

## Review of Electrically Conductive Composites and Films Containing Cellulosic Fibers or Nanocellulose

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Strategic combinations of cellulosic materials with electrically conductive polymers or nanoconductors offer important potential advantages for technological advances, light-weight inexpensive products, applications of novel form factors, and more eco-friendly alternatives to certain forms of smart packaging and electronics. This review of the literature focuses on how such electrically conductive composite systems work, the roles that cellulosic materials can provide in such structures, processes by which electrically-conductive cellulose-based composites and films can be manufactured, and various potential applications that have been demonstrated. Several advantages of cellulose, such as ease of fabrication, compatibility with conductive agents, and sustainability, allow its integration with conductive agents in making conductive composites. Applications of electrically conducting cellulose-based composites for strain sensors, energy storage, solar cells, electrodes, supercapacitors, and smart packaging are discussed.

*Keywords:* Nanocellulose; Conductive material; Composite; Flexibility; Smart Packaging

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### INTRODUCTION

The pace of recent publications reveals intense interest in the production of thinner, cheaper, lighter, and more eco-friendly electro-conductive films and composites. The goal of this article is to review scholarly work leading towards an understanding of electrically conductive composites and films that contain various forms of cellulose, with an emphasis on nanocellulose. Cellulose itself is not a good conductor of electricity, but as a primary ingredient in electrically conductive composites it may serve as an eco-friendly, generally low-cost substrate. However, the combining of a cellulose-based non-conductor with conductive materials presents many challenges or potential advantages in terms of electrical connectivity, tolerance to forces and extension, interfacial adhesion, and chemical stability of the composite materials.

Motivations for the use of cellulosic materials in modern products, displays, and packaging often can be expressed in a negative sense: avoiding higher-cost materials, avoiding heavy structures, and avoiding usage of non-renewable materials, *etc.* (Siqueira *et al.* 2010; Abdul Khalil *et al.* 2012). If one is willing to accept that some classes of manufactured items will be discarded after a single usage (as in the case of a package), then it is important to explore the use of constituent materials that are inherently recyclable and also those that cause minimum harm if discharged to the environment. This pair of challenges will be kept as a subtheme in this article when examining the scholarly literature pertaining to various electrically conductive materials that have been paired with

cellulosics in various studies. Another theme will be to consider the different potentially favorable attributes of cellulose in such applications. The list might include such attributes as fibrillar shape, flexibility, and various chemical details of cellulosic materials.

Certain earlier review articles should be mentioned, either to provide further background or as a means to cut down on the need for detailed discussion of subtopics that already have been well covered by others. Clerc *et al.* (1990) reviewed the AC electrical conductivity of disordered binary composite systems, with an emphasis on semi-random networks of electrical connectivity (percolation) and mathematical modeling. Roldughin and Vysotskii (2000) considered metal-filled films in their review of structures and mechanisms affecting conductivity. The reviews by Bauhofer and Kovacs (2009) and Min *et al.* (2010) deal with the use of carbon nanotubes in conductive composites. Svennersten *et al.* (2011) reviewed the topic of organic bioelectronics in nanomedicine. Tobjörk and Österbacka (2011) reviewed “paper electronics,” covering applications in which paper can be the substrate for printed electronics. Nyholm *et al.* (2011), in their review, covered flexible and paper-based energy storage devices. Irimia-Vladu (2014) reviewed the topic of “green electronics,” with some discussion of electrically conductive polymers and conductive paper. Agate *et al.* (2018) also reviewed recent advances in printed electronics, with particular emphasis on paper as a substrate. Qiu and Hu (2013) reviewed the topic of “smart” materials based on cellulose. Jabbour *et al.* (2013), Shi *et al.* (2015), Ummartyotin and Manuspiya (2015), and Du *et al.* (2017) covered the role of conductive cellulosic systems for use in batteries and other energy-related applications. Terzopoulou *et al.* (2015) as well as Rouf and Kokini (2016) reviewed the roles of graphene, its oxides, and other derivatives in electrically conductive composites containing polysaccharides. The general topic of cellulosic materials in composites and nanocomposites also has been reviewed (Hubbe *et al.* 2008; Siqueira *et al.* 2010; Abdul Khalil *et al.* 2012).

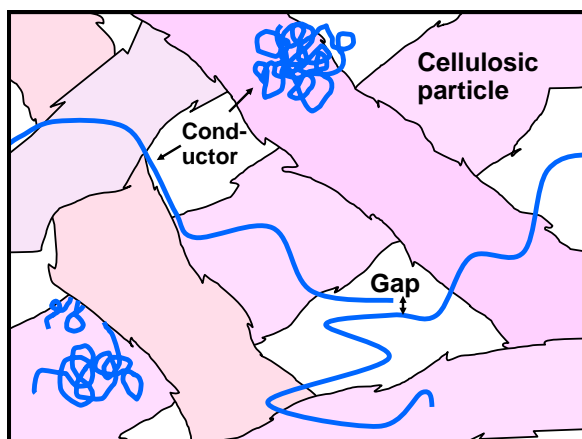
A key motivation for the use of cellulosic materials in various composites has been to reduce reliance on non-renewable materials such as synthetic plastics (Abdul Khalil *et al.* 2012). The wastes of conductive materials based on plastics and inorganic semiconductors are difficult to recycle or decompose; hence they are causing serious environmental problems (Irimia-Vladu 2014). More recently, bio-based materials, such as cellulose and chitin, are receiving a lot attention because of their compostable and cost-competitive characteristics. Cellulose is a polysaccharide of D-glucose. It represents the most abundant polymer in nature and has an annual production of over 150 million metric tons (Zhao and Li 2014). Due to its specific crystalline nature, outstanding mechanical properties, and high surface activity, cellulose and its derivatives are among the most promising biopolymers for many different applications, including but not limited to biomedical devices and wastewater treatment (Grishkewich *et al.* 2017).

## THEORETICAL ASPECTS

### Conductive Composites

Conduction within composite materials depends on the mobility of electrons (Last and Thouless 1971; Wosnitza 1996). As will be described in more detail in the next main section, electrons flow very easily in metals, but also within certain organic polymers such as polypyrrole, graphene, and carbon nanotubes. Most often, when dealing with electrically conducting composites, one of the phases conducts electricity well, whereas the other either is an insulator or a much poorer conductor. So in this review much attention

also will be paid to gaps, defects, and complete lack of contact among the electrically conductive elements in the composite. The envisioned situation is illustrated schematically in Fig. 1, where a nano-scale gap space is represented in the lower-right quadrant.



**Fig. 1.** Schematic illustration of nanostructure within a hypothetical cellulose-based composite containing a conductive component such as carbon nanotubes, which are shown as either being stretched out or agglomerated into bunches

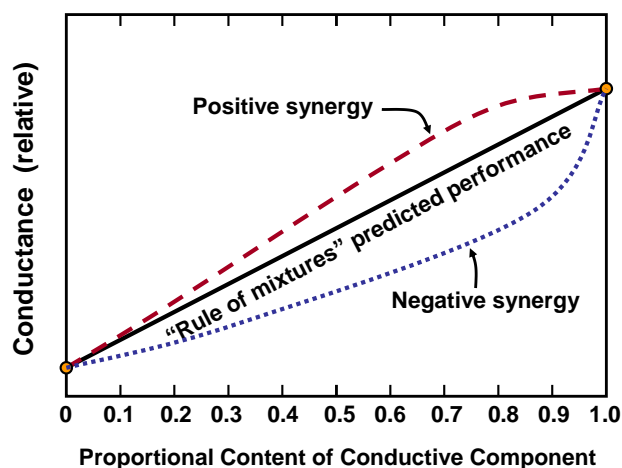
It is not always clear what is the most advantageous size of either the conductive particles or the structural particles (*e.g.* cellulose) in a conductive composite or film. A smaller particle size typically requires a higher energy to prepare the materials and greater costs if there is need for surface modification or the use of a compatibilizer (Lai *et al.* 2003; Qiu *et al.* 2005; Roy and Potiyaraj 2018). Also, depending on how a composite is constructed, there will be cases where higher surface areas may imply a greater requirement and cost of electrically conductive material. Shi *et al.* (2015) listed the following potential advantages of nanostructured conductive polymers for such applications: favorable accommodation of strains, large surface areas, short pathways for charge transport (maybe due to small size of the potential devices), and the availability of a variety of mechanisms of conduction. Though there are reasons to favor different sizes of particles in a composite, a key question will be what combination best meets the performance needs of the application while minimizing costs.

Though the main focus of this review is on composites, it will be important to bear in mind that there are some alternative strategies that can be suggested for future research. For instance, in any mixture of conductive and non-conductive materials there is an inherent risk of inefficient flow of current. Some of the conducting particles may fail to be in electrical contact with other conductors. Such problems often can be minimized by a layered structure, placing the conductive material in layers and then using adjacent layers of structural, binding, or insulating material for support and protection. Though such issues lie beyond the scope of the present review, it seems a promising topic of future research to compare the efficacy and practicality of using layered structures as an alternative to the composite mixtures that will be mainly considered in the present article.

### Rule of Mixtures

One of the simplest, but not necessarily accurate ways to estimate the conductivity of a composite is to sum up the products of the proportional shares of the components and their respective electrical conductances (Du *et al.* 2006; Hubbe 2017). The prediction of

such a “rule of mixtures” calculation is illustrated schematically in Fig. 2. The figure also shows hypothetical results for a system exhibiting positive or negative synergistic effects relative to the expected result based on the rule of mixtures assumption.



**Fig. 2.** Hypothetical plot illustrating what is meant by a “rule of mixtures” relationship, as well as positive and negative synergistic effects

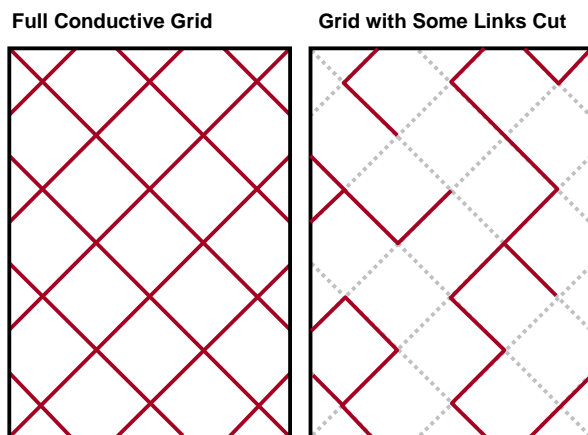
Spitzig *et al.* (1993) observed a rule of mixtures relationship in the case of a heterogeneous amalgam of two metals having unequal conductance. Gaier *et al.* (2003) observed reasonable agreement when predicting the conductance of graphite-polymer composites, but only when testing broad, flat specimens. Narrow specimens showed deviations from the rule, which were attributed to there being too few paths of electrical connections, depending on the size of the specimen. The term “effective medium approximation” has been used when accounting for well-behaved systems in which the conductance properties of composites were predictable based on their composition (Clerc *et al.* 1990; Hsu and Wu 1993; Wang *et al.* 2015c; Xia *et al.* 2017). Similar to the rule of mixtures, the effective medium theory implies that the conductances of the constituents of a mixture are averaged in proportion to their content. Whatever terms and details are used for the calculations, there are some key limitations such approaches, since they do not account well for effects related to shapes of conductive particles, various details related to connectivity, and the statistics of completion of the conductive paths.

### Percolation Theories

The word percolation, as an approach to predicting the electrical conductivity of composites, actually originated in efforts to predict the flow through granular media, as in the case of hot water flowing through coffee grounds (Hunt 2001). The concept of percolation perhaps can be best grasped by considering the experiment conducted by Last and Thouless (1971). These researchers randomly punched holes into conductive paper. They found that conductance went to zero when the proportion of holes approached 0.4. Subsequent researchers have used more sophisticated numerical approaches to perform the same general type of analysis, with options to consider three-dimensional paths of conductance and the effects of differently shaped conductive particles. Excellent reviews of the topic of percolation theory are provided by Kirkpatrick (1973), and Clerc *et al.* (1990). Hunt (2001) reviewed percolation in the case of fluid flow through granular media

with random closure of passages for the fluid. A review article by Bauhofer and Kovacs (2009) provides a listing of “percolation threshold” values, *i.e.* the minimum content of the conductive component required to significantly increase the composite’s electrical conductance relative to that of the non-conductive phase.

The concept of percolation is illustrated in Fig. 3, which is patterned after examples shown by Zallen (1983). The case shown represents the kind of calculation in which electrical connections are systematically (usually randomly) removed from a regular grid, which can be regarded as a system of ordinary resistors. Elimination of links reduces the number of complete paths, until eventually the last complete connection has been lost. In the case shown, for instance, the removal of links completely eliminated left-to-right flow of current crossing the whole grid, and only one path remained for up-to-down current. It is typical for computations to be carried out with very large grids, so as to better represent real systems in which there are very high numbers of possible connections (Zallen 1983).



**Fig. 3.** Illustration of percolation concept, comparing a fully connected grid with a case in which about half of the connections have been eliminated, leading to reduced connections

The traditional approach inherent in percolation theory is an assumption that conductive elements are distributed in a purely random fashion (Last and Thouless 1971; Kirkpatrick 1973; Zallen 1983; Mamunya *et al.* 2002; Bauhofer and Kovacs 2009). For example, Last and Thouless (1971) achieved such an effect by punching random holes into a conductive paper sheet. The results of calculations based on percolation theory have shown quite good agreement with observed conductance measurements for systems that are sufficiently well removed from the critical range of content of the conductive component (Kirkpatrick 1973). Percolation theory predicts much more efficient completion of conductance paths with increasing length-to-width (aspect) ratio of the conductive particles (Kirkpatrick 1973; Mamunya *et al.* 2002; Li *et al.* 2007; Bao *et al.* 2013). Some progress also has been achieved in making predictions within the critical zone, for instance with the concept of a “Green’s function” (Kirkpatrick 1973), a “critical path analysis” (Hunt 2001), and a “magic ratio rule” (Geng *et al.* 2015) to account for connectivity. Roldughin and Vysotskii (2000) introduced the usage of fractal concepts in accounting for connectivity in percolation systems. However, Bauhofer and Kovacs (2009) found large divergence in data obtained from different studies. This can be taken as an indication that the assumption of purely random distribution may be incorrect in many or most cases when applying such calculations to predict experimental results.

Researchers have found it useful to summarize data by means of power laws, as shown in Eqs. 1 and 2 (Grassberger 1999; Mamunya *et al.* 2002; Bauhofer and Kovacs 2009; Min *et al.* 2010),

$$\sigma = \sigma_o \cdot (\varphi - \varphi_c)^t \quad (1)$$

$$\sigma = \sigma_c + (\sigma_m - \sigma_c)[(\varphi - \varphi_c)/(F - \varphi_c)]^t \quad (2)$$

where  $\sigma$  is the electrical conductivity for filler volume contents equal to or larger than a critical value of  $\varphi_c$ ,  $\sigma_c$  is the conductance of the conductive component,  $\sigma_o$  is the conductivity associated with the critical condition,  $\sigma_m$  is the conductivity of the matrix,  $\varphi$  is the volume fraction of conductive particles, and  $F$  is the maximum packing of the conductive filler component. The exponent  $t$  was found empirically to lie within the range of 2.4 to 3.2 (Mamunya *et al.* 2002), which exceeds the theoretically expected value of 1.7. Min *et al.* (2010) reported that in a variety of structures the value of  $t$  can fall in the range between 1.6 and 2 according to various theoretical predictions. Experimentally determined values have been reported in the range of 0.7 and 3.1.

One of the challenges in such models involves how to decide whether or not adjacent conductive elements are in contact or not, since the conventional practice is to regard such contact points as on-off switches for current flow (Kirkpatrick 1973; Min *et al.* 2010). For example, Wang and Chatterjee (2003) assumed that full contact was established whenever the distance between the centers of rod-like particles did not exceed a predetermined value. However, what makes sense mathematically does not necessarily account properly for what actually happens. For instance, Du *et al.* (2006) observed a relatively large interfacial resistance at the junctions between carbon nanotubes that were in physical contact.

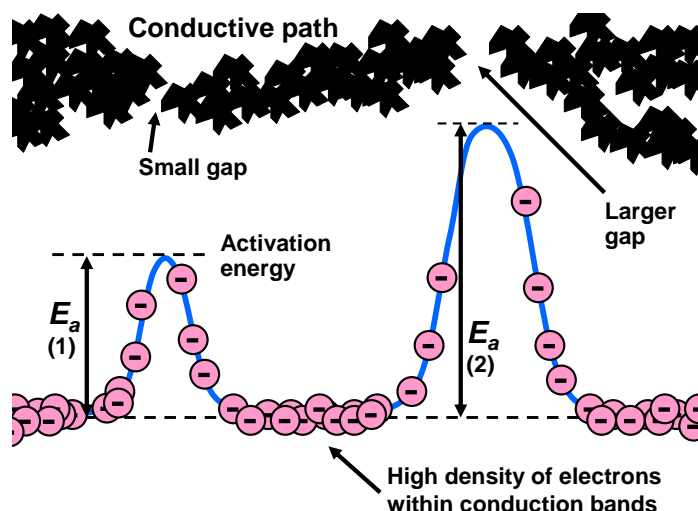
### Hopping and Tunneling Mechanisms of Charge Flow

Since cellulosic materials generally don't conduct electricity well, it is reasonable to expect there to be gaps in the networks of conductive material within cellulose-based conductive composites. To a first approximation, the cellulosic material might be regarded as a perfect resistor, and much attention has been directed towards electron transport related to the conductive substances. Two mechanisms to account for movement of electricity across such gaps are known as hopping and tunneling (Sheng 1980; Du *et al.* 2006; Min *et al.* 2010). Both of these mechanisms entail an activation energy that governs the probability of each unit transport of charge (Hunt 2001). Thus, the amount of current can be expected to follow an Arrhenius relationship,

$$i = A e^{-(E/RT)} \quad (3)$$

where  $A$  is the pre-exponential factor,  $E$  is the activation energy,  $R$  is the gas constant, and  $T$  is the absolute temperature.

Figure 4 envisions a situation in which a certain energy of activation is required for electrons to "hop" across a gap between conductive surfaces. As shown, the expected population of electrons becomes rarer and rarer within a gap of increasing size (occupied by an insulator or empty space) due to less favorable energy, as predicted by the Boltzmann distribution.



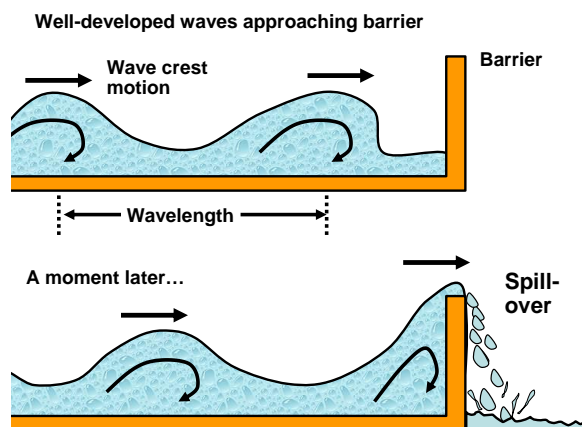
**Fig. 4.** Schematic illustration of the relationship between potential energy (vertical axis) and the expected population densities of electrons, as influenced by nano-scale gaps in a chain of electrically conductive particles

Kaiser *et al.* (2009) found that both mechanisms, hopping and tunneling, are favored by strong local electrical fields. Also, as suggested by Eq. 3, the conductance generally increases with increasing temperature. This is expected because of higher amounts of thermal energy, which increases the likelihood that a given electron will acquire sufficient potential energy to surpass the energy barrier.

The hopping concept applies most appropriately when electrically chargeable sites in a composite are small, in a quantum sense (Sheng 1980). Sato *et al.* (1991) concluded that hopping was the current-limiting factor for conduction within polypyrrole films at high temperature. Based on the observed dependence of current on temperature, Mavinakuli *et al.* (2010) invoked a hopping concept to account for conductivity within a composite of polypyrrole and silicon carbide. Roldughin and Vysotskii (2000) observed a frequency dependence of conductivity in metal-filled polymer films and proposed that this was consistent with a hopping or tunneling mechanism of transport of charge across gaps.

The tunneling concept, by contrast, pertains especially to systems comprised of relatively long conductive paths separated by short gaps (Sheng 1980). Min *et al.* (2010) described such gaps as providing either “contact resistance” or a potential barrier. One can imagine waves of electrical current sloshing back and forth within these pathways, such that the local electrical field varies and sometimes is sufficient to jump the gaps at a rate that can be estimated based on the Arrhenius equation.

The concept is illustrated in Fig. 5, using the analogy of a series of well-developed waves approaching a fixed barrier. This perspective is consistent with the frequency-dependent nature of conductance in such systems (Roldughin and Vysotskii 2000; Xia *et al.* 2017). Whereas hopping mechanisms are strongly associated with higher temperatures, the tunneling mechanism can be important for low to moderate temperature systems (Sheng 1980; Sato *et al.* 1991; Kaiser *et al.* 2009). A tunnel junction can be modeled as a capacitor in series with resistors (Sheng 1980), which suggests that the mechanism may be most effective for conduction of alternating current within favorable ranges of frequency.



**Fig. 5.** Analogy of a well-developed pattern of waves approaching a fixed barrier. In the envisioned example, kinetic energy is converted to sufficient potential energy (higher elevation) as the wave encounters the barrier so that some spill-over occurs.

Toker *et al.* (2003) studied systems that appeared to follow predictions of percolation theory, and yet the charge transport appeared to involve tunneling. The explanation given was that some of the nearest-neighbor distances were too far apart for tunneling to be effective. Wang *et al.* (2015c) likewise attempted to combine the concepts of percolation and tunneling-assisted conductance in the case of agglomerated graphene-containing nanocomposites.

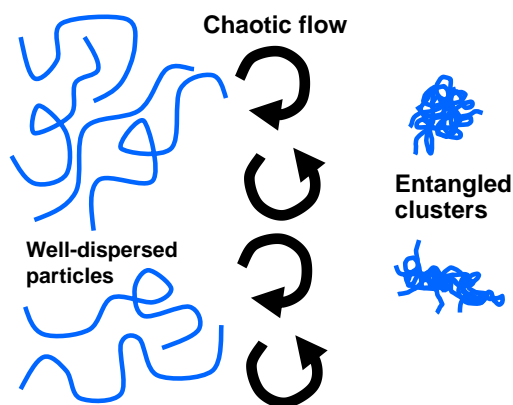
### Biased Distributions of Particles in Composites

Although conventional percolation models usually assume purely random distributions of conductive particles in a matrix, there are many reasons to expect otherwise in practice. For instance, the presence of repulsive forces between solid surfaces can be expected to have a dispersing effect, thus keeping conductive particles from contacting each other within the resulting composite, depending on the process by which the composite is formed. Attractive forces, on the other hand, can be expected to create a bias towards more agglomerated structures within a composite (Wang and Chatterjee 2003; Martin *et al.* 2004; Vigolo *et al.* 2005; Schmidt *et al.* 2007). For instance, Wang and Chatterjee (2003) suggested that such attractions can be included within simulation routines, leading to predictions of higher frequencies of contacts among rods within a homogeneous matrix. Martin *et al.* (2004) were able to achieve a bias towards connectivity among carbon nanotubes within an epoxy matrix by initially using charge-charge stabilization to favor a uniform distribution; this was followed by use of elevated temperatures and modest shearing forces to induce contacts favoring completion of electrical conduction paths.

High levels of agglomeration, leading to very non-uniform distributions, can result from the application of shear, especially in the case of carbon nanotubes, which are flexible and can have very high aspect ratio (Schmidt *et al.* 2007). Shearing of a suspension, even in cases where the fluid phase consists of a melted polymer, can be expected to bring about inter-particle collisions. As illustrated in Fig. 6, if the particles are sufficiently long and flexible, the resulting agglomerates may become entangled. Such effects have been demonstrated in studies of the forming process of wet-laid nonwoven fabrics (Shiffler 1988; Ramasubramanian *et al.* 2008; Hubbe and Koukoulas 2016). As noted by Du *et al.* (2005), a high degree of alignment of rod-like particles can be expected to yield low

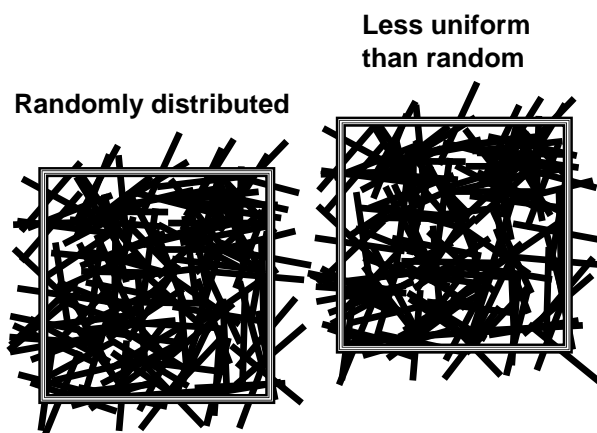


conductivity due to a lack of contact points. Their simulation study showed favorable results associated with a slight degree of alignment compared to a purely random distribution of orientations.



**Fig. 6.** Representation of process of entanglement of long, flexible suspended particles as a result of hydrodynamic shearing

It is important not to confuse a completely “random” distribution of particles with a completely “uniform” distribution. This point is illustrated in Figs. 7 and 8. In each case, the distribution shown in the left-hand frame was obtained with the help of a random number generator. In the case of Fig. 7, in the right-hand frame for the figure each rod-shaped particle was moved by about two pixels so that its center would be closer to that of its nearest neighbor. Despite the very small shifts involved, the overall effect is a decidedly more agglomerated appearance. Likewise, Fig. 8 shows the consequence of the same degree of shifting of locations, but this time in the direction of tending to fill in gaps in the structure. Again, though each component shift was tiny, the overall effect was a distribution that would appear to offer a higher frequency of connections, at least in the case of a two-dimensional structure filled with rod-like conductors placed in random directions.



**Fig. 7.** Graphic example of a two-dimensional distribution of equal rods distributed either according to a random number generator or by moving the center of each rod two pixels closer to its nearest neighbor



**Fig. 8.** Graphic example of a two-dimensional distribution of equal rods distributed either according to a random number generator or by moving the center of each rod two pixels farther away from its nearest neighbor

Though the images portrayed in Figs. 7 and 8 might tend to make one think that a more uniform dispersion of rod-like particles would imply more connections among the rods and hence high overall electrical conductivity in the case of conductive rods, it is important to keep in mind that most composites are inherently three-dimensional. Thus, what may appear to be connections in a two-dimensional view might be near misses, far misses, or possibly connections in the case of a realistic composite structure having three dimensions.

### Hypotheses to be Considered

In light of the theoretical issues just discussed, there are two sets of hypotheses that appear worthy of special focus in this article. The first can be called a “weakest link” hypothesis. It is proposed that the overall conductivity within a typical cellulose-based composite will be governed to a large extent by defects and gaps in its structure. The second can be called an “optimized agglomeration” hypothesis. Here it is proposed that it is often an advantage if the conductive particles have a greater amount of interconnections than would be predicted for a randomly dispersed mixture. On the other hand, a severe level of agglomeration would be unfavorable for electrical connectivity throughout the whole volume of a structure.

#### *Weakest link hypothesis*

In light of the relatively high electrical conductivity of the substances to be considered in the next section, contrasting with the low conductivity of the cellulosic material, it is proposed here that the major determinants of composite conductivity will be related to defects, restrictions, and any other kind of gaps in the network of conductive material. A form of this hypothesis was proposed by Kaiser *et al.* (2009), who studied graphene monolayers and accounted for the net resistances based on Schottky barriers of conduction between adjacent flakes of graphene oxide.

A corollary to the first hypothesis is that the amount of conductive material needs to be at least great enough to provide a theoretical connectivity, *i.e.* probably greater than the predicted percolation threshold (except that the next hypothesis may call that

requirement into question). Another corollary is that, given the much greater conductivity *within* conductive substances compared to the gaps or the cellulosic material, it makes sense to employ relatively long conductive particles, such as nanowires, nanotubes, *etc.* Indeed, many studies have shown advantages of using high aspect ratio conductive particles (Wang and Chatterjee 2003; Bryning *et al.* 2005; Li *et al.* 2007; Rosca and Hoa 2009; Bao *et al.* 2013; Vo *et al.* 2015). Yet a third corollary, which may require future research to validate, is that improving the conductivity of the cellulosic phase may be a promising approach toward achieving higher overall conductivity. As noted by Agate *et al.* (2018), cellulosic material can be made more conductive by suitable doping, as in the case of treatment with iodine or ammonium carbonate or acetate. Such an approach can contribute to conductivity by a proton-hopping mechanism (Rani *et al.* 2014).

#### *Optimized agglomeration hypothesis*

The second hypothesis that appears worthy of examination is that in order to achieve the most favorable conductivity results in a cellulose-based composites there needs to be an optimized level of agglomeration, *i.e.* not a uniformly dispersed system, but also not an over-agglomerated system. It is proposed that, by manipulating factors affecting particle contacts, one can achieve an optimal level of agglomeration of conductive elements within a composite. It is further proposed that the electrical conductivity in such a system can exceed the predictions of percolation theories based on randomly distributed particles.

Published articles have reported both negative and positive effects of agglomeration (or non-uniform distributions) of conductive particles on the conductivity of composites. The following authors observed negative effects of agglomeration on conductivity (Schmidt *et al.* 2007; Liao *et al.* 2008; Bao *et al.* 2013; Yang *et al.* 2014). For instance, Schmidt *et al.* (2007) observed increasing agglomeration of carbon nanotubes within a thermoplastic matrix with increasing time of shearing. Bao *et al.* (2013) explicitly included tangled agglomerates of carbon nanotubes in their excluded volume modeling and predicted a large effect of the dispersion state and the percolation threshold. By contrast, the following articles report positive relationships between the extent of agglomeration of conductive particles and conductivity of the composites (Martin *et al.* 2004; Bryning *et al.* 2005; Du *et al.* 2006; Hu *et al.* 2006; Li *et al.* 2007; Aguilar *et al.* 2010; Wang *et al.* 2015c). Thus, Bryning *et al.* (2005) achieved a very low conductivity threshold, and they attributed this to not only a high aspect ratio of the conductive elements, but also to a bias favoring contacts among them. The lowest percolation thresholds were observed when the carbon nanotubes were given an opportunity to reagglomerate.

Excessive agglomeration of conductive particles seems to be a likely explanation of some counterintuitive findings reported by Liao *et al.* (2008). Those authors observed that conductance values of composites leveled off and even decreased with increasing content of carbon nanotubes in a polypropylene matrix. In fact, the authors noticed “serious aggregation.” The relationship between increasing content of agitated fibers and increasing mechanically induced flocculation leading to the formation of clusters is well known in papermaking science (Kerekes and Schell 1992; Hubbe 2007).

It is clear that hydrodynamic shear can promote agglomeration of elongated particles in suspension. Schueler *et al.* (1997) reported that “light shearing” of carbon black particles dispersed in epoxy resin led to increased conductivity, which was attributed to optimal agglomeration. Vigolo *et al.* (2005) experimented with “sticky nanotubes.” They found that conditions favoring agglomeration gave a lower percolation threshold for electrical conductivity.

*Tools to establish favorable contacts*

Given the findings, as noted above, that increased agglomeration of conductive particles can both hurt and promote higher electrical conductance of composites, it follows that the details of agglomeration must be important. Dense entanglement of conductive particles, leaving most of the composite devoid of the particles, is to be avoided. On the other hand, it would be a great advantage to bias the system in favor of establishing contacts between fibers or chains of conductive particles that span the dimensions of the specimen. Some tools and principles that might be employed to bring about such contacts are included in Table 1, along with some selected references.

**Table 1.** Tools and Principles to Encourage Favorable Contacts to Promote Electrical Conductance in Composites

Tool or Principle	Selected Literature Citations
Van der Waals forces of attraction	Martin <i>et al.</i> 2004
Sparing use of hydrodynamic shear	Martin <i>et al.</i> 2004; Schmidt <i>et al.</i> 2007
Salt addition to encourage coagulation	Schueler <i>et al.</i> 1997
Avoidance of sonication during self-assembly	Bryning <i>et al.</i> 2005
Electric field application	Bauhofer & Kovacs 2009
Magnetic field application	Zhang <i>et al.</i> 2018
Filter-forming (papermaking)	Huang <i>et al.</i> 2005
Conductive-coated cellulosic fibers	Mamunya <i>et al.</i> 2002
Low viscosity, heat, & time for self-assembly	Martin <i>et al.</i> 2004; Bryning <i>et al.</i> 2005

The last item listed in Table 1 merits further discussion. The term self-assembly, if it is favorable, implies that the particles may be able to organize themselves at a nano-scale level such as to achieve more efficient electrical conduction paths (Bryning *et al.* 2005). Conditions under which this is possible will include (a) the system must remain fluid-like long enough to allow significant diffusion of the conductive particles to take place, (b) the viscosity must be low enough for diffusion to take place (Schmidt *et al.* 2007), and (c) there needs to be a net attraction, *e.g.* van der Waals forces drawing the surfaces of the conducting particles towards each other.

## CONDUCTIVE AGENTS

### Metals

Metal, as a highly conductive material, is widely applied in many electronic devices, for example, solar panels and touch screens. Positive features of metals include their generally outstanding electrical conductance, modest costs (in most cases), and ability to be formed into wires and nanowires (Elechiguerra *et al.* 2005; Hu *et al.* 2009; Song *et al.* 2015; Su *et al.* 2017; Lv *et al.* 2018). For example, Hu *et al.* (2009) employed silver wires (nanowires) so small as to be transparent. These were formed into nanopaper in combination with nanofibrillated cellulose, leading to conductive sheets exhibiting high flexibility. Su *et al.* (2017) carried such an approach an additional step further through the use of a conductive polymer (polydopamine) in combination with silver nanowires and nanocellulose. Lv *et al.* (2017) used a filtration method to apply a suspension of silver nanowires to a pre-formed mat of bacterial cellulose.

Metal can continue to function even after being exposed to high forces (Kawaguchi *et al.* 2017). In addition, the oxides of metals can work as conductive agents. For example, indium tin oxide has a very high transparency and it is applied in monitors and photoelectronic materials (Hasan Khondoker *et al.* 2012). The challenge of using metals in conductive materials is that they are hard to recycle. Elechiguerra *et al.* (2005) observed durability problems, which were attributed to the oxidation of silver nanowires. Additionally, the supply of certain metals requires intensive mining, high energy input, and the sources are limited.

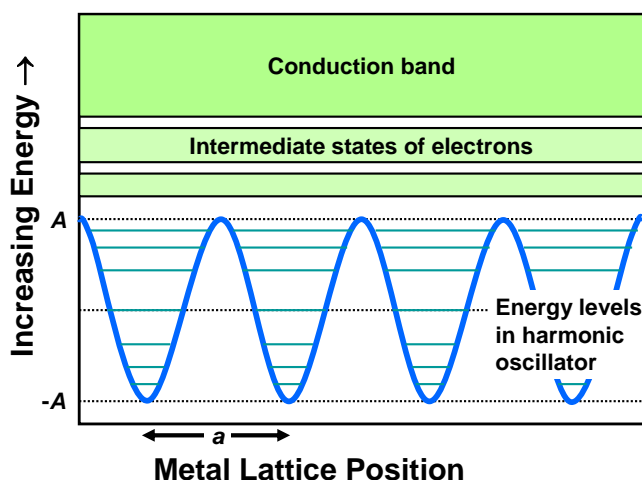
Compared to pure metallic substrates, the use of cellulose in metal-containing composites can provide advantages with respect to cost, flexibility, and degradability. Many studies have been done to prepare conductive materials by adding metals into a nanocellulose matrix and to investigate the electrochemical properties. Table 2 provides highlights from a selection of relevant publications.

**Table 2.** Listing of Studies in Combining Metal Particles and Cellulosic Material in Electrically Conductive Composites or Films

Metal	Highlights of Reported Work	Reference
Ag	Composites of silver and polypyrrole were prepared with different levels of alginate. Conductivity increased with alginate content.	Basavaraja <i>et al.</i> 2010
Ag	Composites of silver and polyaniline were prepared with cellulose. Conductivity exceeded that of pure polyaniline.	Gou <i>et al.</i> 2015
Ag	Conductive paper was prepared by coating it with films of carbon nanotubes and silver nanowires.	Hu <i>et al.</i> 2009
Au	Conductive film was prepared with gold nanoparticles in combination with nanocellulose.	Liu <i>et al.</i> 2015b
Ag	Conductive films were prepared with bacterial cellulose and silver nanowire.	Lv <i>et al.</i> 2018
Cu, Ni	The metal particles were used with epoxy and PVC matrices. Conductance depended on particle shape and dispersion.	Mamunya <i>et al.</i> 2002
Ag	Conductive coatings were prepared with silver-decorated cellulose nanocrystals.	Meulendijks <i>et al.</i> 2017
Cu	Copper films were applied to paper surfaces with low-temperature sintering in air.	Sakurai <i>et al.</i> 2018
Au	Gold particles were dispersed on bacterial cellulose with polyaniline to prepare conductive films.	Sarma <i>et al.</i> 2002
Ag	Silver nanowires were used as filler in a hydroxypropyl methyl-cellulose matrix.	Song <i>et al.</i> 2015
Ag	Silver nanowires were used in combination with polydopamine and nanocellulose to form conductive nanopaper.	Su <i>et al.</i> 2017
Ag	Silver nanoparticles were used with polyaniline to cellulose to prepare aerogels.	Tian <i>et al.</i> 2017
Ni	Electroless nickel plating was used to prepare conductive pulp fiber sheets.	Ueno <i>et al.</i> 2015
Li	Lithium compounds were used in combination with cellulose and polypyrrole to prepare conductive films.	Ummartyotin & Manuspiya 2015
Ag	Silver particle were deposited with dopamine and cellulose nanocrystals to prepare a conductive adhesive.	Wang <i>et al.</i> 2018a
Al, ZnO	Aluminum-doping of ZnO was applied within nanocellulose paper to achieve conductive films with high transparency.	Yang <i>et al.</i> 2009
Ag	Silver nanoparticles were used with polyaniline and nanofibrillated cellulose to form aerogel supercapacitors.	Zhang <i>et al.</i> 2014b

Five of the articles listed in Table 2 stand out as examples in which metal particles were used in combination with conductive polymers to impart electrical conductance to cellulose-based composites (Sarma *et al.* 2002; Zhang *et al.* 2014b; Ummartyotin and Manuspiya 2015; Su *et al.* 2017; Wang *et al.* 2018a). Such approaches are consistent with the hypothesis proposed earlier, that conductance performance may be dominated by issues of poor connections among the conductive particles. In the cited cases the conductive polymers may serve as bridges between the more highly conductive metal particles or nanowires.

The bulk conductance of electricity within metals is due to the relatively free mobility of electrons within conduction bands (Mizutani 2001). As illustrated in Fig. 9, certain electrons are essentially shared among the metal as a whole rather than staying bound to atomic orbitals. As a consequence, these electrons respond freely to applied fields and can participate in bulk-scale currents.



**Fig. 9.** Representation of a conduction band, occupied by highly mobile electrons, within a metal

Resistance within the bulk phase of metals can be attributed, in part, to static imperfections and lattice vibrations, leading to scattering phenomena (Dugdale 2016). As noted by Greenwood (1958), the electrons may interact with scattering centers consisting of irregularities in the metal crystalline structure. Such scattering contributes to some electrical resistance even within the metal itself. However, due to the very high conductivity within metals relative to many other materials that may be present, the gaps between metal structures can be expected to have a greater contribution of resistivity of metal-containing composites than any features within the metals themselves.

Oxidation and corrosion can compromise the durability and performance of certain metals, especially when very thin, as in the case of nanowires. Elchiguerra *et al.* (2005) reported such problems in the case of silver nanowires.

Through magnetron sputtering, Hu *et al.* (2013) prepared a cellulosic conductive material by depositing indium oxide on the nanofibrillated cellulose. The soft conductive nanocellulose material, like a paper film, was found to achieve a 65% transmittance at the 550 nm wavelength of light with a low resistance of 12  $\Omega$ /sq. The conductivity of the paper remained constant after multiple twists. Using the magnetron sputtering technique, Yang *et al.* (2009) deposited ZnO as the conductive agent within in a nanocellulose paper with a

thickness of 250 nm. The resistance of the material was as low as  $4.62 \times 10^{-4} \Omega \cdot \text{cm}$ . The average transmittance of the visible light was reported to be 93.7%.

As a highly conductive agent, silver has been applied in different studies for the preparation of cellulose-based conductive materials. Meulendijks *et al.* (2017) treated cellulose with oxidizing agents TEMPO and NaBr. The oxidized cellulose was mixed with  $\text{SnCl}_2$  and HCl and then centrifuged to obtain the cellulose matrix. After a silver deposition bath treatment, the cellulose-silver cellulosic material had a conductivity as high as  $2.9 \times 10^4 \text{ S/cm}$ . Wang *et al.* (2018a) modified the surface of a cellulose substrate with dopamine via self-polymerization under weak base conditions. The materials were merged into the acetone and treated with UV light to obtain a porous structure. Once silver was deposited onto the porous structure, the composite was found to achieve a low resistance of only  $0.2 \text{ m}\Omega \cdot \text{cm}$ .

Recently there has been a lot of focus on using silver nanowire as the conductive agent in preparing cellulose-based conductive film, achieving high flexibility. Song *et al.* (2015) prepared a kind of nano-paper by integrating bamboo nanocellulose and silver nanowires using hydroxypropyl methylcellulose as the binding agent. With a thickness of  $4.5 \mu\text{m}$ , the nano-paper had a conductivity of  $500 \text{ S/cm}$ . Surface modification of cellulose, such as oxidation with TEMPO, has the potential to improve the bonding strength between matrix and conductive agents significantly. Zhang *et al.* (2018) blended TEMPO-oxidized nanocellulose substrate with 0.2 wt% chitosan and 0.3 wt% nanocellulose. After magnetic field blending, pressure filtering, and low-temperature drying, they obtained a piece of  $7.8 \mu\text{m}$  thick conductive material having a resistivity of  $4.32 \Omega/\text{m}^2$ . It was suggested that chitosan could substantially increase the mechanical properties of the conductive material. When the cellulose:chitosan ratio was 7:3, the maximum strain of the film increased 112% compared to the control. Additionally, coating also has been used in preparing conductive nanocellulose-based material. Su *et al.* (2017) tested the coating of polydopamine on a nanocellulose surface, and then they attached silver nanowires onto the polydopamine. The multi-layer cellulosic product had a transparency of 90.9% of 550 nm light and a film resistance of  $14.2 \Omega/\text{sq}$ .

In addition to silver, other metals with high conductance can also be used to prepare cellulosic conductive materials. For example, Ueno *et al.* (2015) used the Kanigen method and nickel coating on recycled newspaper pulp. The conductive material had a conductivity of  $0.28 \text{ S/m}$  ( $0.0028 \text{ S/cm}$ ). On the other hand, cellulosic board containing 40% of such cellulosic conductive materials was reported to block an electric field of 30 dB at 1000 MHz. Root *et al.* (2018) treated the cellulosic substrate with copper coating. To be more specific, the cellulose matrix was treated with  $\text{CuSO}_4$  solution, and the concentration of  $\text{CuSO}_4$  was 0.0028 mol. The film resistance of the conductive cellulosic materials was affected by the degree of copper electroplating, and the resistance was at the range between 16.5 and  $369.3 \Omega/\text{sq}$ . In other work, Cu was deposited on a cellulose surface, yielding a conductive material with high flexibility (Sakurai *et al.* 2018).

### Conductive Polymers

Conductive polymers are typically macromolecules having highly conjugated  $\pi$  bonds (Svennersten *et al.* 2011). Because of the special electrochemical and photonic properties, low density, and corrosion resistance, some of the conductive polymers (*e.g.* polypyrrole and polyaniline) have been used to make organic light-emitting diodes (OLED) and sensors (Niu *et al.* 2016). The main challenge facing the wider application of conductive polymers in electronic devices is that they are difficult to manufacture.

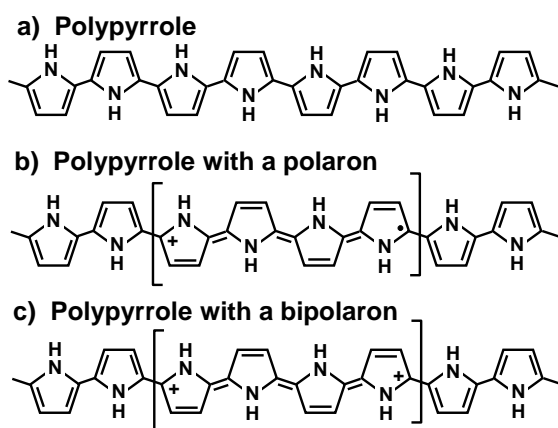
Cellulose, by contrast, has strong mechanical properties and is easy to form into films. It is proposed that mixing the conductive polymers with cellulose could ensure satisfactory mechanical quality. The supporting cellulose structure then could allow the conductive polymers to be in a form that is easy to manufacture. Many studies have been carried out in applying conductive polymers as conductive agent in preparing nanocellulose-based conductive materials (Wistrand *et al.* 2007). Table 3 lists various studies in which polymers such as polypyrrole and polyaniline were used in combination with cellulosic materials to produce electrically conductive composites.

**Table 3.** Listing of Studies in Combining Conductive Polymers and Cellulosic Material in Electrically Conductive Composites or Films

Conductive polymer	Highlights of Reported Work	Reference
EDTP	Composite films were prepared with wood fibers in poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate).	Hafez <i>et al.</i> 2017
PEDOT/PSS	Poly-3,4-ethylenedioxythiophene and polystyrene sulfonate were used with cellulose nanofibers to make nanopaper.	Lay <i>et al.</i> 2017
Poly-dopamine	Polydopamine was coated onto nanocellulose and used with silver nanowires as a composite.	Su <i>et al.</i> 2017
Poly-dopamine	Polydopamine was coated onto nanocellulose and used with silver nanowires as a composite.	Wang <i>et al.</i> 2018a
PEDOT/PSS	Poly-3,4-ethylenedioxythiophene and polystyrene sulfonate were used for polyelectrolyte multilayers with nanocellulose.	Wistrand <i>et al.</i> 2007
PEDOT/PSS	Poly-3,4-ethylenedioxythiophene and polystyrene sulfonate were used with carbon nanotubes in regenerated cellulose.	Zhao <i>et al.</i> 2017

### Polypyrrole

Important progress has been achieved in understanding the electrical conductivity of derivatives of polypyrrole, the structure of which is shown in Fig. 10 (Scott *et al.* 1984).



**Fig. 10.** Molecular structure of polypyrrole: (a) ordinary polypyrrole; (b) containing a polaron feature; (c) containing a bipolaron feature

In addition to showing a representation of pure polypyrrole, the figure also gives an example of a polaron and a bipolaron, which both contribute to electrical conductance (Brédas *et al.* 1984; Scott *et al.* 1984; Sato *et al.* 1991; Jenden *et al.* 1993). Polaron features contribute a single radical cation to the polypyrrole structure, whereas bipolarons



contribute dual-cation features. Note that the “dot” shown in part B of the figure indicates the presence of an unpaired electron. In either case, a key role is played by ionized groups, including both electrons and positive sites, the latter of which can be regarded as “holes” where an electron is missing.

Brédas *et al.* (1984) reported that low oxidation levels of polypyrrole lead to the formation of polarons, whereas higher degrees of oxidation lead to a preponderance of bipolarons, which are associated with a high contribution to conductance. These features were confirmed by Jenden *et al.* (1993), who used FT-Raman spectrographic evidence.

Oxidized compounds related to polypyrrole were further studied by Hegewald *et al.* (2009), who found the best conductivity results after oxidation in a ferric chloride solution. The effects of oxidation are complex, however, since higher levels of oxidation increase the likelihood of defects in the conductive structure.

As noted by Roldughin and Vysotskii (2000), composites that contain conducting polymers tend to be highly disordered systems, in which there is likely to be a high frequency of defects that must be surmounted by quantum-mechanical tunneling and hopping mechanisms. According to Sato *et al.* (1991), the conduction at lower temperatures is mainly due to tunneling, as discussed earlier. Taking a related approach, Wang *et al.* (2018b) found that reductive treatment of graphene oxide decreased the frequency of oxygen-related defects in the structure and therefore yielded easier transport of electric current. Perhaps associated with such redox transitions, one of the negative features of polypyrrole-based conductive materials is poor durability, which may be due either to chemical instability or to effects of swelling and shrinkage in the course of charging and discharging cycles (Shi *et al.* 2015).

In 1977, in work that later led to a Nobel prize, it was found that the conductance of certain organic polymers can be increased by doping with electrolytic substances (Shirakawa *et al.* 1977). Doping of the polypyrrole films with *p*-toluene sulfonate and dodecyl sulfate contributes to conductivity (Jenden *et al.* 1993; Ramelow *et al.* 2001; Mavinakuli *et al.* 2010), which is dependent on charged sites. The sensitivity of conductance to doping treatment was studied further by Ruangchuay *et al.* (2004), who used such effects as the basis for a unique sensing system for acetone vapor. Tezuka *et al.* (1995) studied the reverse problem of “undoping,” including the electrochemical reduction of oxidized polypyrrole.

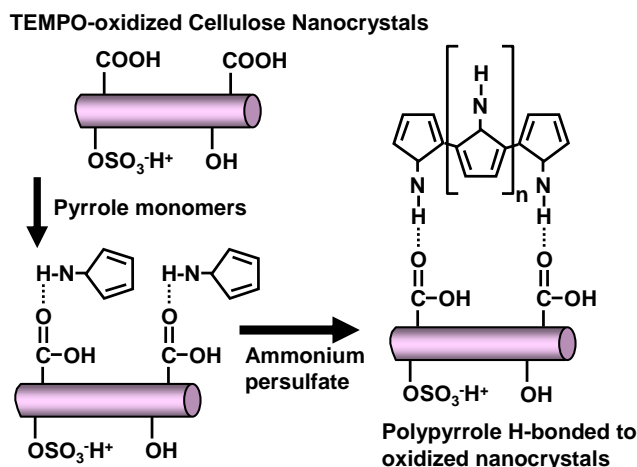
#### *Polypyrrole applications in cellulose composites*

Polypyrrole has been widely used in cellulose-based conductive materials (Mihrianyan *et al.* 2008). Usually the polymerization process of pyrrole monomers has involved the use of  $\text{Fe}^{3+}$  as an oxidative agent in an acidic environment (Fedorkova *et al.* 2010; Lei *et al.* 2013). Nyström *et al.* (2010) homogenized 2 wt% cellulose hydrogel with pyrrole monomer in aqueous solution and added  $\text{FeCl}_3$  solution and 37 wt% HCl to prepare the polypyrrole. The surface-coating of cellulosic matrix was completed with polypyrrole by *in-situ* polymerization. The surface density of the conductive material was  $0.011\text{g/m}^2$  with a conductivity of 1.5 S/m (0.0015 S/cm). Lay *et al.* (2016) fabricated polypyrrole/cellulose composite by *in-situ* polymerization. The cellulosic substrate was bleached softwood pulp that was oxidized with  $\text{FeCl}_3$ . It was found that when the content of polypyrrole reached 20%, the conductivity of the composites was 5.2 S/m (0.052 S/cm).

The preparation methods affect the microstructure, mechanical strength, and conductivity of polypyrrole/cellulose composites (Wang *et al.* 2015b). Saravanan *et al.* (2017) improved the conductivity of polypyrrole/cellulose composite by adding a mixture

of styrene-triazine sulfonate sodium salt and 9,10-anthraquinone-2-sulfonate sodium salt. The results showed a conductivity ranging from 3 K $\Omega$ /sq to 26 K $\Omega$ /sq with different contents of the mixture of styrene-triazine sulfonate sodium salt and 9,10-anthraquinone-2-sulfonate sodium salt. Other oxidizing agents can be added to change the material structure and to improve the performance of conductive polymer. For example, TEMPO oxidizes the hydroxyl groups of cellulose into carboxyl groups. Such treatment was applied to promote the formation of hydrogen bonds between cellulose and pyrrole, thus improving the stability of the composites (Wu *et al.* 2014a). Wu *et al.* (2014b) preprocessed the cellulose by attaching a layer of N-vinylpyrrolidone. This layer of polymer helped the attachment of polypyrrole on the surface of cellulose material, resulting in a conductivity of 36.9 S/cm. Shi *et al.* (2014) introduced supercritical CO<sub>2</sub> as a drying method to process the polypyrrole/cellulose composite from hydrogel into an aerogel. The final material had a low density of 0.41 to 0.53 g/cm<sup>-3</sup> and a conductivity of 0.08 S/cm.

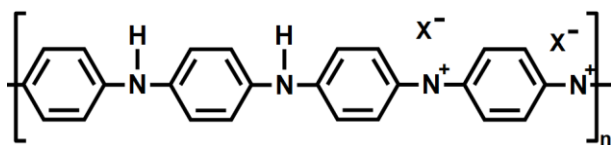
Cellulosic materials that are in non-fibrous form can also be used as the base material and to integrate with polypyrrole. Zhang *et al.* (2017) treated filter paper as the matrix and melted the paraffin-based ink on the surface of the filter paper. Then the ink formed several channels into the filter paper, which were conductive. With the conductive channels, the polymerization of pyrrole monomers was able to be improved, and finally to form a kind of conductive network inside the cellulosic substrate. Several studies have shown that pH is another reason that cellulose/polypyrrole conductive composite changes conductivity. For example, Li *et al.* (2010) found that the conductivity of cellulose/polypyrrole composite decreased under basic conditions but increased under acidic conditions.



**Fig. 11.** Schematic of the reactions between cellulose oxidized with TEMPO and pyrrole monomers. Figure based on one shown by Lay *et al.* (2016), redrawn.

### Polyaniline

Polyaniline, another widely used conductive polymer, has been applied in conductive composites such as electrodes, biosensors, and antistatic coatings (Mi *et al.* 2008). The structure of polyaniline is shown in Fig. 12, which is based on Alonso *et al.* (2018). In the figure, the term "X<sup>-</sup>" indicates a negative ion, such as a chloride ion. Most of the polyaniline has been applied on non-renewable materials, including synthetic rubber, plastics, and fabrics. Other researchers have evaluated cellulose as a potential substitute for petroleum-based base materials (Pettersson and Oksman 2006).



**Fig. 12.** Molecular structure of polyaniline, in its electrically conductive form (figure based on Alonso *et al.* 2018)

The electrical properties of cellulose/polyaniline composites are greatly affected by the content of polyaniline. Luong *et al.* (2013) prepared nanocellulose/polyaniline composites by *in-situ* polymerization and obtained flexible conductive film through vacuum filtration. It was found that when the content of polyaniline was over 4.75%, the conductivity reached  $2.6 \times 10^{-5}$  S/cm, indicating potential applications such as soft electrodes and antistatic coatings. Through *in situ* polymerization of aniline within bleached sulfate pulp, Sharifi *et al.* (2018) treated the kraft pulp as the raw materials and obtained a cellulose/polyaniline film with a density of  $60 \text{ g/m}^2$ . Results obtained with films dried under 800 KPa and  $65 \text{ }^\circ\text{C}$  for 60 min indicated that both polymerization time and the mass ratio of cellulose/aniline affected the conductivity of cellulose/polyaniline films. A maximal conductivity (1.49 S/m or 0.0149 S/cm) was observed after 8 hours of polymerization when the cellulose/polyaniline mass ratio was 1:2. Mo *et al.* (2009) investigated a chemical oxidation method to prepare the cellulose/polyaniline composite. In their study, cellulose was first mixed with a HCl solution containing aniline for activation; then 1 mol/L ammonium persulfate was added into the mixture for the polymerization of aniline monomers. It was found that the conductivity of cellulose/polyaniline composite ranged from  $1.0 \times 10^{-5}$  S/cm to  $3.0 \times 10^{-2}$  S/cm and was closely related to cellulose activation time and aniline dosage during preparation.

Cellulosic materials from different sources have been applied to prepare the cellulose/polyaniline conductive composites. For example, sodium carboxymethyl cellulose and polyaniline will form into hydrogels with semi-interpenetrating polymer network structure using glycerol diglycidyl ether as the crosslinking agent (Li *et al.* 2017). With higher dosages of sodium carboxymethyl cellulose and glycerol diglycidyl ether, the conductivity of the composite hydrogels increased first and then decreased. Bacterial cellulose was studied by Alonso *et al.* (2018) in preparing a cellulose/polyaniline conductive film. A conductivity of  $1.4 \times 10^{-1}$  S/cm was reported.

#### *Other conductive polymers*

Other than polypyrrole and polyaniline, polybenzazole is also used in making conductive composites. Polybenzazole has higher heat stability and redox activity than polypyrrole and polyaniline. Cai *et al.* (2018) prepared a bacterial cellulose/polybenzazole composite by electrospinning. The composite achieved a conductivity of  $4.6 \times 10^{-2}$  S/cm, which was significantly higher than the control with only bacterial cellulose ( $1.5 \times 10^{-8}$  S/cm).

In addition, polythiophene also has been used as the conductive agent in preparing cellulose-based composites. Lay *et al.* (2017) prepared cellulose nanofibers by introducing poly-3,4-ethylenedioxythiophene and polystyrene sulfonate as conductive agents. The electrical conductivity and the specific capacitance of the nanopapers were 2.58 S/cm and 6.21 F/g, respectively. Hafez *et al.* (2017) fabricated composite films by adding wood microfibers to poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate). The mechanical

strength of the composite was improved with higher fiber content. At a wood fiber content of 75%, the resistivity of the composites was the lowest (340  $\Omega$ /sq). Zhao *et al.* (2017) assembled cellulose and poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate) in an ionic liquid and fabricated a flexible and conductive composite matrix. By incorporating multiwalled carbon nanotubes, the composite matrix could achieve higher flexibility and excellent electrochemical properties, including a low resistance of 0.45  $\Omega$  and a high specific capacitance of 485 F/g at 1 A/g.

### Carbon-based Conductive Agents

The two widely-studied forms of carbon having high promise for imparting electrical conductivity to composites are carbon nanotubes and graphene. These materials, in their pure form, share a structural similarity. The structure can be described as either tubular or flat layers of hybridized  $sp^2$  carbons (Zhang *et al.* 2013a; Saeed and Ibrahim 2013; Terzopoulou *et al.* 2015). The molecular structure of graphene and an example of a graphene oxide are illustrated in Fig. 13, which is based on structures shown by Chua and Pumera (2014).

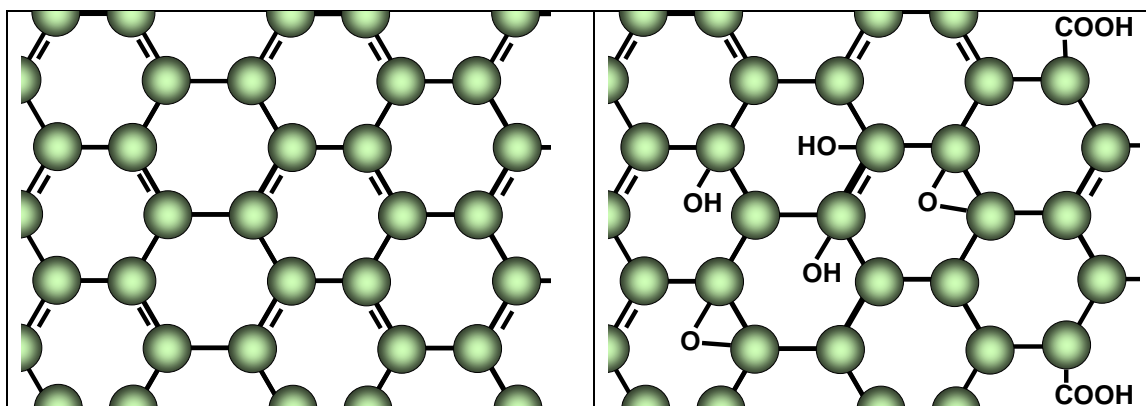


Fig. 13. Molecular structures of graphene (left) and a graphene oxide (right)

Kaiser *et al.* (2009) described the mechanism of current flow as two-dimensional variable-range hopping in parallel with tunneling driven by the electrical field. Their research suggested that highly conductive graphene regions were joined by disordered regions, across which the current flow was wholly dependent on charge-carrier hopping and tunneling, which was sensitive to local electric fields. A much-cited article by Bockrath *et al.* (1999) shows the current within carbon nanotubes rising steadily with increasing applied voltage, but only after exceeding a limiting value of voltage. Dependencies on temperature and applied voltage were consistent with a tunneling mechanism. Within the conducting nanotubes the current flow was consistent with the concept of a Luttinger liquid, describing transport of electricity in one dimension. Yao *et al.* (2000) studied contributions to electrical resistivity within carbon nanotubes at high electrical field strength and concluded that a main contribution to resistance is scattering of electrons associated with emission of light or phonons. However, the major impediments to current flow were associated with poor transfer of current at the ends of nanotubes, even when the nanotubes are directly connected with metal conductors at those ends.

*Carbon nanotubes*

Studies in which carbon nanotubes were incorporated into electrically conductive composites with cellulosic material are listed in Table 4.

**Table 4.** Listing of Studies in Combining Carbon Nanotubes and Cellulosic Material in Electrically Conductive Composites or Films

Conductive Substance*	Highlights of Reported Work	Reference
SWCNT	Aqueous mixtures of single-walled carbon nanotubes and nanocellulose were formed to prepare conductive paper.	Hamedi <i>et al.</i> 2014
CNT	Bacterial cellulose was mixed with carbon nanotubes to prepare light-weight strain sensors.	Hosseini <i>et al.</i> 2018
SWCNT	Single-walled carbon nanotubes and silver wire were coated onto paper to achieve high conductivity.	Hu <i>et al.</i> 2009
CNT	A cationic surfactant was used to disperse the carbon nanotubes, which were used in nanocellulose films.	Huang <i>et al.</i> 2015
CNT	An anionic surfactant was used to disperse the carbon nanotubes to make conductive paper with cellulose fibers.	Imai <i>et al.</i> 2010
CNT	TEMPO-oxidized nanofibrillated cellulose was used together with carbon nanotubes for printable conductive composites.	Koga <i>et al.</i> 2013
MWCNT	Multiwalled carbon nanotubes were used together with cellulose to make conductive and strong composites.	Lee <i>et al.</i> 2016
CNT	Carbon nanotubes in combination with polyaniline were used to prepare conductive coatings for cellulosic paper.	Mao <i>et al.</i> 2018
MWCNT	Cellulose nanocrystals were mixed with the multi-walled carbon nanotubes and filtered to form conductive sheets.	Meng & Manas-Z. 2015
CNT	Conductive aerogels were prepared from carbon nanotubes and cellulose by flash freezing.	Qi <i>et al.</i> 2013
MWCNT	Cellulose nanocrystals were used as a binder with multi-walled carbon nanotubes and graphene and coated on paper.	Tang <i>et al.</i> 2014
CNT	Natural rubber latex and carbon nanotubes were used with cellulose nanocrystals as a binder for strain sensors.	Wang <i>et al.</i> 2016
Carbon black	Carbon black particles were used with natural rubber and cellulose nanocrystals to make strain sensors.	Wu <i>et al.</i> 2016
MWCNT	Bacterial cellulose was rendered conductive by use of carbon nanotubes dispersed with a cationic surfactant.	Yoon <i>et al.</i> 2006
CNT	Nanocellulose and carbon nanotubes were formed into strong and conductive paper for supercapacitors.	Zhang <i>et al.</i> 2013a
MWCNT	Composites with tunicate cellulose were prepared with multi-walled carbon nanotubes and PEDOT:PSS.	Zhao <i>et al.</i> 2017

**Notes:** CNT = Carbon nanotubes, unspecified; SWCNT = Single walled carbon nanotubes; MWCNT = multi-walled carbon nanotubes

Carbon-based conductive agents have very high conductivity, usually higher than that of polymer conductive agents. Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanostructure. There are mainly two types of carbon nanotubes, Single-Wall CNTs (SWCNTs) and Multi-Wall CNTs (MWCNTs) (Lijima 1991). Besides excellent conductivity, CNTs also have outstanding physical properties. A study by Salvetat *et al.* (1999) has shown that the Young's moduli and bending strength of CNTs can be approximately 1 TPa and 100 GPa, respectively, and the conductivity and current capacity can be  $10^7$  S/m ( $10^5$  S/cm) and  $10^9$  A/cm<sup>2</sup>, respectively. CNTs are stable and retain their electrical properties when stretched or bent. As a result of these characteristics, the surface-

modified CNTs have the promising potential to improve the conductivity of chemical and biological polymers with the formation of a conductive network.

A negative aspect of individual carbon nanotubes is their high variability in performance, which can be attributed to differences in chirality and molecular structure (Hu *et al.* 2004). Some tubes act as metal-like conductors, whereas others behave as semiconductors (Bockrath *et al.* 1999). However, as shown by Hu *et al.* (2004), reliable and promising performance can be achieved by the use of networks of carbon nanotubes, wherein the performance is dictated by the ensemble averaging of properties of the individual tubes.

Developers of technology related to carbon nanotubes can choose between single-walled and multi-walled tube products, as well as mixtures thereof. According to Min *et al.* (2010), in the case of MWCNTs the current is carried only by the outermost wall. Though this might be regarded as a penalty in terms of efficiency, one also needs to take into consideration such factors as the length and stiffness of the tubes, which may be key to performance in different applications. Rosca and Hoa (2009) used MWCNTs in epoxy composites to produce “bulky paper” sheets.

Hamedi *et al.* (2014) dispersed 43 wt% of CNTs directly into the nanocellulose. Then the conductive fiber and nanopaper were made through molecular self-assembly of cellulose. Lee *et al.* (2016) described a method to mix 0.5 to 30.0% of multi-wall CNTs with 5 wt% of cellulose and prepare the conductive fiber through solvent-based solution spinning. The reported conductivity can be as high as 2.7 S/cm when there is 30 wt% of multi-wall CNTs. Cellulose-based aerogel was also introduced as conductive material. Qi *et al.* (2013) prepared an aerogel with a mixture of cellulose and CNTs by the flash freezing/lyophilization process. Through adjusting the content of cellulose and CNTs, the Young's modulus could be tuned to reach about 90 MPa with a conductivity of  $2.2 \times 10^{-2}$  S/cm.

During the preparation of conductive material, surface modification of cellulose has the potential to improve the compatibility and the uniformity of dispersion of CNTs in the modified matrix. Koga *et al.* (2013) fabricated transparent, conductive, and printable composites by mixing TEMPO-oxidized nanocellulose and CNTs, indicating a substantial improvement of CNTs dispersion in the TEMPO-oxidized nanocellulose. In addition to TEMPO-oxidization, surface reactant was also found to contribute to the dispersion of CNTs. Huang *et al.* (2015) reported that CNTs were uniformly dispersed in the presence of cetyltrimethylammonium bromide in a NaOH/urea aqueous solution. The compressed nanocomposite film reached a relatively high electrical conductivity (7.2 S/m or 0.072 S/cm) when there was 5 wt% CNTs. Imai *et al.* (2010) found that CNTs disperse more uniformly in the cellulose material previously mixed with anionic surfactant, resulting in a high conductivity of 672 S/m (6.72 S/cm). Oppositely, Yoon *et al.* (2006) dispersed multi-wall CNTs into the cationic cetyltrimethylammonium bromide first and dipped the bacterial cellulose into the CNTs/cetyltrimethylammonium bromide solution. After extraction and drying, the conductivity of the CNTs-incorporated cellulose was  $1.4 \times 10^{-1}$  S/cm at a multi-wall CNTs content of 9.6 wt %.

### Graphene

Graphene, with its high performance in conductivity and mechanics, has recently attracted great interest in the applications of soft conductive materials and supercapacitors (Zhu *et al.* 2011; Wang *et al.* 2014). Two-dimensional nano-scale graphene has extremely high surface-area-to-volume ratio and flexibility. However, the strong  $\pi$ - $\pi$  interaction among graphene particles promotes coalescence, decreasing the surface-area-to-volume ratio (Zhang *et al.* 2012). The hydrophilicity and nanostructure of nanocellulose not only can promote the dispersion of nano graphene, but it also can improve the orientation of polymer and enhance the mechanical property of composites. Studies in which graphene or graphene oxide-type materials were incorporated into electrically conductive composites with cellulosic material are listed in Table 5.

**Table 5.** Listing of Studies in Combining Graphene or Graphene Oxide-related Substances and Cellulosic Material in Electrically Conductive Composites or Films

Conductive Substance*	Highlights of Reported Work	Reference
RGO	Incorporation of reduced graphene oxide into paper prepared with nanofibrillated cellulose gave high electrical conductivity.	Dang & Seppälä 2015
Graphene	The conductance of composite films prepared with bacterial cellulose increased with increasing graphene content.	Feng <i>et al.</i> 2012
GO	Nanocomposites with cellulose nanocrystals and graphene were prepared with cellulose triacetate as an additive.	Ionita <i>et al.</i> 2016
Graphene	Bacterial cellulose was made conductive with the addition of graphene and polypyrrole.	Liu <i>et al.</i> 2015a
RGO	Cellulose nanocomposite paper was prepared with graphene, achieving high strength and electrical conductivity.	Luong <i>et al.</i> 2011
Graphene	Composites prepared with cellulose fibers and graphene showed favorable conductance and cycling ability.	Patel <i>et al.</i> 2014
GO	Coatings with oxidized graphene and carbon nanotubes with nanofibrillated cellulose in paper yielded high conductance.	Tang <i>et al.</i> 2014
Graphene	Films prepared from graphene platelets and cellulose nanocrystals showed high conductance.	Valentini <i>et al.</i> 2014
Graphene	A mixtures of graphene and cellulose nanocrystals was filter-formed, yielding conductive films.	Wang <i>et al.</i> 2015a
Graphene	Starting with graphite and unbleached hardwood pulp, the mixture was reduced with ascorbic acid, filtered to make paper, then annealed.	Wang <i>et al.</i> 2018b
Graphene	Spin coating was used to prepare composites with graphene and cellulose nanocrystals.	Xiong <i>et al.</i> 2015

\* Notes: GO = graphene oxide; RGO = reduced graphene oxide

Cellulose/graphene composites can be made by the homogenization of graphene flakes and cellulose. Figure 14 presents a schematic diagram showing one way in which this can be done. In the first step, stable aqueous suspensions of oxidized graphene and nanocellulose are combined, followed by blending, chemical reduction (to optimize electrical conductance of the graphene), and vacuum filtration (Dang and Seppälä 2015).

A study by Valentini *et al.* (2014) demonstrated the preparation of a highly conductive and optically transparent film by mixing a 0.5 wt% cellulose nanocrystals suspension with a 1 wt% of graphene suspension. Wang *et al.* (2015a) prepared a

conductive composite film by dispersing graphene into a suspension of cellulose nanocrystals. After vacuum filtration, the films were obtained, and the conductivity of the film reached 36 S/cm when the mass ratio of cellulose nanocrystals and graphene was 1:5. Feng *et al.* (2012) fabricated a nanocomposite film consisting of bacterial cellulose and graphene oxide using the vacuum-assisted self-assembly technique. The film was obtained by ultrasonication of the bacterial cellulose and graphene oxide mixture for 30 min with a power of 100 W before vacuum filtration and cool drying. The highest conductivity was  $1.1 \times 10^{-4}$  S/m ( $1.1 \times 10^{-6}$  S/cm), by controlling the graphene content in the range of 1 to 5%.

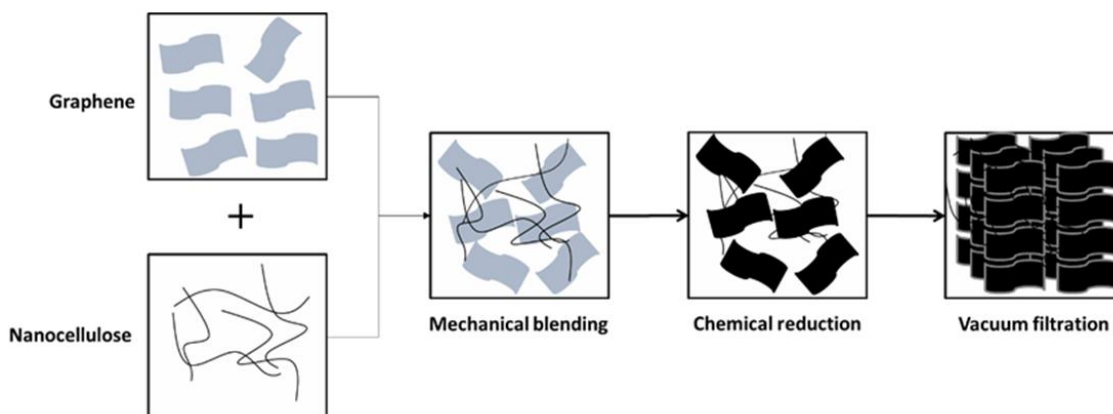


Fig. 14. Preparation process of conductive composites based on nanocellulose and graphene

Poor dispersion of reinforcing nanostructures can lead to failure of the cellulose/graphene nanocomposites. In order to improve mechanical strength, Xiong *et al.* (2015) explored spin coating in preparing the cellulose nanocrystal/graphene composites, which increased the Young's modulus to  $169 \pm 33$  GPa. Other components, such as cellulose triacetate, were also studied to improve the properties of cellulose nanocrystal/graphene composites conductive films (Ionita *et al.* 2016).

### Combinations

Each kind of conductive agent described above was able to increase the conductivity of the composites. However, composites with a single conductive agent usually have limitations. For example, silver nanowires with excellent conductivity and flexibility are prone to oxidation, while CNTs are robust to the oxygen, acid, and salts (Elechiguerra *et al.* 2005; Jeong *et al.* 2016). Thus, the types of conductive agents need to be selected with care, depending on the intended application.

One of the cases most studied is the combination of silver metal and a conductive polymer. Tian *et al.* (2017) first carried out an *in-situ* polymerization of aniline monomer onto the cellulose scaffolds. Then, Ag nanoparticles were electrodeposited onto the obtained conductive composites. This method increased the conductivity of the cellulose/polyaniline from  $3.45 \times 10^{-2}$  S/cm to 0.94 S/cm. The work not only demonstrated a way to improve the conductivity of polymer nanohybrids, but it also suggested a strategy in the application of nanocomposite in energy storage. Gou *et al.* (2015) fabricated a cellulose/Ag/polyaniline conductive composite through mixing 1.0 mol/L aniline (dissolved in HCl) into a solution prepared by ultrasonication of  $\text{Ag}(\text{NH}_3)_2\text{OH}$ , isopropanol, and cellulose. The conductivity of the cellulose/Ag/polyaniline composite



was up to 0.348 S/cm, which was much higher than pure polyaniline (0.142 S/cm) and cellulose/polyaniline composites ( $3.0 \times 10^{-2}$  S/cm). A similar method was applied by dispersing gold nanoparticles into bacterial cellulose/polyaniline film (Sarma *et al.* 2015; Faria-Teschler *et al.* 2016). It was found that the addition of gold nanoparticles improved the surface chemistry as well as the electrochemical properties of the conductive film.

The combination of CNTs and graphene helps to reduce the required usage level of graphene, which saves costs and maintains a high conductivity. Jabbour *et al.* (2012) prepared conductive papers by incorporating graphite particles and carbon fibers through a conventional paper making process. Carbon fiber and graphene were dispersed in the carboxymethyl cellulose (CMC) and then homogenized with cellulose. The highest conductivity of the paper was 964 S/m (9.64 S/cm) with a graphene, carbon fiber, and cellulose mass ratio of 56:24:20. Tang *et al.* (2014) combined the multi-layer CNTs with oxidized graphene at a mass ratio of 4:1 and applied nanocrystalline cellulose as a binder between the two conductive agents. The oxidized graphene was found to promote the distribution of CNTs in the aqueous solution. Through the coating process, the cellulose conductive paper with the two conductive agents had a homogenized structure and the conductivity was 892 S/m (8.92 S/cm).

The combination of conductive polymer and carbon also has been found to improve the conductivity of cellulosic substrates. Mao *et al.* (2018) studied the coating of carbon nanotubes/polyaniline nanocomposite layers on cellulosic paper and found that the conductivity of electro-surface-coated paper could reach 46.4 S/cm when the CNTs content was 10 wt %.

While the application of polythiophene was lower than that of polypyrrole and polyaniline, it also could be used as conductive agents. Lay *et al.* (2016) prepared conductive nanopapers with poly(3,4-ethylenedioxythiophene) and polystyrene sulfonate. The reported conductivity and capacitance of the nanopapers were 2.58 S/cm and 6.21 F/g, respectively. Further coating of polypyrrole substantially improved the electrical conductivity (10.55 S/cm) and the specific capacitance (315.5 F/g) of the nanopapers.

## CELLULOSE AND ITS ROLE IN CONDUCTIVE COMPOSITES

### Cellulose in General

When one's goal is to prepare an electrically conductive composite, the role of conductive substances such as polypyrrole, graphene, or carbon nanotubes is obvious. But what is the role of the cellulosic material? To begin to answer that question, it is important first to note the highly diverse range of cellulosic materials that could be employed. As has been well explained in recent reviews and texts, cellulosic materials range from nanomaterials, to intermediate sized "fines", to fibers, and larger particles or strands of wood, etc.

Table 6 provides a listing of various cellulosic materials that might be used in various composites, their general sizes, and some selected citations for textbooks or review articles for each category. Since these materials have been well reviewed in the cited sources, no further descriptions will be given here.

In addition to the cellulosic particles listed in Table 6, one might also consider such materials as bacterial cellulose, which has been explicitly used in preparation of electrically conductive composites (Sarma *et al.* 2002; Yoon *et al.* 2006; Feng *et al.* 2012; Xu *et al.* 2013; Liu *et al.* 2015a; Faria-Tischer *et al.* 2016; Alonso *et al.* 2018; Cai *et al.* 2018;

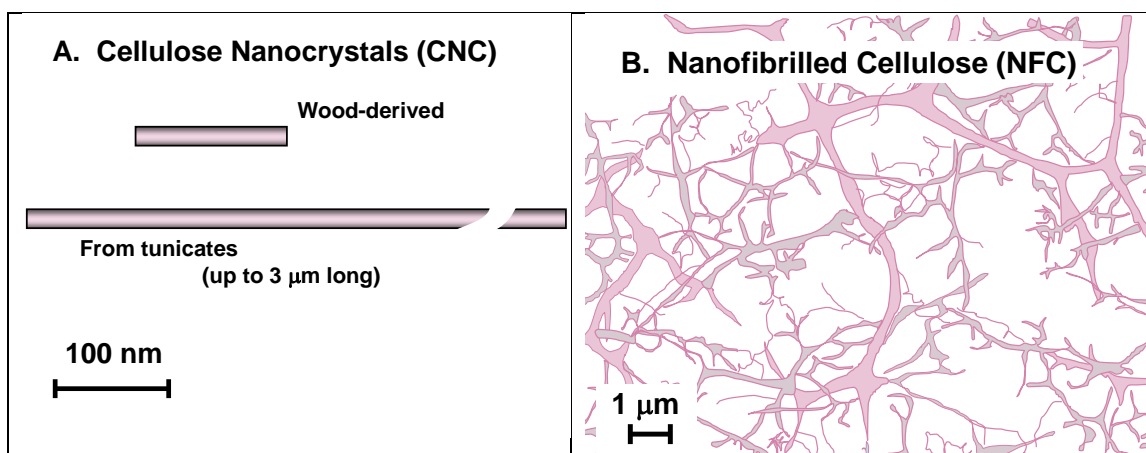
Hosseini *et al.* 2018; Lv *et al.* 2018). For example, Feng *et al.* (2012) used vacuum application to create a layered structure with bacterial cellulose and graphene oxide. In addition to electrical conductance, the graphene oxide application also contributed to mechanical strength. The dimensions of bacterial cellulose can be expected to be highly dependent on both the culture conditions and on any hydrodynamic shear that is applied after biosynthesis (Gallegos *et al.* 2016).

**Table 6.** Categories of Possible Cellulosic Entities to Consider for the Preparation of Composites

Cellulosic Entity	Typical width	Typical length	Selected references
Cellulose nanocrystals	3.5 to 15 nm	0.1 to 0.3 $\mu\text{m}$	Lima & Borsali 2004; Beck-Candanedo <i>et al.</i> 2005; Eichhorn <i>et al.</i> 2010; Boluk <i>et al.</i> 2011
Nanofibrillated cellulose	< 100 nm	< 10 $\mu\text{m}$	Eichhorn <i>et al.</i> 2010; Kangas <i>et al.</i> 2014
Microfibrillated cellulose	< 100 nm	< 100 $\mu\text{m}$	Eichhorn <i>et al.</i> 2010; Kangas <i>et al.</i> 2014
Cellulosic fines	5 to 20 $\mu\text{m}$	20 to 100 $\mu\text{m}$	Kangas & Kleen 2004
Cellulosic fibers	10 to 30 $\mu\text{m}$	1 to 3 mm	Parham & Gray 1982
Wood particles	0.1 to 1.3	1.3 to 13 mm	Marra 1992
Wood strands	6 to 20 mm *	13 to 76 mm	Marra 1992

\* Note: Wood strand thickness is given as about 0.25 to 0.64 mm.

Figure 15 illustrates some typical sizes and shapes of some of the types of cellulose particles most studied for the preparation of cellulose-based electrically conductive composites.



**Fig. 15.** Representation of typical sizes and shapes of cellulosic materials often reported in studies of cellulose-based conductive materials. A: Cellulose nanocrystals (CNC); B: Nanofibrillated cellulose (NFC). The figures previously appeared in Hubbe *et al.* (2017b).

Figure 15A depicts the rod-like shape and tiny sizes of the cellulose nanocrystals (CNCs), which are most often obtained by digesting cellulose fibers in concentrated sulfuric acid. Though their sizes and cross-sectional shapes (*e.g.* rectangular or trapezoidal) depend to some extent on the cellulosic source material and the processes used in isolation, the properties of CNC can be generally summarized by noting that (a) they are very tiny, (b) they are simple in shape, and (c) they tend to be rather uniform within a given

batch. Figure B represents a typical batch of nanofibrillated cellulose (NFC) obtained by TEMPO-mediated oxidation of  $\alpha$ -cellulose fibers followed by intense mechanical shearing (Crawford *et al.* 2012). Consistent with scanning electron micrographic images obtained in many such studies, the material has the form of a network with multiple branch points and a wide range of fibril diameters.

### Considerations Regarding the Size of the Cellulosic Entities

Given the diverse size ranges shown in Table 6, researchers and developers of electrically conductive cellulosic composites have many options. Some general principles can be mentioned:

- a. Larger cellulosic particles are typically cheaper to produce.
- b. Larger cellulosic particles have a lower surface area per unit mass, and this may lower the cost if any surface treatment is needed to aid interfacial compatibility within the composite.
- c. Smaller particles may be needed for certain applications, for instance the need for material to pass through tiny nozzles in 3D printing.
- d. Nano-scale particle size may be needed for certain transparent films.

### Possible Roles of the Cellulosic Particles

Likely roles of the cellulosic component of electrically conductive composites will be considered next. First, some published evidence suggests that the cellulose can serve as a template or support for deposition or reinforcement of the conductive substance, helping to maintain its connectivity. Second, the cellulosic material may contribute to the overall strength or flexibility of the composite.

#### *Template and support for the conductive substance*

In a composite it is common for one of the main ingredients to serve as an essentially continuous matrix and the other to serve as a reinforcement (Gupta and Gupta 2019). When one of the ingredients is cellulosic, due to the inherently crystalline nature of such materials, it usually serves as a reinforcement (Lee *et al.* 2014). As such, it is worth considering whether or not the cellulosic component, in a given case, is acting as a kind of support or template on which the conductive material can remain intact and capable of serving as a somewhat continuous contributor to current flow. Such a relationship is especially clear in certain cases in which the conductive substance is intentionally coated onto cellulosic fibers or nanofibers (Patel *et al.* 2014; Zhou *et al.* 2014; Liu *et al.* 2015a; Su *et al.* 2017; Tian *et al.* 2017; Wang *et al.* 2018a). For instance, Patel *et al.* (2014) attached graphene flakes securely onto cellulosic surfaces using polysulfides. By this means they achieved sufficient durability for use in sulfur batteries. In principle, a secure substrate having stable dimensions would be expected to stabilize fragile conductive deposited films (Shi *et al.* 2015). Su *et al.* (2017) carried out in-situ polymerization of poly-dopamine in an aqueous suspension of nanofibrillated cellulose, such that the NFC became coated with the conductive material. As another example, Wang *et al.* (2018a) oxidized the surfaces of cellulose nanocrystals as a first step in coating the CNC particles with silver. Cellulosic materials also can provide a contiguous extended or branched structure, such that conductive material coated on its surface will have continuous paths to follow.

Certain attributes of cellulose can be expected to make it especially suitable as a substrate for deposition of conductive materials at the nano scale. In particular, it is well

known that the cellulose macromolecule, as a result of its biosynthesis, becomes organized into relatively smooth, regular, and continuous nanofibrils having widths in the range of about 4 to 10 nm, and that these likewise become organized into larger fibrils. Thus, nanomaterials obtained by acid hydrolysis or by mechanical shearing of cellulosic materials tend to produce fibrillar structures that seem well suited for support of relatively long and continuous chains or layers of conductive materials. On a larger scale, the fibrils are wrapped as a series of layers that comprise fibers. Again, these structures tend to have a relatively high aspect ratio (often in the range 50 to 200), which may be advantageous as a support for conductive materials that need to be connected as continuous paths for current.

A second potentially advantageous attribute of cellulose, in terms of serving as a support for conductive materials, is its dimensional stability, especially in the lengthwise dimension. Cellulose fibers typically swell or shrink in the long dimension by only a couple of percentage points when the humidity changes over wide ranges (Courchene *et al.* 2006; Larsson and Wågberg 2008). This may be expected to be important when serving as a support for relatively fragile conductive materials such as graphene (Zhang *et al.* 2014a; Shi *et al.* 2015).

#### *Physical attributes of the composite*

The overall physical properties of the composite, including elastic modulus, breaking strength, and maximum extension before failure can be expected to be affected by each major component, and the cellulosic component is no exception. The use of cellulosic materials has been shown to provide increased strength to structures involving conductive materials (Hafez *et al.* 2017). In the case of graphene, the conductive component of nanocomposites has been found to increase the modulus of films prepared from nanofibrillated cellulose (Luong *et al.* 2011; Dang and Seppälä 2015). Likewise, Meng and Manas-Zloczower (2015) found that the addition of carbon nanotubes to cellulose nanocrystals increased the strength of electrically conductive composites compared to the strength of the cellulosic component alone. Related findings with carbon nanotubes and nanocellulose were reported by others (Qi *et al.* 2013; Zhang *et al.* 2013a).

## PROCESSING ASPECTS

### Explaining Scatter in Experimental Data

While the contents, *e.g.* a conductive substance and a cellulosic material, clearly play key roles regarding the resulting properties of electrically conductive composites, the manner in which the materials are brought together also have been found to play a decisive role. Processing aspects affecting such results have been discussed in a recent review article (Du *et al.* 2017). Important differences in composite properties, depending on preparation procedures, have been reported (Li *et al.* 2007; Hernandez *et al.* 2009). As was noted earlier, sometimes processing conditions that lead to more uniform dispersion of conductive particles have had the perverse effect of decreasing the conductivity at selected levels of composition (Li *et al.* 2007). Sato *et al.* (1991) showed that stretching of a composite in the course of its processing sometimes can increase conductance in the processing direction.

Evidence of the dominant effect of processing conditions on conductance of composite materials was assembled by Bao *et al.* (2013). They present an extensive table

showing very large differences in percolation threshold for different sets of composites, where each set was prepared with the material types kept constant but the processing conditions varied. Li *et al.* (2007) found that published data for percolation thresholds of composites containing carbon nanotubes spanned a range of 0.002% to 4%, and that the best explanation was differences in detailed structure due to processing differences. As was noted earlier, conditions tending to favor a more uniform distribution of conductive particles generally made the composites less efficient in conducting electricity, in terms of the amount of conductive material required. Schueler *et al.* (1997) summarized the main factors governing the effectiveness of electrically conductive composites during processing as particle-particle interactions, the dynamics of agglomeration, and the structure of agglomerates.

### Composite Preparation

Among the methods that have been used to prepare cellulose-containing composites, many of them can be placed in the categories of doping, coating, casting, extrusion, filtration, and papermaking (Hubbe *et al.* 2017a).

#### *Coating the cellulose*

The word “coating” typically implies a process in which a fluid mixture is applied to a surface, after which a suspending liquid either may be absorbed into the bulk of the substrate or evaporated into the gaseous phase, leading to immobilization (Brodin *et al.* 2014; Hubbe *et al.* 2017a). In principle, there can be advantages to coating conductive substances onto cellulose particles, thereby rendering the cellulosic entities fully conductive on their exposed outer surface. This approach was explained most clearly by Mamunya *et al.* (2002), who showed how metal powders deposited onto larger non-conducting elongated particles can serve as conducting elements as core-shell structures. More typically, conductive materials have been applied to coat cellulosic surfaces by adsorption or particle deposition from solution (Hu *et al.* 2009; Zhou *et al.* 2014; Shi *et al.* 2015; Meulendijks *et al.* 2017; Sakurai *et al.* 2018; Wang *et al.* 2018a). For example, Meulendijks *et al.* (2017) prepared cellulose nanocrystals to which silver particles has been applied to the surface by *in-situ* precipitation. For larger structures, metal coatings can be applied to cellulosic surfaces by electroless plating (Kelly *et al.* 2007; Ueno *et al.* 2015; Root *et al.* 2018). However, conventional wet coating processes such as spin coating or rod coating may cause uneven distribution of the conductive materials due to self-aggregation in the course of solvent drying, a phenomenon known as the coffee-ring effect (Deegan *et al.* 1997; Hu *et al.* 2010; Han and Lin 2012; Kim *et al.* 2013; Koga *et al.* 2013).

#### *Casting*

When it comes time to form a composite from prepared conductive particles in a suspension with cellulosic particles, many of the systems considered in this review article involved a process that can be classified as casting. In these cases the mixture was applied to an impervious surface, and a solvent (such as water) was then evaporated (Schmidt *et al.* 2007; Gou *et al.* 2015; Lee *et al.* 2016). Schmidt noted that time and viscosity may play critical roles in determining whether or not conductive particles are able to self-assemble, thereby establishing electrical connections prior to drying of the composite, at which point the structure will have become fixed. If the viscosity is low enough and the time before curing is long enough, then the van der Waals forces presumably will tend to draw adjacent conductive particle surfaces into contact.

### *Electrospinning*

The electrospinning procedure reported by Cai *et al.* (2018) offers a way to prepare ultrathin filaments containing one or more component. The approach has been used frequently in the lab with nanoparticles suspended in a solution of another component. In principle, the same method could be used to prepare conductive fibers reinforced by nanocellulose particles. In the cited work, polybenzazole was the conductive polymer, and it was dissolved together with cellulose in an ionic liquid. However, such a strategy does not necessarily achieve the most advantageous type of structure, as mentioned earlier, in which the conductive material is facing outwards and is thus more able to achieve electrical connections. There is motivation to consider solvent systems that leave the cellulosic material in particulate form, thus minimizing the likelihood that the conductive material might be entirely covered by a skin of the more hydrophilic regenerated cellulose.

### *Papermaking/infusion*

The papermaking process can be defined as the preparation of a particle suspension, followed by removal of most of the water by drainage through a screen, followed by drying (Hubbe *et al.* 2017a). The process has obvious importance as a way to prepare relatively inexpensive, highly recyclable sheets of cellulosic fibers at high rates of production, and there are many reports in which electrically conductive coatings have been applied to such paper sheets (Hu *et al.* 2009; Nyholm *et al.* 2011; Tobjörk and Österbacka 2011; Agate *et al.* 2018). However, it is also possible to incorporate electrically conductive particles during the paper forming process (Huang *et al.* 2005; Jabbour *et al.* 2012). The same can be achieved by mixing very small conductive particles such as graphene or carbon nanotubes with nanocellulose, then forming “nanopaper” sheets on a suitable membrane filter (Hu *et al.* 2013; Luong *et al.* 2013; Zhang *et al.* 2013b; Hamedi *et al.* 2014; Lay *et al.* 2016). For example, Hu *et al.* (2013) prepared transparent and conductive nanopaper using either tin-doped indium oxide, carbon nanotubes, or silver nanowires applied to a mat of nanofibrillated cellulose by a filtration method. Similar work was carried out by Luong *et al.* (2013) using suspensions of nanofibrillated cellulose with polyaniline. Likewise, Lay *et al.* (2016) report the preparation of nanopaper from oxidized nanofibrillated cellulose and pyrrole, with *in-situ* polymerization to poly-pyrrole, followed by formation of nanopaper by filtration.

A key potential advantage of using a papermaking procedure is that it may be one of the best ways to achieve a highly connected skeleton of electrically conductive fibers, which thereafter can be infused with a suitable matrix to achieve the desired toughness or other film properties. Though a somewhat different procedure was used, the potential benefits of such an approach were demonstrated by Du *et al.* (2006), who started their procedure with a composite of electrically conductive carbon nanotubes in a polymethylmethacrylate matrix. By using solvent to dissolve the matrix, they were able to achieve a simple, well-formed mat of the conductive fibers, which then could be compressed and brought into contact as a highly conductive sheet. The high conductance was preserved even when the sheet was filled with epoxy resin, which was allowed to cure.

One of the most significant challenges in the processing and development of high-performance conductive composites is improvement of the electrical conductivity while maintaining sufficient flexibility of the resulting structures.

## APPLICATIONS

Cellulose-based conductive composites have several advantages over conventional conductive materials. Because of their high flexibility and biodegradability, cellulose-based conductive composites represent an attractive alternative to the traditional conductive materials and have been applied in different areas (Nyholm *et al.* 2011; Svennersten *et al.* 2011; Tobjörk and Österbacka 2011; Zschieschang *et al.* 2011; Muskovich and Bettinger 2012; Jabbour *et al.* 2013; Irimia-Vladu 2014; Terzopoulou *et al.* 2015; Ummartyotin and Manuspiya 2015; Du *et al.* 2017; Agate *et al.* 2018; Li *et al.* 2018). Due to their flexible, light, and nontoxic nature, materials based on cellulose have great potential in applications such as flexible wearable devices and energy storage devices. In addition, by replacing the use of traditional conductive materials, conductive cellulose composites could potentially reduce the environmental footprint of electronic devices and improve their sustainability (Sequeira *et al.* 2010). Some key areas of application to be highlighted here are strain sensors, energy storage devices, photovoltaic (PV) devices such as solar cells, electrodes, and super-capacitors.

### Strain Sensors

Strain sensors require material that is electrically sensitive to mechanical strains. They have a wide range of application potential, such as performance monitoring (Helmer *et al.* 2011). The systems work due to a changing electrical conductance upon the application of pressure. For instance, Mohan *et al.* (2016) found that films prepared from graphene oxide that had been compressed exhibited higher conductance. For most conventional strain sensors, the sensory materials have been either coated onto or embedded into a soft fabric. Those methods, although widely applied, require complicated and costly processes (Toprakci *et al.* 2013). Cellulose nanocrystals, instead, have high mechanical strength and provide an attractive alternative in making flexible conductive materials. Wu *et al.* (2016) and Wang *et al.* (2016) fabricated conductive nanocomposites with a unique 3D hierarchical conductive structure. In their research, natural rubber and CNTs were uniformly dispersed under ultrasonic suspension. With the help of latex assembly technology, the dispersed mixture was then integrated with cellulose nanocrystals to prepare the nanocomposites, which could be applied as strain sensors. Hosseini *et al.* (2018) applied in-situ polymerization and synthesized bacterial cellulose/multi-wall CNTs composites. In their work, the composite hydrogels were converted to the conductive aerogels via the supercritical CO<sub>2</sub> method. The strain sensing revealed a linear trend as a function of the resistance.

### Energy Storage Devices

Nyholm *et al.* (2011) reviewed paper-based systems for energy storage, with emphasis on supercapacitors and batteries. Shi *et al.* (2015) reviewed the prospects for use of various electroconducting polymers in these applications. Such systems show promise to mitigate the energy crisis due to low reduction potential, low density, and large capacity (Jabbour *et al.* 2013).

Nowadays, Li-ion batteries are among the most widely used energy storage devices. Papers made from lignocellulose are renewable, recyclable, biodegradable, and porous, and they have been deployed in the manufacturing of Li-ion batteries - the so-called “paper batteries”. However, the functions of such “paper batteries” are usually restricted by the thickness of the paper. Different from paper cellulose, nanocellulose has much smaller

dimension (the diameter of the nanocellulose is around 10 to 30 nm). Note that such dimensions are close to those of most reactants inside the Li-ion batteries. This allows nanocellulose to become a part of the batteries (Pushparaj *et al.* 2007; Fu *et al.* 2016). The nanocellulose can contribute to the stability and mechanical strength of polymer matrix inside cellulose-based Li-ion batteries. Ummartyotin and Manuspiya (2015) mixed a small amount of Li-ion/Li-oxide (in the forms of  $\text{Li}_4\text{Ti}_5\text{O}_{15}$  and  $\text{LiFePO}_4$ ) with cellulose and polypyrrole, and formed the paper by vacuum filtration. The fabricated cellulose-based Li-ion battery had significant higher chemical stability over the traditional Li-ion battery.

### PV/Solar Cells

Cellulosic materials are also applied in fabrication of PV and solar cells. Given the fact that the minimum dimension of regular cellulose is much higher than the wavelengths of visible light, ordinary cellulosic fibers can be used only as base material in cellulose-based PV and solar cells. For example, Li *et al.* (2018) prepared the solar cell electrodes by sputtering indium tin oxide on regenerated cellulose film. On the other hand, nanocellulose has a diameter as low as 10 nm and is transparent to visible light. This allows nanocellulose to become an excellent material in making translucent electrodes (Hu *et al.* 2013). Zhou *et al.* (2014) deposited the conductive polymer onto the nanocellulose surface by a film-transfer lamination technique. The power conversion efficiency of solar cells fabricated with the coated nanocellulose could reach up to 4.0%. The incorporation of low-cost cellulosic materials and large scale manufacturing will be beneficial for the PV/solar cells industry since the current technology requires a useful operating life of over 25 years for PV devices to reach a desirable amortized energy cost.

### Electrodes

Electrodes are important for electronic devices such as soft monitors and touch-screens (Puetz and Aegerter 2008). A qualified electrode should ensure that the light transition and electronic conductivity remain stable with minimal effects from the surroundings (MacDonald 2004). Cellulose meets that requirement and could be applied as the base material for production of low density and renewable soft electrodes. Hasan Khondoker *et al.* (2012) fabricating indium tin oxide (ITO) electrodes onto cellulose film using spin-coating. The results showed that the optimal concentration of ITO particles was 15 wt%. At that concentration, the transparent cellulose had a low resistivity of  $5.0 \times 10^3 \Omega/\text{sq}$  and high transmittance of 74% at 800 nm. A study by Xu *et al.* (2013) showed that the conductive cellulose membranes fabricated from bacterial cellulose/polypyrrole could achieve a high electrical conductivity of 3.9 S/cm. The membrane had a maximum discharge capacity of 101.9 mAh/g at 0.16 A/g current density. Different methods could be used to obtain cellulose-based electrodes with different properties, such as improving the fabrication process, optimizing specific surface area, and changing the conductive agents. Liu *et al.* (2015b) prepared a hybrid conductive film of gold nanoparticles (20 nm in diameter) and nanocellulose. With its stable electrochemical properties, the conductive film showed a great potential as an electrode material.

### Supercapacitors

Supercapacitors, because of their high power density and short charging cycle, have attracted great interest in different applications (Zhang *et al.* 2014b; Liu *et al.* 2015a). Based on the electron storage mechanisms, supercapacitors could be categorized into electrochemical double-layer capacitors made of carbon-based materials, and oxidation



and reduction capacitors made of transition metal oxides and conductive polymers (Rudge *et al.* 1994). The use of graphene in systems for supercapacitors is consistent with the molecular-scale mechanisms that have been proposed for such materials (Xia *et al.* 2017); each junction between a graphene sheet and the adjacent material can be modeled as its own tiny capacitor, as part of a dense network of capacitors.

Carbon nanotubes and nanocellulose have shown great potential in making flexible solid-state supercapacitors because of their high specific surface area compared to conventional capacitors (Lu *et al.* 2014). In addition, supercapacitors made of CNTs and nanocellulose show substantially higher mechanical properties over the conventional supercapacitors. For example, a study by Zhang *et al.* (2013a) presented excellent mechanical properties of CNTs and nanocellulose supercapacitors with tensile strength being 1 MPa and Young's modulus being 123 MPa. Similar to CNTs, graphene also has suitable properties of conductivity and porous structure. The covalent bonds formed between nanocellulose and graphene promote the uniform distribution of the graphene inside the composites. Due to the large specific surface and low mass density, cellulose aerogels also have attracted increasing interest in producing supercapacitors. Zhang *et al.* (2014b) synthesized solid-state flexible aerogel supercapacitors from cellulose nanofibrils (CNF), silver nanoparticles, and polyaniline (PANI) nanoparticles. The same specific capacitance was obtained at 176 mF/cm<sup>2</sup> at 10 mV/s after repeated bending.

## CLOSING STATEMENTS

Cellulose, as one of the most abundant, biodegradable, and renewable natural materials, has shown great potential in the fabrication of conductive flexible composites. The cellulose-based composites can be environmentally friendly and have high-quality in photonic and electrical properties. Cellulose-based composites have favorable prospects in the applications of green electronics and energy storage devices. Challenges must be overcome to achieve wide application of cellulose-based composites, however. The current nanocellulose preparation processes are generally expensive and have relatively low yields. Accordingly, future research and the development of cellulose-based composites are needed, especially in the following areas:

(1) *Developing new dispersion systems for nanocellulose in combination with electroconductive substances.* The optimum distribution of the cellulosic component is critical in preparing high quality cellulose-based composites. The current methods in cellulose surface modification include silane coupling, cationic modification, and surface oxidation. These methods could improve the distribution of nanocellulose particles, but the dispersing efficiency often drops with the increasing nanocellulose concentration within various plastic matrices.

(2) *Preparing nanocellulose particles with high degrees of polymerization.* Higher polymerization generally implies higher mechanical strength and durability of the nanocellulose. Acid hydrolysis, as a means to prepare CNC, removes the amorphous region of the cellulose, but it inevitably leads to breakage of some of the inherent structure of nanocellulose. That breakdown not only results in less nanocellulose yield, but also it negatively affects the mechanical strength and weather resistance. Therefore, finding new processes to reduce the destruction of nanocellulose is critical to improve the crystallinity of nanocellulose, and ultimately improve the electrochemical properties of the conductive nanocellulose composites.

(3) *Establishing a system of multiple conductive agents.* A complex system that integrates different conductive polymers, metal nanowires, and graphene, for instance, could help to achieve a more robust system with less susceptibility to performance loss due to discontinuities between conductive elements. More attention is needed on the effects of stretching and environmental conditions on the long-term performance of cellulose-containing composite structures intended for electronic applications.

(4) *Focus of future research on “weak links” of electrical connection.* As shown by multiple researchers, the incorporation of diverse materials, including non-conductors such as cellulosic materials in electrically conductive composites often results in structures with numerous gaps or poor electrical contacts among the electrically conductive particles. There is a need for research that specifically addresses ways to improve the transfer of current at the inevitable gaps or non-ideal contact interfaces between different kinds of electro-conductive materials.

(5) *Focus of future research on achieving optimal degrees of agglomeration with self-assembly of favorable electrical connections.* The literature provides multiple evidence, both theory-based on results-oriented, pointing to a critical role of agglomeration of electrically conductive particles, relative to the conductance performance of the composites. Some of the most promising approaches provide opportunities for the conductive particles to establish electrical connections efficiency by means of a diffusion-based self-assembly process. There is a need for focused research to better understand such approaches. Also, there appears to be a potential advantage in forming well-connected mats of conductive particles and then infusing matrix material (as a binder, *etc.*) in such a way as to preserve the high levels of conductivity.

(6) *Smart packaging.* The integration of sensors such as temperature, humidity, oxygen indicators into food packaging can be used for food shelf-life and safety and typically comprise cellulose based materials that enable recycling at end-of-life. In this case, cellulose fibers can be exploited to provide a host matrix for the conductive material that can adhere to a paper substrate.

(7) *Displays.* Nanocellulose can be used as a substrate for light-emitting diodes and displays. Okahisa *et al.* (2009) reported successful fabrication of an organic light-emitting diode (OLED) device using acetylated cellulose nanofibrils composites. The fabrication of the device involved application of a coating to a nanocellulose-based flexible film (Okahisa *et al.* 2001).

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