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Development, application and commercialization of transparent paper

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Abstract
Transparent paper made of cellulose for next generation 'green' electronic devices is a completely new concept that has attracted great attention over the past decade due to a variety of prominent properties of cellulose such as its natural origin, environmental safety and renewability. Various proof-of-concept transparent paper-based electronics have been demonstrated by scientists from all over the world. In this article, we first discuss the natural cellulose-based materials for transparent paper. We then summarize recent advances in the fabrication of transparent paper, including filtration, casting, extrusion and impregnation. The latest developments in transparent and flexible paper electronic devices are also demonstrated, such as photovoltaic devices, transistors, organic light emitting diodes and displays. Finally, we discuss the economically efficient routes for the mass production of transparent paper.

Keywords: transparent paper, cellulose, electronic devices, scalable production

1. Transparent paper: a renewable material

We are surrounded by a world of electronic devices that are an indispensable part of daily life, such as portable computers, mobile phones, televisions, solar cells, displays and cameras. The increasing demand for electronics poses a growing environmental problem due to the wide use of plastics, glass and silicon as the substrates. To achieve the sustainability of electronics, increased attention has been directed towards 'green' electronics that are fabricated from natural materials using economically efficient production routes [1, 2]. Integrating transparent paper into flexible electronics has become a hot research area recently that has attracted widespread interest in the scientific community because of its potential capacity to enable the scalable and sustainable production of transparent and flexible electronics by roll-to-roll methods [3]. In the

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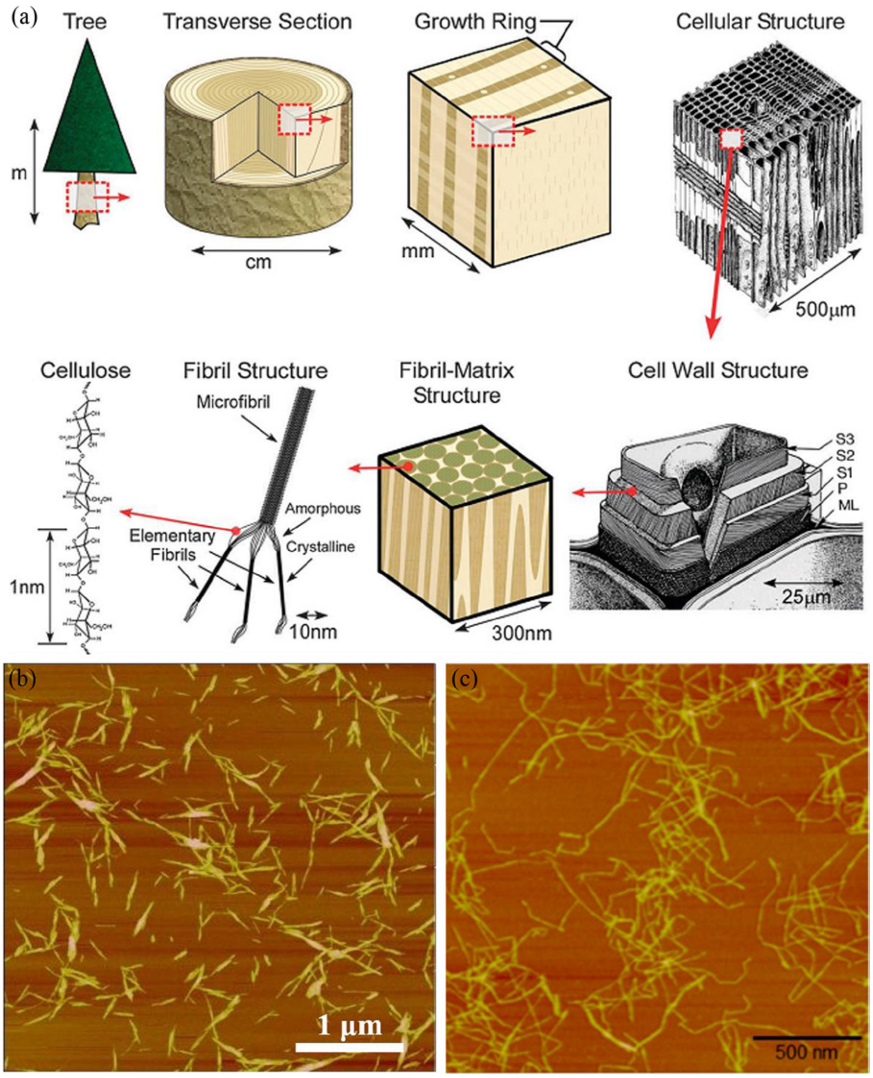

Figure 1. (a) The hierarchical structure of wood from the tree to the cellulose molecular structure; and an AFM height image of (b) cellulose nanocrystals (CNC) and (c) nanofibrillated cellulose (NFC) [34, 38, 39].

past five years, scientists from research institutes have continually demonstrated proof-of-concept of devices on transparent paper such as displays [4, 5], transistors [6, 7], organic light-emitting diodes (OLEDs [8, 9]), touchscreens [10], lithium ion batteries [11], solar cells [12–17], transparent conductive electrodes [13, 18, 19] and antennas [20].

Cellulose was first discovered by Anselme Payen in the laboratory in 1838 [21]. It is the most abundant biomaterial on Earth. Its outstanding characteristics such as biodegradability, renewability, low cost, light weight, nontoxicity and even biocompatibility make it universally accepted [22–24]. Cellulose is extensively found in many natural materials such as trees, plants, bacteria and animals, and provides approximately 1.5×10^{12} tons of the entire biomass production, which has been used by humans as engineering material for several centuries [22, 25–27]. Note that cellulose fibers and cellulose in this review are primarily extracted from wood pulp. Figure 1(a) shows the hierarchical structure of a tree. A cellulose chain is comprised of several hundred to more than 10 000 anhydroglucose units by β-1, 4 linkages. About 36 cellulose chains self-assemble into elementary fibrils with a diameter of 3.5 ~ 5 nm containing both amorphous and crystalline regions, and these elementary fibrils are further bundled into microfibrils that constitute the cell wall of micro-sized cellulose fibers [28–32]. In this article, three types of cellulose fibers are mentioned: microsized fiber, nanocrystal cellulose (NCC), also known as whiskers [33, 34], and nanofibrillated cellulose (NFC), also named microfibrillated cellulose, nanofibrils or microfibrils [24, 35, 36]. To keep the terms consistent in this paper, we have used the terminologies NFC and NCC. The microsized fibers are elongated hollow cells isolated from the tree through chemical and/or mechanical treatments under high processing temperature and pressure, and the separated wood pulp is then bleached several times to remove as much of the residual lignin within the pulp as possible. NCC is produced by acid hydrolysis of wood fibers, plant fibers and so on. It is a rod-like and highly crystalline cellulose nanofiber (CN) with widths and lengths of 5–70 nm and 50–500 nm (figure 1(b) [33]), respectively, and contains a high fraction of Iβ crystal structure. NFC is normally produced from wood pulp and plant fibers by combining mechanical processes (homogenization, grinding, ultrasonification, etc) with pretreatments (enzymatic, alkaline, oxidation treatments) and is 5–60 nm wide and 500–2000 nm long, including both amorphous and crystalline regions (figure 1(c) [24, 25, 35–37]).

Cellulose is a colorless polysaccharide due to the absence of groups in cellulose that will absorb light in the visible range [25]. Hence, cellulose-based materials such as regenerated cellulose and cellulose fiber with a diameter of micro/nanoscale size can be used to prepare transparent paper by casting, filtration, extrusion, etc [3, 40]. It has been verified that the optical properties of paper are related to its surface textures, porosity, pore size, thickness, packing density and fiber dimensions [41–43], and the paper shows low absorptive losses [16]. The feasible way to attain highly optical total transmittance of paper is by eliminating the microcavities in the fiber network [10, 43]. In comparison to common papers such as copy paper, printing paper, paperboard and tissue, which are ubiquitous in daily life, transparent paper not only exhibits better optical and mechanical properties but also presents better barrier performance [44–53]. Chemical treatments, mechanical processing and impregnation are used to make paper transparent by effectively reducing light scattering behavior between fibers and air within substrates [54–57]. A schematic showing the mechanism to make paper transparent is depicted in figure 2: a beam of light strikes regular paper made out of wood pulp and the incident light is heavily reflected by the porous architecture due to the intensive light scattering effect caused by the mismatched refractive indices between air (1.0) and cellulose (1.5). Only a small percent of incident light propagates through the regular paper, which causes the opacity of regular paper (see figure 2(a)). As the void spaces in the microsized fiber network are thoroughly infiltrated with NFC, most of the incident light can easily pass through the paper (see figure 2(b)). By conspicuously replacing microscale cavities with nanoscale pores in paper using transparent materials with a similar refractive index of cellulose, the light scattering occurring at the interfacial area between microsized fibers and air is consequently significantly suppressed, resulting in the high total transmittance [10]. Note that the optical transmittance mentioned in the following text refers to optical total transmittance unless otherwise specified.

2. Development of transparent paper

Transparent paper such as parchment paper, cellophane, tracing paper, nanopaper and glassine is one type of specialty paper exhibiting excellent optical transparency that was first developed in the middle of the 19th century [3]. It was initially developed to use as a support for a variety

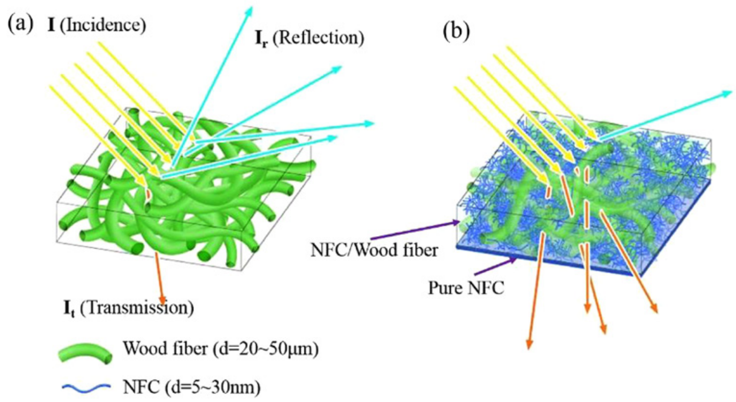

Figure 2. Schematic of (a) regular paper made of micro-sized wood fibers and (b) the porous structure of regular paper infiltrated with NFC to decrease internal light scattering [10].

of materials. Architectural drawings, fine art paintings and technical artistic designs, which are ubiquitously conserved in modern libraries, archives and museums, were drawn on transparent paper due to its transparency and relatively low cost [55, 57]. The first article that fundamentally studied the transparentizing effect of various liquids on paper in detail was published by Vaurio in 1960 [58], with the latest one published by Yano *et al*, where acetylated pulp paper was impregnated with acrylic resin to prepare transparent cellulose-based composites [59]. Transparent papers have emerged in many applications such as food packaging, maps, release labels, wrapping and bookbinding due to superior optical, mechanical and barrier properties. New applications will be constantly expanded in the near future resulting from frequent interdisciplinary research. In this review, transparent paper is defined as any cellulose-based substrates having a total transmittance higher than 70% regardless of the optical haze. We elaborated primarily on three types of transparent papers developed by using wood cellulose with dimensions ranging from nanoscale to microscale size: transparent paper made of microsized fibers, cellulose solution (regenerated cellulose film) and CNs (nanopaper).

2.1. Transparent paper made of microsized cellulose fibers

Transparentizing paper is the procedure of removing inside pores in an efficient and low-cost manner. Transparent paper made of microsized cellulose fibers has been developed for more than 150 years. Originally, wet-laid or woven paper was impregnated with resins, oils, varnishes, gums and mixtures to reduce internal void spaces. In the mid 19th century, a chemical method was introduced to prepare transparent paper by immersing a formed paper into a bath of sulfuric acid or sometimes zinc chloride to gelatinize or partially dissolve the fiber network, followed by several washes in water to remove residue chemicals [55, 60]. This transparent paper, also named vegetable parchment, presents a similar appearance to traditional parchment and strong mechanical properties, which has attracted a lot of attention due to the reduced requirement for energy-intensive fiber treatment. Nishino *et al* introduced all-cellulose composites (ACCs) that have since been the focus of numerous recent works that explore two distinct strategies: a one-step method and a two-step method [61, 62]. The one-step method refers to a surface selective dissolution of conventional paper using dominant non-derivatized solvents such as lithium

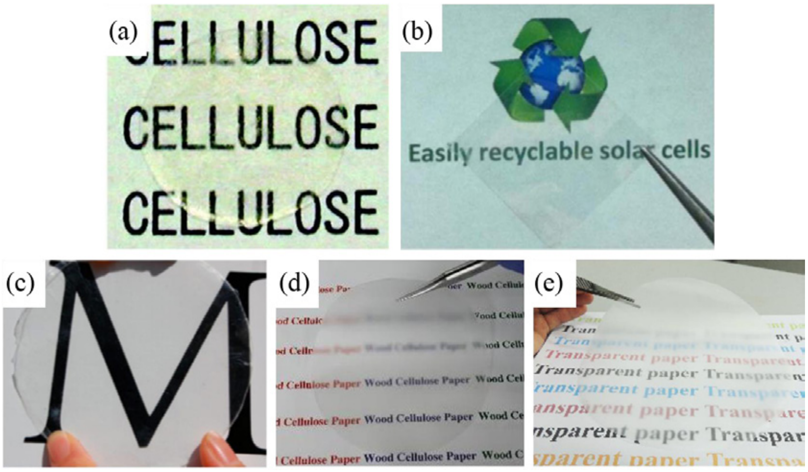

Figure 3. Photographs of various transparent papers made of (a) partially dissolved wood fibers, (b) CNC, (c) TEMPO-oxidized NFC, (d) TEMPO-oxidized NFC and micro-sized wood fibers and (e) TEMPO-oxidized wood pulp [7, 10, 12, 14, 64].

chloride/N, N'-dimethylacetamide (DMAc [63–67]), NaOH/poly(ethylene glycol [68]) and ionic liquids [69–71]. The two-step method involves dissolving a part of cellulose that is then coagulated in the fiber network, and figure 3(a) displays an all-cellulose composite produced by partially dissolving fiber surface using DMAc/LiCl solvent, which exhibits optical transparency and superior tensile strength of 211 Mpa [64]. In addition, the mechanical treatment of wood pulp was proposed to improve the optical transparency of paper 100 years ago [55], and was widely adopted in the production of transparent paper: the fibers were crushed and fibrillated rather than being cut after intensive beating, tending to form fiber networks with high packing density during the paper-making procedure. The transparency of paper fabricated through this method, however, is usually less than 60%, so additional steps were necessary to enhance the transparency of paper further, such as calendaring, supercalendering and impregnation. There are many approaches to make paper made of microsized fibers transparent, but no complete optical properties were demonstrated in the literature.

2.2. Regenerated cellulose film

Using regenerated cellulose to fabricate transparent regenerated cellulose film (RCF) is another crucial approach. Schweitzer discovered that solid cellulose could dissolve in $Cu(OH)_2/NH_3$ solvent in 1857 [72], which opened up the area of using cellulose solutions to prepare cellulosic film by extrusion. Cross *et al* first used viscose prepared from full dissolution of cellulose in $NaOH/CS_2$ solution to make RCF in the laboratory [73], and the large-scale production of RCF was founded by Brandenberger in 1908 [74]. The interest has since been concentrated on the preparation of cellulose solution in a simple, environmentally benign and economical way [75]. Dissolving cellulose in solvents with/without changes to the molecular structure are two principles for preparing cellulose solution [26, 27]. Hundreds of solvents based on the two mechanisms are explored to efficiently dissolve cellulose in economical and ecological ways, such as $NaOH/CS_2$, ionic liquids [76–80], a N-methylmorpholine-n-oxide (NMMO) solution [75], DMAc/LiCl [81] and an aqueous NaOH solution [82–85]. The prepared cellulose solution is then coated onto plastic or extruded through a slit into the regenerated solution or by other production methods to produce RCF [86–88]. Qi *et al* recently reported a 'green' process to prepare a cellulose solution by dissolving cotton into aqueous NaOH/urea solution, which was then casted on a glass plate to fabricate transparent RCF [88]. Transparent paper made from regenerated cellulose presents excellent optical transparency (~90%) that matches the appearance of plastics and has superior barrier properties, but its tensile strength and stiffness are lower than that of nanopaper or ACCs [8, 49].

2.3. Nanopaper

Recently, transparent paper made of CNs (NCC and NFC) had a representative thickness of 25–100 μm and a density of 0.8–1.5 g cm^{-3}, and attracted great attention because of its unique properties such as excellent flexibility [3, 5, 6, 8, 89–92], superior surface smoothness [7, 8, 91], thermal stability [93, 94], high optical transmittance [5, 8, 15, 43, 94, 95], strong tensile strength [44, 45, 47–49] and superior gas barrier performance in dry conditions [51–53, 87, 96–99]. These fascinating properties meet the stringent requirements of fabricating next generation 'green', transparent and flexible electronics on nanopaper. The cell wall of a wood fiber consists of a primary wall and three secondary wall layers, and each of these layers is composed of millions of CNs with a specific arrangement [28]. Efficiently disintegrating CNs from the fiber cell wall through chemical treatments and/or mechanical processes is thus a key step to prepare nanopaper. Additionally, CNs can also be isolated from bacteria, tunicates and algae in order to be used as reinforcement materials to improve the thermal stability and mechanical strength of transparent composites [4, 67, 95, 100–102]. We will focus on CNs extracted from wood due to limited space in this article.

The reports of colloidal suspensions of cellulose prepared from sulfuric acid degradation of cellulose fibers appeared in the 1950s [103–106]. NCC is generated by removing amorphous areas of purified cellulose with the assistance of acid hydrolysis, always followed by a step of ultrasonic processing. It appears to be a promising material with a strengthening effect and superior optical properties that may find potential use in coating, food packaging, gas barriers, security paper, nanocomposites, etc [24, 37, 107]. Yang *et al* developed a new method to produce electrosterically stabilized nanocrystalline cellulose (ENCC) without the use of intensive mechanical processes. After a modification of ENCCs by oxidation, an ion exchange treatment and cross linking, nanopaper fabricated from various modified ENCCs by vacuum filtration shows an increase in tensile strength and thermal stability, yet a decrease in water vapor transmission rates and optical transmittance compared to original ENCC film [108]. There are a few reports on the application of NCC film on electronic devices. Zhou *et al* prepared a nanopaper made of NCC and glycerol (see figure 3(b)) by the casting method to fabricate organic solar cells, and this nanopaper exhibits a root mean square (RMS) surface roughness of 1.8 ± 0.6 nm [12], which is much more suitable for the direct fabrication of electronics.

Acid hydrolysis of wood pulp to produce NCC only has a yield of 30–50% [109] and the pure NCC film indicates a fragile and stiff performance due to the high stiffness of whisker-like NCC that restricts the application of NCC film in flexible electronics. NFC exhibits a high aspect ratio (100–150), large specific surface area (100–200 m^2 g^{-1}), high strength and good elastic performance [110]. The inherent strength of cellulose crystals within NFC combined with the strong interactions between NFCs during drying enable the production of much tougher and more flexible neat NFC than pure NCC film [111]. The liberation of NFC from the cell wall of wood fibers by mechanical processes was first reported by Herrick and Turbak in 1983 [112–114]. Most research efforts have since focused on energy-efficient disintegration of individual NFC with minimum mechanical damage. Currently, pretreatments (alkali treatments, oxidation, enzymatic treatments) along with mechanical treatments (homogenization, grinding, microfluidization, ultrasonic treatments, cryo-crushing) are utilized to obtain NFC with desirable properties [25, 36, 37, 52, 115–118].

There has been an increased interest in pure NFC film over the past decade. It was not until 1997 that Taniguchi first reported the use of natural microfibrillated fibers with a diameter of 20–90 nm to produce a new film with a translucent appearance and dramatically enhanced tensile strength, but no complete data was provided [119]. The first literature elucidating in detail the fascinating properties of a new paper made of CNs from trees was published by Nogi *et al* After delignification of wood flour, the residue was pretreated with 5% potassium hydroxide to remove hemicellulose, followed by a grinding procedure. The obtained NFC was used to prepare nanopaper by vacuum filtration, exhibiting a maximum optical transmittance (71.6% at 600 nm), minimal coefficient of thermal expansion (8.5 ppm K-1) and high tensile strength (223 Mpa [42]). The excellent oxygen and oil resistance of this nanopaper are also described in the literature [51, 99]. Wang and his co-workers utilized cellulosic solid residue from the waste stream of acid hydrolysis of hardwood pulp to produce NFC by a homogenization in a microfluidizer. This procedure shows a conspicuous decrease in energy consumption of nanofibrillation compared to original hardwood pulp and achieves the full use of cellulose during the production of cellulose nanocrystals. The prepared NFC was then used to produce a neat NFC film with an optical transmittance greater than 90% in the visible range [50]. Note that the paper's density is an important parameter that influences the optical, mechanical and barrier properties of transparent paper [45, 53, 98]. The density of paper should therefore be taken into consideration as the optical and mechanical properties of diverse samples are contrasted.

Due to the strong interfibrillar hydrogen bonding, separating NFC from the fiber cell wall is an energy-intensive process that causes serious damage to the fiber morphologies, which becomes a major impediment for commercial applications. To alleviate the fiber damage and reduce energy consumption during mechanical processes, various pretreatments are applied to the wood pulp, such as enzymatic treatments, alkali processing and chemical oxidation. As a result, the power required to produce one ton of NFC from sulfite pulp significantly decreases from 20 000–30 000 kWh to 500 kWh [24, 116]. In recent years, a promising and effective method was proposed by Isogai *et al* to pretreat wood pulp using 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated oxidation under aqueous conditions prior to grinding or homogenization [35, 98, 120–124]. Through this pretreatment, individual NFCs were easily disintegrated from microscopic wood fibers by the electrostatic repulsion between the negatively charged carboxylate ions introduced in the subsequent mechanical processing that attaches carboxyl groups in the C6 position of cellulose.

Transparent paper made of TEMPO-oxidized NFC exhibits excellent optical transmittance and high barrier properties. Isogai *et al* reported a transparent paper fabricated from softwood TEMPO-oxidized NFC, which presented an optical transparency up to 90% at the wavelength of 600 nm, a tensile strength of ~233 MPa and Young's modulus of ~6.9 GPa, and a low coefficient of thermal expansion of approximately 2.7 ppm K^{-1} m. A thin layer (0.4 μm) of NFC was coated on 25 μm thick polylactic acid (PLA) film, displaying a vigorous decrease in oxygen permeability from 746 mL m^{-2} d^{-1} Pa^{-1} to 1 mL m^{-2} d^{-1} Pa^{-1} [98]. Hu *et al* demonstrated a carboxymethylated NFC-based nanopaper for solar cells. It not only indicated an excellent transparency of ~90% similar to that of commercial polyethylene terephthalate (PET) plastic, but also presented the light scattering behavior that is desired for optoelectronics [15]. Figure 3(c) displays a transparent paper fabricated from TEMPO-oxidized NFC by Huang and his colleagues for a flexible transistor, exhibiting a 90% transparency, a tensile strength over 200 MPa and a root mean square roughness (RMS) of 1 nm [43]. Zhu *et al* reported a nanopaper also made of TEMPO-treated NFC for OLED showing an optical transmittance of 93% and transmission haze of 50% at 550 nm, and a maximum tensile strength of 287 MPa. Additionally, this transparent paper-based OLED displayed anti-glaring effects in sunshine due to the light scattering behavior of paper substrate [8].

In addition to the aforementioned transparent paper made of macroscopic cellulose fibers, cellulose nanofibers or regenerated cellulose, there are other types of transparent papers developed recently that present a ~90% optical total transmittance. It will take a long time to prepare a piece of nanopaper with a filtration due to the poor drainability of the NFC suspension. Furthermore, the thickness of nanopaper fabricated from vacuum filtration is generally less than 60 μm, resulting in insufficient stiffness for the fabrication of some electronic devices. A bistructural transparent paper with a total transmittance of 91.5% (at 550 nm) using NFC and microsized wood pulp by filtration was proposed by Fang *et al* aimed at solving the problem (figure 3(d) [10]). A thin film layer of NFC ensures the nanoscale surface roughness that fulfils the requirement for fabricating electronic devices, while the NFC-infiltrated hybrid layer assures the high stiffness and shape stability of fabricated transparent paper. However, this procedure still takes several hours to filter a piece of transparent paper. Hu's research group made a great step forward in the fast fabrication of transparent paper. Unbeaten wood fibers were treated with TEMPO/NaBr/NaClO and the TEMPO-oxidized wood fibers were then used to fabricate novel transparent paper by a vacuum filtration process (see figure 3(e)). This transparent paper not only presents both high optical total transmittance (~96%) and transmission haze (~60%) but also illustrates strong tensile strength (~105 Mpa), which demonstrates promising potential in optoelectronics such as OLED light systems, signage and solar cells, where optical transmittance and haze are both needed [14].

3. Device integration

Transparent paper electronics attract broad interest both in the academic and industrial community for their disposability, sustainability, light weight, excellent optical properties, flexibility and low cost. A variety of proof-of-concept transparent paper-based electronic devices have been demonstrated over the past three years. In this article, we mainly discuss three types of transparent paper devices: organic field-effect transistors (OFETs), solar cells and OLEDs.

3.1. Organic field-effect transistors

Transistors are one of the most important semiconductor devices used to amplify and switch electronic signals or electrical power. Nanopaper made of NFC exhibits strong mechanical strength, superior surface texture, remarkable optical properties and can render many types of electronics that are not possible on regular paper. People have reported the architecture and the performance of a memory card based on a single field-effect transistor built on transparent paper. Huang *et al* have demonstrated flexible transparent OFETs with carbon nanotube-coated conductive nanopaper as the gate and substrate (see figure 4(a)), showing an optical transmittance

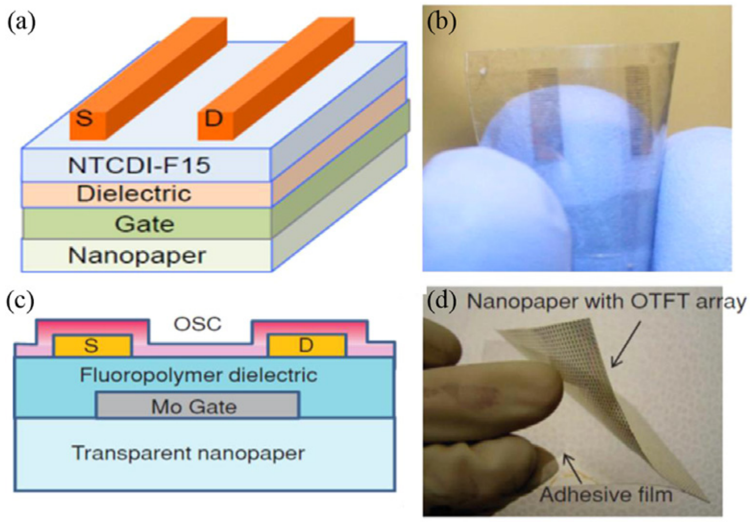

Figure 4. (a) A schematic drawing of a nanopaper organic field-effect transistor; (b) a picture of a fabricated transparent and flexible transistor; (c) schematic illumination and cross section of a fabricated organic thin-film transistor (OTFT); and (d) the fabricated nanopaper-based OTFT array can be readily peeled off from the support glass [6, 7].

up to 83.5% [7]. As shown in figure 4(b), the device is transparent and flexible. Both good electrical characteristics and excellent mechanical flexibility were observed, which may be due to the large binding energy between polymer dielectric and cellulose nanopaper and the effective stress release from the fibrous substrate. Only a 10% decrease in mobility was observed when the nanopaper transistors were bent. In addition, Fujisaki demonstrated an organic thin-film transistor (OTFT) array on the transparent nanopaper, which was laminated on the support glass and the corresponding structure is displayed in figure 4(c) [6]. The bottom-contact OTFT array based on a fluoropolymer gate dielectric and a soluble small molecular OSC was fabricated using a lithographic and solution-based process. The nanopaper can easily be peeled off from the support glass with integrated devices with no fracturing (figure 4(d)). These excellent results suggest the great potential of nanopaper transistors in flexible and green electronics.

3.2. Solar cells

A significant advance in transparent paper-based solar cells has been witnessed in the past several years. Researchers from the Massachusetts Institute of Technology used tracing paper as a substrate to fabricate solar cells by combining oxidative chemical vapor deposition with *in situ* shadow masking, followed by encapsulation [16]. As shown in figure 5(a), the light directly struck on solar cells showing a power conversion efficiency (PCE) of less than 1.5% and having a life time (half-life) of over 500 h. Hu and his colleagues first applied the high transparent nanopaper (~90% at 550 nm) to demonstrate solar cells with a ~0.21% PCE (figure 5(b) [15]). Figure 5(c) shows the recyclable solar cells on cellulose nanocrystal substrate demonstrated by Zhou *et al*, which not only displayed a high PCE of 2.7% but also showed the recyclability of paper-based solar cells [12]. These solar cells only used transparent paper as a flexible and affordable substrate rather than as a component and the incident light directly reaches the active layer of solar cells without using the optical properties of transparent paper. Fang *et al* developed a novel transparent

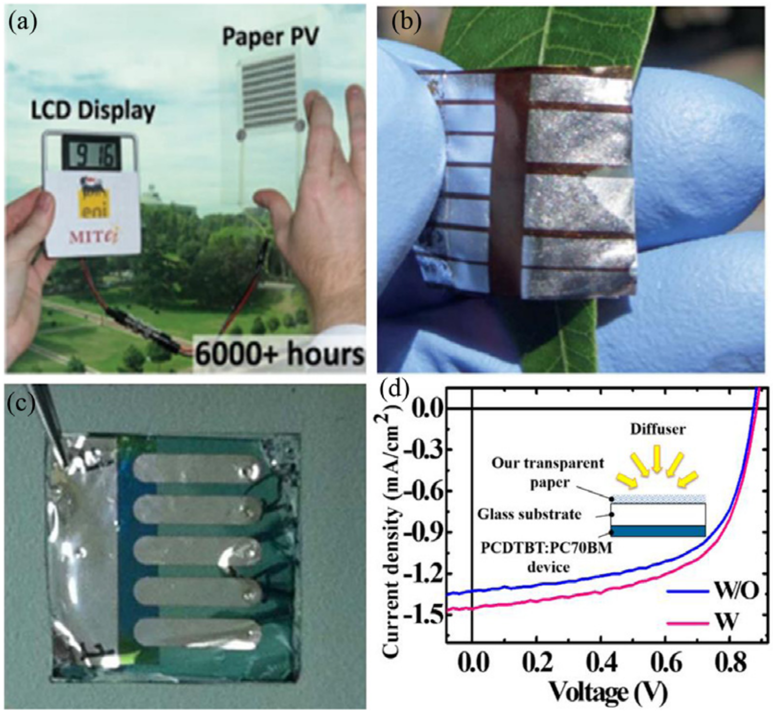

Figure 5. (a) Laminated paper solar cells power the LCD displayer; (b) solar cells based on transparent and conductive nanopaper; (c) recyclable solar cells fabricated on a cellulose nanocrystal substrate. Reprinted with permission from Macmillan Publishers Ltd (Y Zhou, C Fuentes-Hernandez, T M Khan, J-C Liu, J Hsu, J W Shim, A Dindar, J P Youngblood, R J Moon and B Kippelen 2013 Recyclable organic solar cells on cellulose nanocrystal substrates *Sci. Rep.* **3** 1536). (d) The I–V characteristics and schematic of a transparent paper-based organic solar cell [12, 14–16].

paper with both high optical transmittance and strong light scattering behavior, which can be attached to solar cells to increase light harvesting of organic solar cells resulting in an increased PCE from 5.34% to 5.88% (figure 5(d) [14]). Dongheon and colleagues used transparent paper as an anti-reflection layer of photovoltaics to improve light trapping ability. Through simply laminating transparent paper on the top of GaAs solar cells, it presents an increased PCE from 13.55% to 16.79% while showing angle independent behavior in the visible range [17].

3.3. Organic light-emitting diodes

OLEDs are a versatile platform for electronic displays ubiquitous in daily life. Flexible and even foldable displays attract worldwide attention. Traditionally, OLEDs are fabricated on rigid glass or flexible plastic such as polyethylene terephthalate (PET) and polyethylene naphthalate (PEN) substrates. The rigidity and density of glass not only increases the cost on the manufacturing line but also brings inconvenience for the device carriers. Glass is not a promising substrate for roll-to-roll manufacturing. The biggest challenge of plastic substrates is their thermal stability. Most plastic has a large coefficient of thermal expansion (CTE), which causes the destruction of functional materials of the OLED layers during temperature fluctuation in the device assembly and mounting processes. Paper is an attractive substrate for flexible electronics because of its excellent thermal stability, recyclability, sustainability, light weight, flexibility and mature

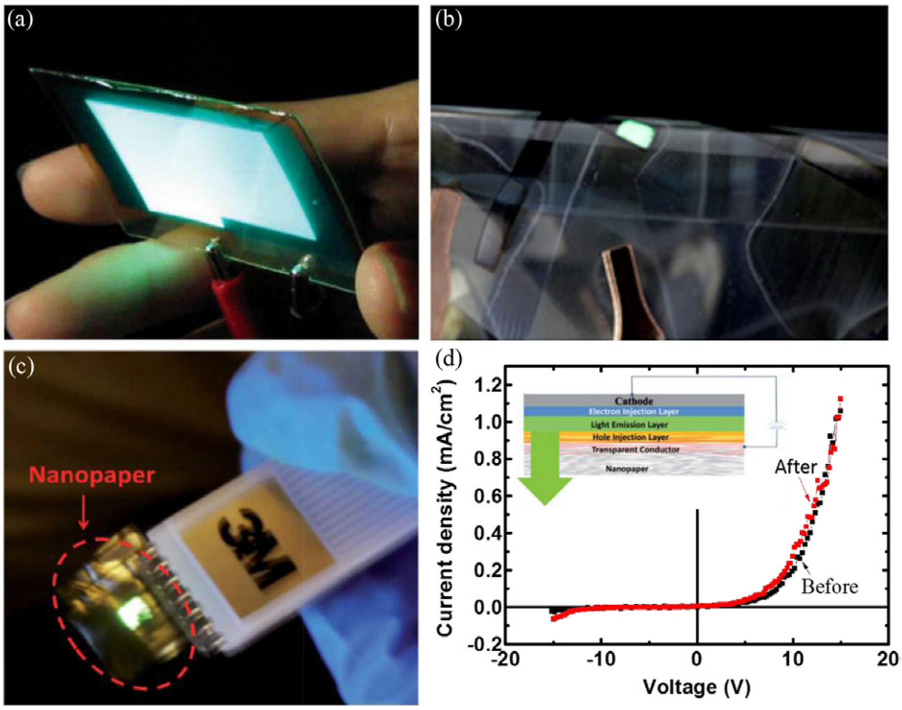

Figure 6. (a) Luminescence of an organic light-emitting diode (OLED) deposited onto a transparent bacterial cellulose nanocomposite; (b) OLEDs operating on transparent paper made of regenerated cellulose films; (c) image of an OLED deposited directly on a cellulose nanopaper; (d) I–V curve of the flexible OLED in the flat and bent states, respectively. The bending radius is 1.5 mm. Inset is the structure of OLEDs [4, 8, 9].

roll-to-roll large scale manufacturing technology. The opaque and large surface roughness of regular paper becomes an impediment for use in the OLED device. Recently, transparent nanopaper has attracted broad interest for its high optical transmittance, low CTE and excellent mechanical strength. Nogi *et al* demonstrated an OLED deposited onto bacterial cellulose reinforced matrix resin in figure 6(a) [4]. Figure 6(b) is a flexible phosphorescent OLED fabricated on RCF reported by Sumit *et al* showing high brightness, high current density and luminous efficiencies [9]. Figure 6(c) shows the powered OLED on nanopaper [8]. The inset in figure 6(d) illustrates the structure of the device, which consists of a 20 nm calcium (Ca) electron injection layer, a light-emitting layer of green polyfluorene, a 10 nm molybdenum oxide (MoO_3), 30 nm PEDOT:PSS (poly(3,4 ethylenedioxythiophene): poly(styrenesulfonate)) hole injection layer and two conductive layers. I–V curves of the flexible OLED at flat and bending states are demonstrated in figure 6(d). There is little difference between the regressions before and after bending [8]. We can see that nanopaper is a promising substrate for transparent and flexible OLED devices. The nanopaper is not only lighter, stronger and more thermally stable, but also possesses high transmittance and can be applied in roll-to-roll large scale manufacturing.

4. Scalable manufacturing of transparent paper

Filtration, extrusion and impregnation are three primary approaches to produce transparent paper on a large scale. Commercial transparent paper such as tracing paper and glassine are currently

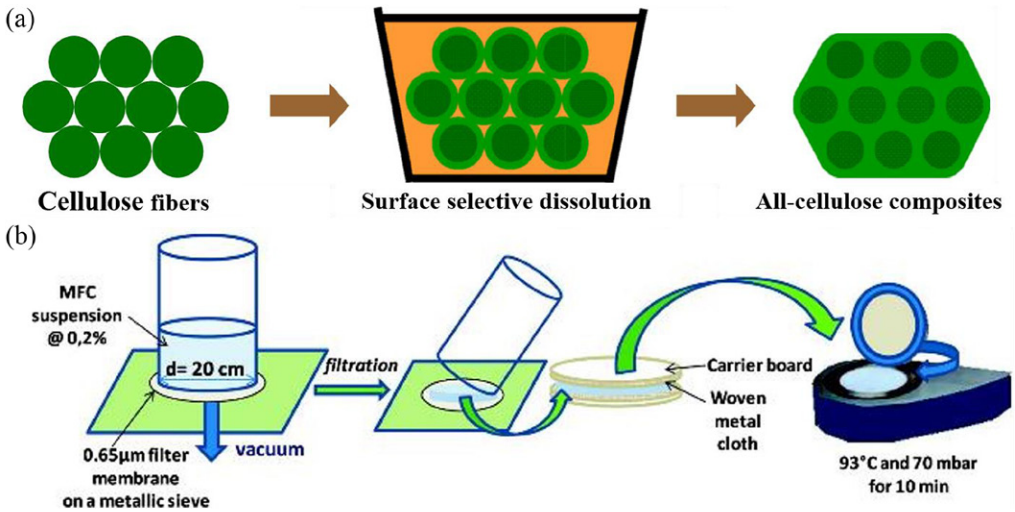

Figure 7. Methods for the production of transparent paper. (a) Selective dissolution of the fiber surface; (b) filtration [64, 126].

produced by a traditional paper-making technology followed by a process of supercalendering or impregnation that significantly reduces the microcavities within paper. Parchment paper is one type of paper widely used in baking that aims to replace traditional wax paper and is made by immersing formed paper into a bath of sulfuric acid or sometimes zinc chloride to partially dissolve the fiber surface. For cellophane made of dissolved cellulose widely used in food packaging, the fully dissolved cellulose solution is extruded through a slit to form a flat sheet, which then coagulates in a precipitation bath followed by several steps of washing to remove the additional materials. Since these transparent papers have been developed for more than a century, their scalable technologies are quite mature. In this review, we will not discuss them in detail.

The original transparent paper was produced by impregnating a formed sheet into oils, resins, wax, etc [55, 57]. This technology further evolved into chemical treatments of shaped paper using sulfuric acid or $ZnCl_2$, showing great potential in the preparation of transparent paper. Nishino *et al* proposed a method to prepare transparent paper with high optical transmittance via chemical treatments of paper made of microsized cellulosic fibers or CNs [64, 65, 67, 71] and the schematic illustrating the mechanism of this method is displayed in figure 7(a). Filter paper was immersed in LiCl/DMAc solvent to partially dissolve the fiber surface [64]. More solid cellulose was dissolved with increasing immersion time of the paper in the LiCl/DMAc solvent and the dissolved cellulose penetrated into the inside pores, which resulted in the enormous increase in the paper's transparency. However, several challenges should be overcome prior to industrial production of transparent paper via this method; for example, it takes a long time to activate the cellulosic fibers and partially dissolve the activated paper, which limits its industrial exploitation. Wang *et al* report a new procedure to prepare transparent bioplastics. Cotton linter pulp was first dissolved in NaOH/urea aqueous solution, and the prepared cellulose solution was then evenly spread on a glass followed by a process of coagulation [86]. The formed cellulose physical hydrogel was rinsed in water several times and dried under pressure at a temperature of 90–190 °C. The final cellulose film has a thickness of 300 μm, which is much higher than that of commercial cellophane. This method is quite suitable for producing thick transparent paper.

There is increasing interest in the fast preparation of transparent paper made of NFC due to its unique properties. NFC is a gel-like aqueous dispersion and has a concentration of ≤2% due to its high hydrophilicity. It is impossible to prepare nanopaper by a regeneration method because of its low concentration and indissoluble properties. Paper-making is a process of dewatering by gravity, vacuum draw, squeezing and heating, which is considered the most efficient and economical approach to produce paper on a large scale; therefore, a similar approach was used to prepare nanopaper. A typical procedure used in the laboratory is as follows: an NFC suspension forms a wet film on filter membranes with different pore sizes by pressurized filtration and the wet NFC film was then placed between two stacks of filter paper to remove free water by pressing followed by drying at room temperature [7, 53, 98, 111]. Manufacturing nanopaper by this method, however, is not practically feasible due to the time- and energy-consuming procedure caused by the low drainability of the NFC dispersion [42, 49]. In particular, for the nanopaper fabricated from TEMPO-oxidized NFC, it will take a much longer time and more energy to fabricate it due to the smaller fiber diameters and greater dispersion stability of cellulose fibers in the suspension [125].

Large-scale manufacturing of nanopaper has been hindered by the gel-like nature of the NFC suspension. To produce nanopaper on an industrial scale, alternative manufacturing technologies for rapid removal of water in NFC suspension are needed. Recently, several research groups from various universities and institutes have concentrated on fast preparation of nanopaper driven by its unique properties. Sehaqui *et al* reported a rapid water-based preparation procedure for large, flat, smooth and optically transparent nanopaper with a diameter of 200 mm using a semiautomatic sheet former, only taking 1 h to fabricate a piece of 60 μm thick nanopaper with a tensile strength of 232 MPa [126]. Figure 7(b) is the schematic for the preparation procedure, which consists of three steps: vacuum filtration, wet film transfer and drying under a vacuum. This method is not suitable for the continuous production of transparent paper because of the long time required to remove most of the free water in the NFC suspension. A quick way to prepare transparent nanopaper with excellent barrier properties and solvent resistance by pressurized filtration was proposed by scientists from Finland [49]. A 137 cm^2 large nanopaper with a thickness of 125 μm and tensile strength of 230 MPa was prepared in less than 1 h with this method, taking a major step towards commercial production.

Although a great amount of progress has been made over the last five years on the preparation of nanopaper by pressurized filtration, extremely low dewatering of NFC suspension and poor surface roughness of nanopaper left by filter membranes and wires used for filtration make this route difficult [127]. A casting method was proposed by Aulin *et al* to prepare nanopaper by pouring an NFC dispersion onto polystyrene Petri dishes with a diameter of 14 cm and drying at a temperature of 23 °C and a relative humidity (RH) of 50% [51]. A casting method avoids the filtration process while eliminating the influence of membranes and wires on the surface roughness of nanopaper. Scientists from the VTT Technical Research Center of Finland and Aalto University have gone a step further by developing a semi-industrial roll-to-roll pilot line to produce transparent nanopaper with superior surface smoothness and excellent evenness based on a similar principle avoiding slow dewatering and shrinkage [127]. NFC suspensions were prepared by a combination of enzymatic or chemical and mechanical processes (figure 8(a)), which were evenly coated on plastic films and dried at a temperature preferably in a range of 25 to 60 °C followed by hot pressing at a temperature of 80 °C. Figure 8(b) is the drying section of the semi-industrial roll-to-roll pilot line, and the obtained NFC film is displayed

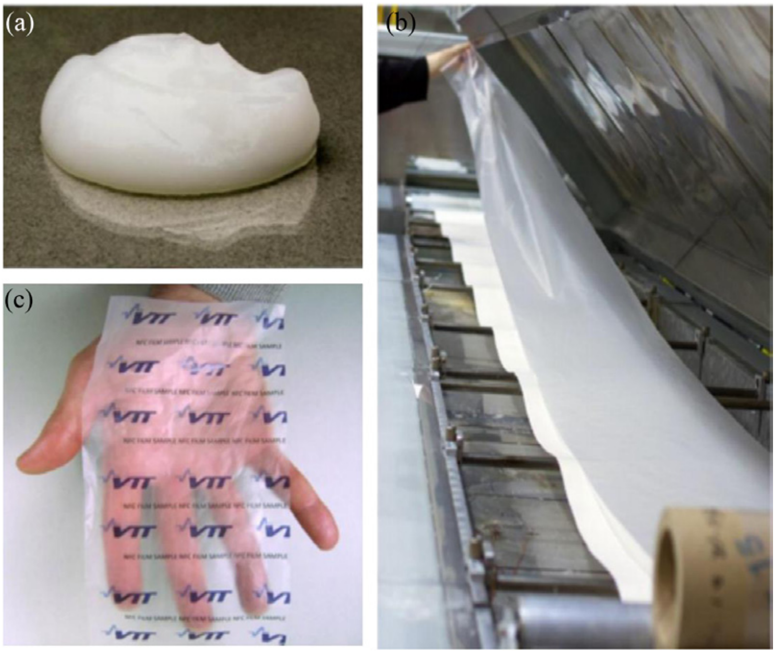

Figure 8. (a) NFC suspension; (b) a semi-industrial roll-to-roll pilot-line for NFC film developed by the cooperation of VTT and Aalto University; and (c) an NFC film [128].

in figure 8(c). This method may pave the way to industrial-scale production of nanopaper with excellent properties.

5. Cost analysis

In general, the price of commercial transparent paper is much higher than that of common paper due to the energy- and time-consuming manufacturing procedure as well as the requirement for extra equipment and chemicals to obtain excellent optical transmittance. For instance, transparent tracing paper available in the market normally costs approximately USD \$1300~\$2000 per ton; the price of cellophane usually used in food packaging is in the range of \$3000 to \$6000 per ton, which is much more expensive than common paper, which has a price ranging from \$500 to \$1500 per ton. To apply transparent paper in high-tech areas, in addition to considering the potential manufacturing technologies for large-scale production of transparent paper, affordable price is also an important factor that affects its industrialization. In this section, we focus on the cost analysis of transparent paper made of NFC, which is a hot research area showing great potential in food packaging and printed electronics. Normally, the cost of production of transparent paper involves raw materials, chemicals, energy, capital costs and so on.

Transparent paper fabricated from NFC has been a hot research area for several years; however, there is a lack of scalable manufacturing techniques and equipment and it is therefore impossible to evaluate the capital costs for the production of transparent paper. Wood pulp is the primary raw material for the production of transparent paper. There are two types of original wood pulp: bleached softwood pulp (BSP) and bleached hardwood pulp (BHP), and the marketing price of original BSP is approximately \$810~\$910 and BHP is \$750~\$850, which will fluctuate with the change in supply and demand of pulp across the world. These numbers are obtained from *World Pulp Monthly*, released by RISI Inc in January 2013 [129]. Enzymatic or chemical pretreatments were generally applied to treat the wood pulp before mechanical treatments to facilitate the isolation of NFC from the fiber cell wall. Meyer *et al* at CTP (Centre Technique du Papier) calculated the production costs of NFC based on their laboratory and pilot scale results, and concluded that the production costs of NFC with a TEMPO pretreatment were more expensive than that of NFC with enzymatic pretreatment (no exact numbers for the production costs were provided in the report) [130]. TEMPO oxidation was widely considered a promising and efficient method to pretreat wood pulp [35, 98, 123, 124]. Taking the recipe described by Huang and Zhu for example [8, 41], the price in the Chinese market for TEMPO, sodium hypochlorite and sodium bromide is approximately \$100 Kg^{-1} [131], \$0.17 Kg^{-1} (10 wt % [132]) and \$1.30 Kg^{-1} [133], respectively, and the total chemical cost for producing one ton of NFC is around \$2700. High chemical costs hinder the up-scaling of TEMPO pretreated NFC. Fortunately, some reports showed that the NaBr and expensive TEMPO served as a catalyst during the oxidation procedure and can be recycled from spent liquid, which has the potential to reduce the production costs of TEMPO-oxidized NFC [33, 134]. The energy for the production of transparent paper was primarily divided into two parts: liberation of NFC and removal of water in NFC suspension. Considering a variety of approaches for the preparation of NFC and transparent paper, it is difficult to calculate the cost of energy consumption. Therefore, we will not investigate the energy costs for the production of transparent paper in this article.

Summary

Transparent paper for electronics is becoming an increasingly hot research topic in scientific communities as a new area for next generation 'green' electronics that meet the requirement for the sustainable development of human society. A great amount of recent progress has been made, including: (1) cellulose materials with dimensions spanning from the microscopic scale to nanoscale have been used to fabricate transparent paper with superior mechanical and optical properties; (2) filtration, casting, impregnation and chemical treatments can be used to make transparent paper depending on the requirements of its eventual use; (3) various proof-of-concept devices have been demonstrated using transparent paper as a substrate or component showing competitive performance; (4) fabricating nanopaper by efficient methods is ongoing from the laboratory scale to pilot scale; and (5) tailored properties of transparent paper for specific electronic devices. There are still many challenges that must be overcome for the preparation of transparent paper, which include but are not limited to the following: (1) current time- and energy-consuming fabrication processes for transparent paper with superior mechanical and optical properties; (2) the poor dimensional stability and bad water resistance of transparent paper due to the hydrophilic property of cellulose; (3) affordable cost for the isolation of NFC from the fiber cell wall and mass production approaches of nanopaper; and (4) the weather durability of transparent paper.

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