more [107–110]. For example, Csoka *et al.* demonstrated that thin CNC films demonstrated a piezoelectric effect with an effective shear piezoelectric constant of $2.1 \text{ \AA/V}$, which is comparable to a reference ZnO film [109]. Jeon *et al.* demonstrated that bacterial cellulose films exhibited electrically driven bending deformation, which could be enhanced by chemical modification [110]. Nanocellulose-based actuators and electroactive devices have enormous potential, but there exists a fairly wide gap in fundamental understanding of these effects as well as a lack of effective demonstration of these materials in devices compared to existing materials.

9 MAGNETIC CELLULOSE NANOCOMPOSITES IN AEROGELS AND NANOPAPER

Composite materials offer a unique opportunity of combining two or more materials that retain their individual properties but when combined can produce new features. An example of this composite approach is the efforts to integrate magnetic particles within cellulose materials. A hydrophobic cellulose aerogel composite was previously prepared with magnetic nanoparticles for oil absorption applications [111]. The principle of this composite is that the cellulose would absorb the oil from a spill and then be magnetically retrieved. The aerogel produced was able to absorb oil up to about 28 times of its own weight within 10 minutes and could be easily removed and recovered from the water surface by an external magnet. Olsson *et al.* were able to make magnetic aerogels and nanopaper using cellulose nanofibrils as templates by facilitating the growth of ferromagnetic cobalt ferrite nanoparticles [112]. The nanocellulose is then compacted to make stiff magnetic nanopaper. The nanofibrils act as templates for the ferromagnetic nanoparticles. Their flexibility, high porosity and surface area make them attractive for use in microfluidics or electronic actuators. Researchers have also shown the ability to

incorporate magnetic particles with cellulose materials by coprecipitation methods [113–115]. Cobalt ferrite nanotubes with an average diameter of 217 nm were synthesized by coprecipitation using freeze-dried bacterial nanocellulose as template [116]. The metal precursors (Fe^{3+} and Co^{2+} ions) bind to cellulose nanofibrils via electrostatic interactions between the hydroxyl groups (electron-rich oxygen atoms) of the nanocellulose and electropositive transition metal cations. The authors were able to show magnetic behavior at room temperature that they attributed to the fraction of nanoparticles in superparamagnetic state.

10 MAGNETOSTRICTIVE CELLULOSE NANOCOMPOSITES FOR ACTUATION AND SENSING

In ferromagnetic materials, magnetostriction leads to the variation of their physical geometries according to an external magnetic field. The magnetostrictive effect is usually negligible for regular materials like nickel. The advent of rare earth iron alloys, such as Terfenol-D, that exhibit giant magnetostrictive effect has led to the promising development of sensors and energy harvesting devices requiring higher energy density, faster response and better precision. Additionally, the magnetostrictive effect has been used in transducers for applications in sonars [117–119], energy harvesting [120–123], active vibration control [124–126] and position control systems [127, 128]. However, the monolithic Terfenol-D materials are heavy and not easily moldable into desirable shapes for sensor and actuator fabrication; they are still relatively brittle and can only withstand small strains to failure [129]. A potential remedy is to take advantage of the superb mechanical properties of the nanocellulose matrix to form a magnetostrictive composite with magnetostrictive particles. The structure of the cellulose nanofibers provides a layered substrate for magnetostrictive materials. Since the resulting composite is in the form of film and inherit magnetic properties from magnetostrictive particles, it is known as magnetostrictive nanocellulose membrane (MNM).

For magnetostriction, the Joule effect describes the change in length due to a change in the magnetization state of the material. Consequently, the magnetic field can be used to actuate or morph the flexible MNM. Whereas through the inverse magnetostrictive effect (also known as the Villari effect), the mechanical stress will change the magnetic susceptibility of a material. Since the film is expected to respond to changes in the external mechanical stresses by changing its magnetic state, these changes in the magnetic state can induce voltage in coil(s) in accordance with Faraday's law, which can then be readily used to deliver power to an

electrical load. Moreover, a magnetic field can be used to optimize magnetostrictive properties of the composite by favorably aligning particles [130–133] during the processing stage (Figure 11). Figure 12 shows a unimorph nanocellulose composite that is actuated by a magnetic field and the Joule effect. The magnetic field is cycled from 0 to 2 kOe and back down in 200 Oe increments.

The composite material fabrication procedure generally followed the CNF preparation procedure discussed in earlier literature [134], with additional steps for introducing Terfenol-D particles. Filtration was carried out until approximately 80% of the water by volume was removed from the composite. An identical volume of CNF slurry was then added atop the partially filtered layer, this time without any Terfenol-D particles. This was done to create a unimorph structure which would allow the material to bend instead of linearly deforming under an applied magnetic field. Filtration was again carried out until approximately 80% water was removed from the material. At this point, the sample was removed from the filtration vessel, and sandwiched between two sheets of wax paper with absorptive pads on either side. The stack was then pressed at 100 N for 24 hours while sitting atop a layer of silica gel desiccant which drew out remaining water.

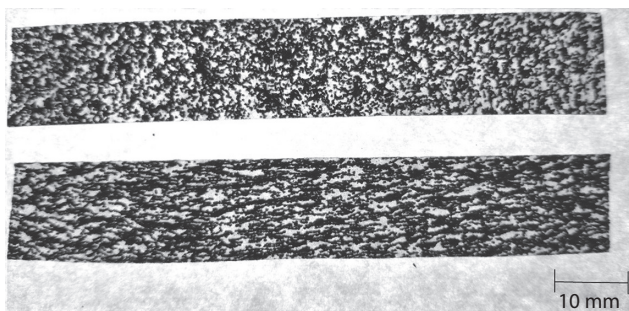


Figure 11 Nanocellulose membranes with magnetostrictive materials (top: random and bottom: aligned).

Testing of the composite was performed via a video extensometry method, using DC magnetic fields inside a laboratory electromagnet to actuate the sample. The magnet was placed atop a damped optics table to eliminate random vibrations from the environment. An optical microscope (Stemi 2000-C, Carl Zeiss AG, Germany) equipped with a digital camera (AxioCam ICc 1, Carl Zeiss AG, Germany) was mounted to the electromagnet for the purpose of non-contact displacement measurement. A black and white grating pattern was painted at the tip of both edges of the particle-containing sample. The sample was then cantilevered within the center of the electromagnet air gap, with length direction along the central axis of the pole pieces. Ten cycles of a low frequency AC magnetic field were applied to the sample in order to relax any residual stresses introduced during the mounting procedure. DC current was supplied to the electromagnet such that the magnetic field strength incremented by 200 Oe, completing a full loop between -2 kOe and 2 kOe. An optical microscope image of the sample was captured at each increment. The image sequence obtained was then converted to a video file, and the angular displacement of the sample as a function of magnetic field strength was extracted by tracking the painted-on grating with open source video analysis software (Tracker). The process was repeated with the sample flipped over in its holder, and its other edge in view of the microscope. A total of five trials were performed for each sample at each orientation. Images of a sample with grating being analyzed in Tracker can be seen in Figure 12.

Figure 13 shows the angular deflection data for a 30% volume fraction Terfenol-D/CNF unimorph composite film compared with a control sample containing an equal volume of non-magnetostrictive grade 68 ferrite particles. In addition to lacking appreciable magnetostrictive properties, the 68 ferrite has comparable initial DC magnetic permeability to that of Terfenol-D. As such, the control sample experiences

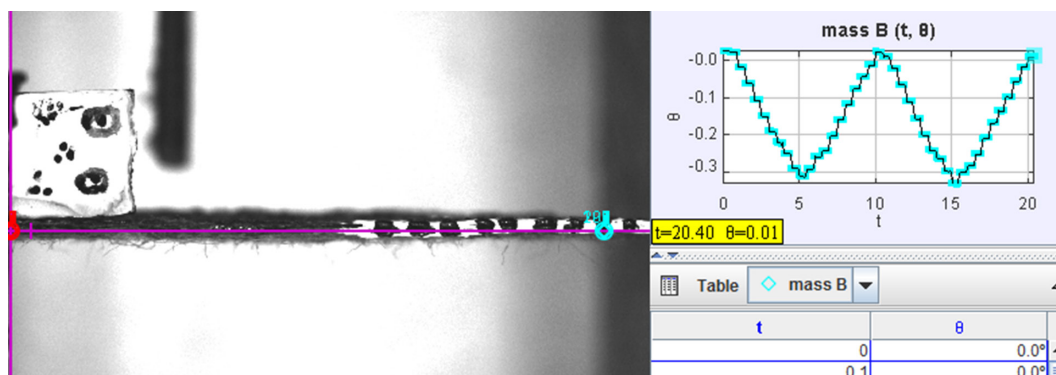


Figure 12 Angular deflection data being extracted from microscope images of samples during testing.

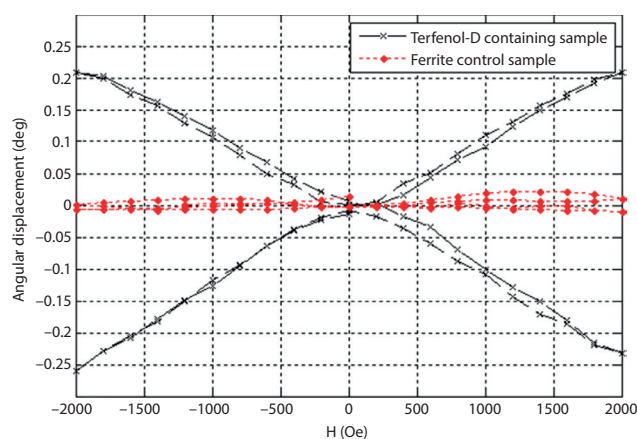


Figure 13 Angular deflection data comparing unimorph CNF composite films containing magnetostrictive and non-magnetostrictive particles.

an approximately equivalent attractive force in a static magnetic field. The data shows both positive and negative angular deflections for the Terfenol-D-containing sample, due to the fact that the sample was flipped over as mentioned previously. This reversal, one indicator of magnetostriction, is in contrast to the unidirectional deflection caused by magnetic attraction. Peak angular deflections at 2 kOe magnetic field of 0.26° and 0.21° were observed depending on sample orientation. The difference is likely attributable to imperfect sample alignment with the magnetic field direction, caused by some deformations of the composite film during the drying stage of the manufacturing procedure. In addition, it has been previously reported that localization and boundary effects relative to the distribution of the Terfenol-D particles in a composite may contribute to the variability in the response [135]. Regardless, the virtually nonexistent response of the control sample and the deflection reversal when the Terfenol-D sample is flipped strongly indicate that a magnetostrictive response is being observed in the fabricated unimorph specimens.

11 CONCLUSIONS

Cellulose nanomaterials are a relatively new class of materials that are receiving increased attention for a wide variety of applications because of their sustainability and unique properties. Cellulose nanofibrils and cellulose nanocrystals have been used in electronics, display devices, including organic light-emitting diodes, energy harvesting devices, such as photovoltaics, magnetic and magnetostrictive composites, as battery electrodes and separators, and many other functional or advanced applications. In addition to potentially improving the environmental impact and

sustainability of function materials, cellulose nanomaterials often provide improved functionality and/or durability for these applications. Films from cellulose nanomaterials have high transparency, high optical haze, low thermal expansion coefficient and good mechanical properties, thus offering some advantages over traditional materials, such as thermoplastics. As the economics and availability improve, these nanomaterials are expected to find a variety of commercial applications in functional devices.

REFERENCES

1. S. Innami and Y. Fukui, Additive composition for foods or drugs, US Patent 4659388, assigned to Daicel Chemical Industries, Ltd. (April 21, 1987).
2. C.J. Grande, F.G. Torres, C.M. Gomez, and M.C. Bañó, Nanocomposites of bacterial cellulose/hydroxyapatite for biomedical applications. *Acta Biomater.* **5**(5), 1605–1615 (2009).
3. N. Lin and A. Dufresne, Nanocellulose in biomedicine: Current status and future prospect. *Eur. Polym. J.* **59**, 302–325 (2014).
4. P. Gatenholm and D. Klemm, Bacterial nanocellulose as a renewable material for biomedical applications. *MRS Bull.* **35**(03), 208–213 (2010).
5. N. Petersen and P. Gatenholm, Bacterial cellulose-based materials and medical devices: Current state and perspectives. *Appl. Microbiol. Biotechnol.* **91**(5), 1277–1286 (2011).
6. A.P. Mathew, K. Oksman, D. Pierron, and M.F. Harmand, Biocompatible fibrous networks of cellulose nanofibres and collagen crosslinked using genipin: Potential as artificial ligament/tendons. *Macromol. Biosci.* **13**(3), 289–298 (2013).
7. A.P. Mathew, K. Oksman, D. Pierron, and M.-F. Harmad, Crosslinked fibrous composites based on cellulose nanofibers and collagen with in situ pH induced fibrillation. *Cellulose* **19**(1), 139–150 (2012).
8. D. Klemm, F. Kramer, S. Moritz, T. Lindström, M. Ankerfors, D. Gray, and A. Dorris, Nanocelluloses: A new family of nature-based materials. *Angew. Chem. Int. Ed.* **50**(24), 5438–5466 (2011).
9. F.W. Brodin, Ø.W. Gregersen, and K. Syverud, Cellulose nanofibrils: Challenges and possibilities as a paper additive or coating material—A review. *Nord. Pulp Pap. Res. J.* **29**(1), 156–166 (2014).
10. C. Hii, Ø.W. Gregersen, G. Chinga-Carrasco, and Ø. Eriksen, The effect of MFC on the pressability and paper properties of TMP and GCC based sheets. *Nord. Pulp Pap. Res. J.* **27**(2), 388–396 (2012).
11. K. Mörseburg and G. Chinga-Carrasco, Assessing the combined benefits of clay and nanofibrillated cellulose in layered TMP-based sheets. *Cellulose* **16**(5), 795–806 (2009).
12. R. Guimond, B. Chabot, K.N. Law, and C. Daneault, The use of cellulose nanofibres in papermaking. *J. Pulp Pap. Sci.* **36**(1), 55–61 (2010).

13. K. Syverud, A novel application of cellulose nanofibrils for improving the water resistance of commercial paints, in: *Eleventh International Conference on Wood and Biofiber Plastic Composites*, (2011).
14. K. Dimic-Misic, T. Salo, J. Paltakari, and P. Gane, Comparing the rheological properties of novel nanofibrillar cellulose-formulated pigment coating colours with those using traditional thickener. *Nord. Pulp Pap. Res. J.* **29**(2), 253–270 (2014).
15. K. Dimic-Misic, P.A.C. Gane, and J. Paltakari, Micro- and nanofibrillated cellulose as a rheology modifier additive in CMC-containing pigment-coating formulations. *Ind. Eng. Chem. Res.* **52**(45), 16066–16083 (2013).
16. J. Cowie, E.M. Bilek, T.H. Wegner, and J.A. Shatkin, Market projections of cellulose nanomaterial-enabled products – Part 2: Volume estimates. *TAPPI J.* **13**(6), 57–69 (2014).
17. J.A. Shatkin, T.H. Wegner, E.M. Bilek, and J. Cowie, Market projections of cellulose nanomaterial-enabled products – Part 1: Applications. *TAPPI J.* **13**(5), 9–16 (2014).
18. J.-F. Revol, L. Godbout, and D.G. Gray, *Solidified Liquid Crystals of Cellulose with Optically Variable Properties*, US Patent 5,629,055, assigned to Pulp and Paper Research Institute of Canada, (May 13, 1997).
19. J.P.F. Lagerwall, C. Schütz, M. Salajkova, J. Noh, J.H. Park, G. Scalia, and L. Bergström, Cellulose nanocrystal-based materials: From liquid crystal self-assembly and glass formation to multifunctional thin films. *NPG Asia Mater.* **6**(1), e80 (2014).
20. S. Beck, J. Bouchard, and R. Berry, Controlling the reflection wavelength of iridescent solid films of nanocrystalline cellulose. *Biomacromolecules* **12**(1), 167–172 (2010).
21. N. Lavoine, I. Desloges, A. Dufresne, and J. Bras, Microfibrillated cellulose – Its barrier properties and applications in cellulosic materials: A review. *Carbohydr. Polym.* **90**(2), 735–764 (2012).
22. E.L. Bradley, L. Castle, and Q. Chaudhry, Applications of nanomaterials in food packaging with a consideration of opportunities for developing countries. *Trends Food Sci. Technol.* **22**(11), 604–610 (2011).
23. E. Fortunati, I. Armentano, Q. Zhou, A. Iannoni, E. Saino, L. Visai, L.A. Berglund, and J.M. Kenny, Multifunctional bionanocomposite films of poly(lactic acid), cellulose nanocrystals and silver nanoparticles. *Carbohydr. Polym.* **87**(2), 1596–1605 (2012).
24. E. Fortunati, M. Peltzer, I. Armentano, L. Torre, A. Jiménez, and J.M. Kenny, Effects of modified cellulose nanocrystals on the barrier and migration properties of PLA nano-biocomposites. *Carbohydr. Polym.* **90**(2), 948–956 (2012).
25. J. George, High performance edible nanocomposite films containing bacterial cellulose nanocrystals. *Carbohydr. Polym.* **87**(3), 2031–2037 (2012).
26. E.-L. Hult, M. Iotti, and M. Lenes, Efficient approach to high barrier packaging using microfibrillar cellulose and shellac. *Cellulose* **17**(3), 575–586 (2010).
27. N. Lavoine, I. Desloges, and J. Bras, Microfibrillated cellulose coatings as new release systems for active packaging. *Carbohydr. Polym.* **103**, 528–537 (2014).
28. J.-H. Seo, T.-H. Chang, J. Lee, R. Sabo, W. Zhou, Z. Cai, S. Gong, and Z. Ma, Microwave flexible transistors on cellulose nanofibrillated fiber substrates. *Appl. Phys. Lett.* **106**(26), 262101 (2015).
29. J. Huang, H. Zhu, Y. Chen, C. Preston, K. Rohrbach, J. Cumings, and L. Hu, Highly transparent and flexible nanopaper transistors. *ACS Nano* **7**(3), 2106–2113 (2013).
30. R. Sabo, J.-H. Seo, and Z. Ma, Cellulose nanofiber composite substrates for flexible electronics, in: *2012 TAPPI International Conference on Nanotechnology for Renewable Materials*, Montreal, Quebec, Canada (2012).
31. Y.H. Jung, T.-H. Chang, H. Zhang, C. Yao, Q. Zheng, V.W. Yang, H. Mi, M. Kim, S.J. Cho, and D.-W. Park, High-performance green flexible electronics based on biodegradable cellulose nanofibril paper. *Nat. Commun.* **6**, article no. 7170, DOI: 10.1038/ncomms8170 (2015).
32. H. Zhu, B.B. Narakathu, Z. Fang, A. Tausif Aijazi, M. Joyce, M. Atashbar, and L. Hu, A gravure printed antenna on shape-stable transparent nanopaper. *Nanoscale* **6**(15), 9110–9115 (2014).
33. Z. Fang, H. Zhu, Y. Yuan, D. Ha, S. Zhu, C. Preston, Q. Chen, Y. Li, X. Han, and S. Lee, Novel nanostructured paper with ultrahigh transparency and ultrahigh haze for solar cells. *Nano Lett.* **14**(2), 765–773 (2014).
34. L. Hu, G. Zheng, J. Yao, N. Liu, B. Weil, M. Eskilsson, E. Karabulut, Z. Ruan, S. Fan, J.T. Bloking, M.D. McGehee, L. Wagberg, and Y. Cui, Transparent and conductive paper from nanocellulose fibers. *Energ. Environ. Sci.* **6**(2), 513–518 (2013).
35. Y. Luo, J. Zhang, X. Li, C. Liao, and X. Li, The cellulose nanofibers for optoelectronic conversion and energy storage. *J. Nanomater.* **2014** (2014).
36. Y. Zhou, T.M. Khan, J.-C. Liu, C. Fuentes-Hernandez, J.W. Shim, E. Najafabadi, J.P. Youngblood, R.J. Moon, and B. Kippelen, Efficient recyclable organic solar cells on cellulose nanocrystal substrates with a conducting polymer top electrode deposited by film-transfer lamination. *Org. Electron.* **15**(3), 661–666 (2014).
37. U.S. Environmental Protection Agency, Electronics waste management in the United States through 2009, U.S.E.P. Agency <http://www.epa.gov/wastes/conserve/materials/ecycling/docs/fullbaselinereport2011.pdf> (2011).
38. M. Iguchi, S. Yamanaka, and A. Budhiono, Bacterial cellulose—a masterpiece of nature's arts. *J. Mater. Sci.* **35**(2), 261–270 (2000).
39. G. Guhados, W. Wan, and J.L. Hutter, Measurement of the elastic modulus of single bacterial cellulose fibers using atomic force microscopy. *Langmuir* **21**(14), 6642–6646 (2005).
40. C. Legnani, C. Vilani, V.L. Calil, H.S. Barud, W.G. Quirino, C.A. Achete, S.J.L. Ribeiro, and M. Cremona, Bacterial cellulose membrane as flexible substrate for organic light emitting devices. *Thin Solid Films* **517**(3), 1016–1020 (2008).
41. M. Nogi and H. Yano, Transparent nanocomposites based on cellulose produced by bacteria offer potential innovation in the electronics device industry. *Adv. Mater.* **20**(10), 1849–1852 (2008).

42. L. Deng, R.J. Young, I.A. Kinloch, A.M. Abdelkader, S.M. Holmes, D.A. De Haro-Del Rio, and S.J. Eichhorn, Supercapacitance from cellulose and carbon nanotube nanocomposite fibers. *ACS Appl. Mater. Interfaces* **5**(20), 9983–9990 (2013).
43. R.J. Moon, A. Martini, J. Nairn, J. Simonsen, and J. Youngblood, Cellulose nanomaterials review: Structure, properties and nanocomposites. *Chem. Soc. Rev.* **40**(7), 3941–3994 (2011).
44. I. Sakurada, Y. Nukushina, and T. Ito, Experimental determination of the elastic modulus of crystalline regions in oriented polymers. *J. Polym. Sci.* **57**(165), 651–660 (1962).
45. S.J. Eichhorn, C.A. Baillie, N. Zafeiropoulos, L.Y. Mwaikambo, M.P. Ansell, A. Dufresne, K.M. Entwistle, P.J. Herrera-Franco, G.C. Escamilla, L. Groom, M. Hughes, C. Hill, T.G. Rials, and P.M. Wild, Review: Current international research into cellulosic fibres and composites. *J. Mater. Sci.* **36**(9), 2107–2131 (2001).
46. M.A.S. Azizi Samir, F. Alloin, and A. Dufresne, Review of recent research into cellulosic whiskers, their properties and their application in nanocomposite field. *Biomacromolecules* **6**(2), 612–626 (2005).
47. I. Siró and D. Plackett, Microfibrillated cellulose and new nanocomposite materials: A review. *Cellulose* **17**(3), 459–494 (2010).
48. T. Saito, M. Hirota, N. Tamura, S. Kimura, H. Fukuzumi, L. Heux, and A. Isogai, Individualization of nano-sized plant cellulose fibrils by direct surface carboxylation using TEMPO catalyst under neutral conditions. *Biomacromolecules* **10**(7), 1992–1996 (2009).
49. Y. Qing, R. Sabo, J.Y. Zhu, U. Agarwal, Z. Cai, and Y. Wu, A comparative study of cellulose nanofibrils disintegrated via multiple processing approaches. *Carbohydr. Polym.* **97**(1), 226–234 (2013).
50. MatWeb. Tensile property testing of plastics, <http://www.matweb.com/reference/tensilestrength.aspx> (2016).
51. S.H. Jin, Y.-B. Park, and K.H. Yoon, Rheological and mechanical properties of surface modified multi-walled carbon nanotube-filled PET composite. *Compos. Sci. Technol.* **67**(15–16), 3434–3441 (2007).
52. Y. Sun and J.A. Rogers, Inorganic semiconductors for flexible electronics. *Adv. Mater.* **19**(15), 1897–1916 (2007).
53. H. Fukuzumi, T. Saito, T. Iwata, Y. Kumamoto, and A. Isogai, Transparent and high gas barrier films of cellulose nanofibers prepared by TEMPO-mediated oxidation. *Biomacromolecules* **10**(1), 162–165 (2009).
54. A.N. Nakagaito, M. Nogi, and H. Yano, Displays from transparent films of natural nanofibers. *MRS Bull.* **35**(03), 214–218 (2010).
55. M. Nogi, S. Iwamoto, A.N. Nakagaito, and H. Yano, Optically transparent nanofiber paper. *Adv. Mater.* **21**(16), 1595–1598 (2009).
56. Y. Okahisa, A. Yoshida, S. Miyaguchi, and H. Yano, Optically transparent wood–cellulose nanocomposite as a base substrate for flexible organic light-emitting diode displays. *Compos. Sci. Technol.* **69**(11), 1958–1961 (2009).
57. S. Iwamoto, A.N. Nakagaito, and H. Yano, Nanofibrillation of pulp fibers for the processing of transparent nanocomposites. *Appl. Phys. A: Mater. Sci. Process.* **89**(2), 461–466 (2007).
58. H. Yano, J. Sugiyama, A.N. Nakagaito, M. Nogi, T. Matsuura, M. Hikita, and K. Handa, Optically transparent composites reinforced with networks of bacterial nanofibers. *Adv. Mater.* **17**(2), 153–155 (2005).
59. C. Preston, Z. Fang, J. Murray, H. Zhu, J. Dai, J.N. Munday, and L. Hu, Silver nanowire transparent conducting paper-based electrode with high optical haze. *J. Mater. Chem. C* **2**(7), 1248–1254 (2014).
60. E.D. Cranston and D.G. Gray, Morphological and Optical Characterization of Polyelectrolyte Multilayers Incorporating Nanocrystalline Cellulose. *Biomacromolecules* **7**(9), 2522–2530 (2006).
61. T. Nishino, I. Matsuda, and K. Hirao, All-cellulose composite. *Macromolecules* **37**(20), 7683–7687 (2004).
62. S. Ifuku, M. Nogi, K. Abe, K. Handa, F. Nakatsubo, and H. Yano, Surface modification of bacterial cellulose nanofibers for property enhancement of optically transparent composites: Dependence on acetyl-group DS. *Biomacromolecules* **8**(6), 1973–1978 (2007).
63. H. Yagyu, T. Saito, A. Isogai, H. Koga, and M. Nogi, Chemical modification of cellulose nanofibers for the production of highly thermal resistant and optically transparent nanopaper for paper devices. *ACS Appl. Mater. Interfaces* **7**(39), 22012–22017 (2015).
64. X. Zheng, Y. Zhou, J. Liu, and A. Li, Use of nanomechanical fracture-testing for determining the interfacial adhesion of PZT ferroelectric thin films. *Surf. Coat. Tech.* **176**(1), 67–74 (2003).
65. Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya, and M. Nakamura, Lead-free piezoceramics. *Nature*, **432**(7013), 84–87 (2004).
66. C.D. Richards, M.J. Anderson, D.F. Bahr, and R.F. Richards, Efficiency of energy conversion for devices containing a piezoelectric component. *J. Micromech. Microeng.* **14**(5), 717–721 (2004).
67. S. Roundy, P.K. Wright, and J. Rabaey, A study of low level vibrations as a power source for wireless sensor nodes. *Comput. Commun.* **26**(11), 1131–1144 (2003).
68. E.-M. Anton, W. Jo, D. Damjanovic, and J. Rödel, Determination of depolarization temperature of $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ -based lead-free piezoceramics. *J. Appl. Phys.* **110**(9), 094108 (2011).
69. T. Bove, K. Liang, and W. Wolny, Experimental study of temperature & pressure effects on high-porosity PZT materials, in: *Ultrasonics Symposium (IUS), 2012 IEEE International*, IEEE (2012).
70. K. Franke, H. Huelz, and M. Wehnacht, Stress-induced depolarization in PZT thin films, measured by means of electric force microscopy. *Surface Science* **416**(1), 59–67 (1998).
71. Q. Jiang and L. Cross, Effects of porosity on electric fatigue behaviour in PLZT and PZT ferroelectric ceramics. *J. Mater. Sci.* **28**(16), 4536–4543 (1993).
72. A. Gruverman, O. Auciello, and H. Tokumoto, Nanoscale investigation of fatigue effects in Pb (Zr, Ti) O₃ films. *Appl. Phys. Lett.* **69**(21), 3191–3193 (1996).
73. G. Chinga-Carrasco, D. Tobjörk, and R. Österbacka, Inkjet-printed silver nanoparticles on nano-engineered

- cellulose films for electrically conducting structures and organic transistors: Concept and challenges. *J. Nanopart. Res.* **14**(11), 1–10 (2012).
74. T. Shimaoka, Development of transparent cellulose nano fiber film for flexible displays, in: *2015 TAPPI International Conference on Nanotechnology for Renewable Materials*, Atlanta, GA (2015).
 75. K. Torvinen, J. Sievänen, T. Hjelt, and E. Hellén, Smooth and flexible filler-nanocellulose composite structure for printed electronics applications. *Cellulose* **19**(3), 821–829 (2012).
 76. S. Couderc, O. Ducloux, B.J. Kim, and T. Someya, A mechanical switch device made of a polyimide-coated microfibrillated cellulose sheet. *J. Micromech. Microeng.* **19**(5), 055006 (2009).
 77. T.T. Nge, M. Nogi, and K. Suganuma, Electrical functionality of inkjet-printed silver nanoparticle conductive tracks on nanostructured paper compared with those on plastic substrates. *J. Mater. Chem. C* **1**(34), 5235–5243 (2013).
 78. H. Koga, T. Saito, T. Kitaoka, M. Nogi, K. Suganuma, and A. Isogai, Transparent, conductive, and printable composites consisting of TEMPO-oxidized nanocellulose and carbon nanotube. *Biomacromolecules* **14**(4), 1160–1165 (2013).
 79. M. Singh, H.M. Haverinen, P. Dhagat, and G.E. Jabbour, Inkjet printing-process and its applications. *Adv. Mater.* **22**(6), 673–685 (2010).
 80. A. Yoshida, A. Sugimoto, T. Miyadera, and S. Miyaguchi, Organic light emitting devices on polymer substrates. *J. Photopolym. Sci. Tec.* **14**(2), 327–332 (2001).
 81. S. Beck-Candanedo, M. Roman, and D.G. Gray, Effect of reaction conditions on the properties and behavior of wood cellulose nanocrystal suspensions. *Biomacromolecules* **6**(2), 1048–1054 (2005).
 82. C. Teters, W. Kong, M. Taylor, J. Simonsen, M. Lerner, T. Plant, and G. Evans, The cellulose nanocrystal electro-optic effect, in: *International Conference on Nanotechnology for the Forest Products Industry*, Knoxville, TN, (2007).
 83. H. Oulachgar, M. Bolduc, G. Chauve, Y. Desroches, P. Beaupre, J. Bouchard, and P. Galarneau, Fabrication and electro-optical characterization of a nanocellulose-based spatial light modulator. *MRS Advances*, (2015). DOI: 10.1557/adv.2015.34
 84. L. Jabbour, C. Gerbaldi, D. Chaussy, E. Zeno, S. Bodoardo, and D. Beneventi, Microfibrillated cellulose-graphite nanocomposites for highly flexible paper-like Li-ion battery electrodes. *J. Mater. Chem.* **20**(35), 7344–7347 (2010).
 85. L. Jabbour, R. Bongiovanni, D. Chaussy, C. Gerbaldi, and D. Beneventi, Cellulose-based Li-ion batteries: A review. *Cellulose* **20**(4), 1523–1545 (2013).
 86. M. Schroers, A. Kokil, and C. Weder, Solid polymer electrolytes based on nanocomposites of ethylene oxide–epichlorohydrin copolymers and cellulose whiskers. *J. Appl. Polym. Sci.* **93**(6), 2883–2888 (2004).
 87. L. Hu, N. Liu, M. Eskilsson, G. Zheng, J. McDonough, L. Wågberg, and Y. Cui, Silicon-conductive nanopaper for Li-ion batteries. *Nano Energy* **2**(1), 138–145 (2013).
 88. S. Leijonmarck, A. Cornell, G. Lindbergh, and L. Wågberg, Single-paper flexible Li-ion battery cells through a paper-making process based on nanofibrillated cellulose. *J. Mater. Chem. A* **1**(15), 4671–4677 (2013).
 89. A. Chiappone, J.R. Nair, C. Gerbaldi, L. Jabbour, R. Bongiovanni, E. Zeno, D. Beneventi, and N. Penazzi, Microfibrillated cellulose as reinforcement for Li-ion battery polymer electrolytes with excellent mechanical stability. *J. Power Sources* **196**(23), 10280–10288 (2011).
 90. G. Nyström, A. Razaq, M. Strømme, L. Nyholm, and A. Mihranyan, Ultrafast all-polymer paper-based batteries. *Nano Lett.* **9**(10), 3635–3639 (2009).
 91. S.-J. Chun, E.-S. Choi, E.-H. Lee, J.H. Kim, S.-Y. Lee, and S.-Y. Lee, Eco-friendly cellulose nanofiber paper-derived separator membranes featuring tunable nanoporous network channels for lithium-ion batteries. *J. Mater. Chem.* **22**(32), 16618–16626 (2012).
 92. L. Nyholm, G. Nyström, A. Mihranyan, and M. Strømme, Toward flexible polymer and paper-based energy storage devices. *Adv. Mater.* **23**(33), 3751–3769 (2011).
 93. Y. Zhou, C. Fuentes-Hernandez, T.M. Khan, J.-C. Liu, J. Hsu, J.W. Shim, A. Dindar, J.P. Youngblood, R.J. Moon, and B. Kippelen, Recyclable organic solar cells on cellulose nanocrystal substrates. *Sci. Rep.* **3** (2013).
 94. G. Zheng, Y. Cui, E. Karabulut, L. Wågberg, H. Zhu, and L. Hu, Nanostructured paper for flexible energy and electronic devices. *MRS Bull.* **38**(4), 320–325 (2013).
 95. H. Choi and H. Yoon, Nanostructured electrode materials for electrochemical capacitor applications. *Nanomaterials* **5**(2), 906–936 (2015).
 96. K.-Y. Lee, H. Qian, F.H. Tay, J.J. Blaker, S.G. Kazarian, and A. Bismarck, Bacterial cellulose as source for activated nanosized carbon for electric double layer capacitors. *J. Mater. Sci.* **48**(1), 367–376 (2013).
 97. H. Wang, E. Zhu, J. Yang, P. Zhou, D. Sun, and W. Tang, Bacterial cellulose nanofiber-supported polyaniline nanocomposites with flake-shaped morphology as supercapacitor electrodes. *J. Phys. Chem. C* **116**(24), 13013–13019 (2012).
 98. X.D. Zhang, Z.Y. Lin, B. Chen, W. Zhang, S. Sharma, W.T. Gu, and Y.L. Deng, Solid-state flexible polyaniline/silver cellulose nanofibrils aerogel supercapacitors. *J. Power Sources* **246**, 283–289 (2014).
 99. S.Y. Liew, W. Thielemans, and D.A. Walsh, Electrochemical capacitance of nanocomposite polypyrrole/cellulose films. *J. Phys. Chem. C* **114**(41), 17926–17933 (2010).
 100. J. Peng, H. Zhang, Q. Zheng, C.M. Clemons, R.C. Sabo, S. Gong, Z. Ma, and L.-S. Turng, A composite generator film impregnated with orientated cellulose nanocrystals for enhanced triboelectric performance. *Nano Energy*, (submitted) (2016).
 101. J. Peng, Nanocellulose as reinforcement and nucleating agents for solid and foamed component and as dielectric filler for triboelectric generator, in: *Mechanical Engineering*, University of Wisconsin: Madison, WI, pp. 99–123 (2015).

102. P. Tingaut, T. Zimmermann, and G. Sèbe, Cellulose nanocrystals and microfibrillated cellulose as building blocks for the design of hierarchical functional materials. *J. Mater. Chem.* **22**(38), 20105–20111 (2012).
103. L.J. Nielsen, S. Eyley, W. Thielemans, and J.W. Aylott, Dual fluorescent labelling of cellulose nanocrystals for pH sensing. *Chem. Commun.* **46**(47), 8929–8931 (2010).
104. J.V. Edwards, N. Prevost, K. Sethumadhavan, A. Ullah, and B. Condon, Peptide conjugated cellulose nanocrystals with sensitive human neutrophil elastase sensor activity. *Cellulose* **20**(3), 1223–1235 (2013).
105. L. Zhang, Q. Li, J. Zhou, and L. Zhang, Synthesis and photophysical behavior of pyrene-bearing cellulose nanocrystals for Fe³⁺ sensing. *Macromol. Chem. Phys.* **213**(15), 1612–1617 (2012).
106. X. Qiu and S. Hu, “Smart” materials based on cellulose: A review of the preparations, properties, and applications. *Materials* **6**(3), 738–781 (2013).
107. J.-H. Kim, B.S. Shim, H.S. Kim, Y.-J. Lee, S.-K. Min, D. Jang, Z. Abas, and J. Kim, Review of nanocellulose for sustainable future materials. *Int. J. Precis. Eng. Man.-Green Technol.* **2**, 197–213 (2015).
108. Z. Abas, H.S. Kim, J. Kim, and J.-H. Kim, Cellulose electro-active paper: From discovery to technology applications. *Frontiers in Materials* **1**(17), 1–4 (2014).
109. L. Csoka, I.C. Hoeger, O.J. Rojas, I. Peszlen, J.J. Pawlak, and P.N. Peralta, Piezoelectric effect of cellulose nanocrystals thin films. *ACS Macro Lett.* **1**, 867–870 (2012).
110. J.-H. Jeon, I.-K. Oh, C.-D. Kee, and S.-J. Kim, Bacterial cellulose actuator with electrically driven bending deformation in hydrated condition. *Sensor. Actuat. B: Chem.* **146**, 307–313 (2010).
111. S.F. Chin, A.N.B. Romainor, and S.C. Pang, Fabrication of hydrophobic and magnetic cellulose aerogel with high oil absorption capacity. *Mater. Lett.* **115**, 241–243 (2014).
112. R.T. Olsson, M.A. Samir, G. Salazar-Alvarez, L. Belova, V. Ström, L.A. Berglund, O. Ikkala, J. Nogues, and U.W. Gedde, Making flexible magnetic aerogels and stiff magnetic nanopaper using cellulose nanofibrils as templates. *Nat. Nanotechnol.* **5**(8), 584–588 (2010).
113. C.H. Chia, S. Zakaria, K.L. Nguyen, V.Q. Dang, and T.D. Duong, Characterization of magnetic paper using Fourier transform infrared spectroscopy. *Mater. Chem. Phys.* **113**(2), 768–772 (2009).
114. A.C. Small and J.H. Johnston, Novel hybrid materials of magnetic nanoparticles and cellulose fibers. *J. Colloid Interface Sci.* **331**(1), 122–126 (2009).
115. C. Chia, S. Zakaria, K. Nguyen, and M. Abdullah, Utilisation of unbleached kenaf fibers for the preparation of magnetic paper. *Ind. Crop. Prod.* **28**(3), 333–339 (2008).
116. S. Menchaca-Nal, C. Londoño-Calderón, P. Cerrutti, M. Foresti, L. Pampillo, V. Bilovol, R. Candal, and R. Martínez-García, Facile synthesis of cobalt ferrite nanotubes using bacterial nanocellulose as template. *Carbohydr. Polym.* **137**, 726–731 (2016).
117. M.B. Moffett, A.E. Clark, M. Wun-Fogle, J. Linberg, J.P. Teter, and E.A. McLaughlin, Characterization of Terfenol-D for magnetostrictive transducers. *J. Acoust. Soc. Am.* **89**(3), 1448–1455 (1991).
118. F. Claeysen, N. Lhermet, R. Le Letty, and P. Bouchilloux, Actuators, transducers and motors based on giant magnetostrictive materials. *J. Alloys and Compd.* **258**(1), 61–73 (1997).
119. J.H. Goldie, M.J. Gerver, J. Oleksy, G.P. Carman, and T.A. Duenas, Composite Terfenol-D sonar transducers, in: 1999 *Symposium on Smart Structures and Materials*, International Society for Optics and Photonics (1999).
120. P. Li, Y. Wen, P. Liu, X. Li, and C. Jia, A magnetoelectric energy harvester and management circuit for wireless sensor network. *Sensor. Actuat. A: Phys.* **157**(1), 100–106 (2010).
121. M.E. Staley and A.B. Flatau, Characterization of energy harvesting potential of Terfenol-D and Galfenol, in: *Proceedings of SPIE*, International Society for Optical Engineering (2005).
122. T. Ueno and S. Yamada, Performance of energy harvester using iron–gallium alloy in free vibration. *IEEE Trans. Magn.* **47**(10), 2407–2409 (2011).
123. L. Wang and F. Yuan, Vibration energy harvesting by magnetostrictive material. *Smart Mater. Struct.* **17**(4), 045009–045014 (2008).
124. M. Goodfriend and K. Shoop, Adaptive characteristics of the magnetostrictive alloy, Terfenol-D, for active vibration control. *J. Intell. Mater. Syst. Struct.* **3**(2), 245–254 (1992).
125. T.-Z. Wang and Y.-H. Zhou, Nonlinear dynamic model with multi-fields coupling effects for giant magnetostrictive actuators. *Int. J. Solids Struct.* **50**(19), 2970–2979 (2013).
126. S.-J. Moon, C.-W. Lim, B.-H. Kim, and Y. Park, Structural vibration control using linear magnetostrictive actuators. *J. Sound Vibration* **302**(4), 875–891 (2007).
127. A.-G. Olabi and A. Grunwald, Design and application of magnetostrictive materials. *Mater. Design* **29**(2), 469–483 (2008).
128. R.C. Fenn, J.R. Downer, D.A. Bushko, V. Gondhalekar, and N.D. Ham, Terfenol-D driven flaps for helicopter vibration reduction. *Smart Mater. Struct.* **5**(1), 49–57 (1996).
129. T. Duenas and G. Carman, Large magnetostrictive response of Terfenol-D resin composites. *J. Appl. Phys.* **87**(9), 4696–4701 (2000).
130. I.D. Mayergoyz and G. Engdahl, *Handbook of Giant Magnetostrictive Materials*, Academic Press, San Diego, CA (1999).
131. C. Rodríguez, A. Barrio, I. Orue, J. Vilas, L. León, J.M. Barandiarán, and M.F.-G. Ruiz, High magnetostriction polymer-bonded Terfenol-D composites. *Sensor. Actuat. A: Phys.* **142**(2), 538–541 (2008).
132. J. Kaleta, D. Lewandowski, and R. Mech, Magnetostriction of field-structural composite with Terfenol-D particles. *Arch. Civ. Mech. Eng.* (2015).
133. R. Elhajjar, V. La Saponara, and A. Muliana, *Smart Composites: Mechanics and Design*, CRC Press (2013).
134. Y. Qing, R. Sabo, Y. Wu, and Z. Cai, High-performance cellulose nanofibril composite films. *Bioresources* **7**(3), 3064–3075 (2012).
135. R.F. Elhajjar and C.T. Law, Magnetomechanical local-global effects in magnetostrictive composite materials. *Model. Simul. Mater. Sci. Eng.* **23**(7), 075002 (2015).