

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

4,800

Open access books available

122,000

International authors and editors

135M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.

For more information visit www.intechopen.com



Coating of Conducting Polymers on Natural Cellulosic Fibers

Saiful Izwan Abd Razak, Nor Syuhada Azmi,
Khalida Fakhrudin, Farah Nuruljannah Dahli,
Izzati Fatimah Wahab,
Noor Fadzliana Ahmad Sharif,
Abdul Halim Mohd Yusof and
Nadirul Hasraf Mat Nayan

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/63304>

Abstract

The process of combining natural cellulosic fibers with conducting polymers (CPs) is being pursued by scientist and researchers for their achievable synergistic electrical and biofriendly properties. CPs can be deposited on to a wide variety of cellulosic substrate and fibers, thus achieving good interactions between them. Various methods of deposition include in situ polymerization, physical coating, multilayering, and printing. Such materials are used for achieving more sustainable and low-cost CP-based applications.

Keywords: conducting polymers, cellulosic fibers, coating, paper, electrical conductivity, polyaniline, polypyrrole

1. Introduction

Since the discovery of conducting polymers (CPs), extensive researches have been carried out to explore the interesting properties of this relatively new and exciting material. Their ease of preparation, low cost, and good electronic properties have lead to the discovery of many CP-related applications. Due to their uniqueness and versatility, CPs are being deposited onto

many type surfaces to induce their properties to the template or substrate material. Among those substrates, plant-based cellulosic fibers have gained wide scientific interest. In comparison with synthetic fibers, cellulosic fibers are eco-friendly and more abundant. Conductive cellulosic fibers produced by coating with CPs are being explored for various applications including supercapacitors and batteries, conductive paper and packaging, fillers in polymer composites, transistors and conductive wires, adsorbents, and actuators. Here, we discuss recent and past reports on the research activities regarding coating of CPs on cellulosic fibers and their directed applications.

2. Cellulosic fibers

Cellulosic fibers derived from plant have drawn much attention due to their sustainability and renewability. Plant fibers find applications in many fields. Conventional synthetic fibers like glass, carbon, and aramid can be produced with a definite range of properties, whereas the characteristic properties of natural fibers vary considerably. In general, cellulosic fibers may be bast, leaf, or seed including wood or nonwood types. The major constituents of lignocellulosic fibers are cellulose, hemicelluloses, and lignin. Cellulose is the most abundant natural polymer which contain D-anhydroglucose units (cellobiose) and are joined by β -1,4-glycosidic linkages at C_1 and C_4 positions. The chemical structure is shown in **Figure 1**. The main functional groups of cellulose are its hydroxyl groups (primary and secondary). These hydroxyl groups are involved in a number of intra- and intermolecular hydrogen bonds which result in various ordered crystalline arrangements. In fibers, cellulose chains are aligned along the fiber length, which make them high in flexural and tensile strength [1]. Hemicelluloses can consist of various monomeric units such as glucose, mannose, galactose, xylose, and arabinose. Depending on the monomeric unit, they can vary in structure and are highly branched with much lower degree of polymerization than that of cellulose giving them a non-crystalline structure. Hemicelluloses act as supportive matrix for cellulose fibers. Lignin is an amorphous, high molecular weight phenolic compound, which function as a structural supporting material in plant. Their structure varies and do not have predictable, continuous, and uniform properties. Though the exact chemical structure of lignin still remains unestablished, the high carbon and low hydrogen content suggested that the compound is highly unsaturated or aromatic [2].

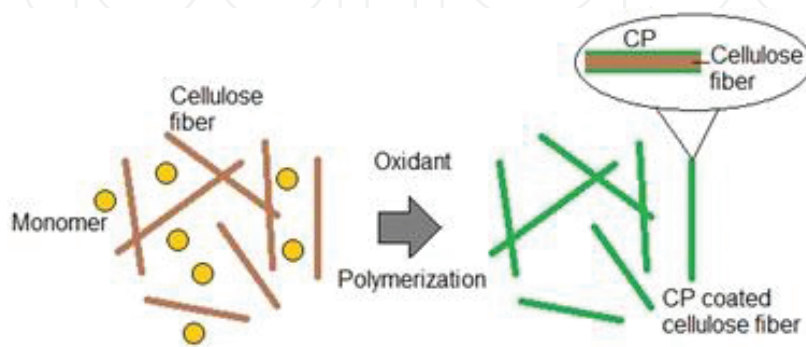


Figure 1. In situ polymerization of CP on cellulosic fibers.

3. Polyaniline, polypyrrole, and PEDOT, PEDOT:PSS

Polyaniline (PANI), polypyrrole (PPY), poly (3,4-ethylenedioxythiophene) (PEDOT), and poly (3,4-ethylenedioxythiophene):poly (styrenesulfonate) (PEDOT:PSS) can be regarded as the most explored CPs up to date. PANI has the longest history among the CPs. It is one of the oldest artificial CPs and its high electrical conductivity among organic compounds has attracted continuing attention. The green protonated emeraldine salt has conductivity many orders of magnitude higher than that of common polymers, which ranges from 10^{-10} to 10^1 S/cm but lower than that of typical metals [3]. PPY is another interesting CP with conductivity ranging from 10^{-4} to 10^{-2} S/cm. It has been studied in many electrochemical and sensor applications [4]. Another extensively explored family of CPs is PEDOT. It has high conductivity reaching 300 S/cm. Despite being described as more environmentally friendly compared to other CPs, they have the disadvantage being insoluble water and infusible [5]. PEDOT can be imbedded in poly(4-styrenesulfonic acid) (PSS) to form a more processable water-based PEDOT:PSS complex. This CP forms a stable dispersion that allow for coating process, which include spin coating. The conductivity can be from 10^{-5} to 1 S/cm depending on the PEDOT:PSS ratio [6].

4. CPs on cellulosic fibers

In situ polymerization is regarded the most popular method of depositing CPs on cellulosic fibers. The method varies widely depending on the types of oxidants, medium, dopants, monomers, the ratio between them, and the processing steps and parameters. In most cases, the in situ polymerization can be simplified as having the monomers of CPs being polymerized in a reactor or medium in the presence of the cellulose fibers (**Figure 1**). CPs will be formed on the bulk fibers or surface depending on the arrangement of the fibers.

Wood-based celluloses have been explored widely with the modification of CPs. PPYs deposited on crosslink cellulose have conductivity reaching 1.1 S/cm with good mechanical properties. The crosslink structure might keep the rigid PPY in a good conductive state due to the weaker interaction between the crosslinked cellulose and the PPY [7]. Aniline monomer has been described to penetrate all areas of wood veneer structures during in situ polymerization. In situ PANI formation was more prominent in cell walls and middle lamella. PANI modification resulted in the reduction of mechanical properties due to the prohibition of secondary interactions within the cell wall. The conductivity was anisotropic, mostly along the direction of wood fibers. Furthermore, the lignin component of the wood and PANI formed strong interaction as described by increase in glass transition temperature of lignin [8]. Lignin is a major component of wood; it contains the structures of phenol, carboxyl, and aldehyde groups, among others. Its hydrophobic character and presence of aromaticity facilitates the interaction with the hydrophobic PANI. Blends of emeraldine base of PANI (36%) and lignin film have shown good homogeneous blend and good oxidation/reduction potential characteristics. The interaction occurs mainly between amine of PANI and carbonyl of lignin; imine of PANI and hydroxyl of lignin [9, 10].

Due to the vast growing effort of reducing wood-based resource, bamboo has been explored as the substitute to replace wood. Peeled bamboo veneers have shown increase in conductivity from 10^{-4} to 10^{-3} S/cm when coated with PANI, tuned by the phosphate acid doping concentration. Cellulose structure of bamboo was intact but with a slight reduction in the degree of crystallinity [11]. Curauá fiber, natural vegetal fibers of amazonic origin have shown increase in conductivity from 10^{-8} to 10^{-4} S/cm when in situ coated with PANI doped with sulfuric acid. PANI-modified fibers achieved conductivity changes of approximately 20,000% when tested for its compression sensitivities due to the high contacts. The modified fiber has potential applications as a pressure-sensing material by the function of its conductivity to applied pressure [12]. Similarly, mango fiber was reported to achieve conductivity by modification with PANI. The coated fiber was reported to achieve magnetic properties, being attracted by magnetic field [13]. It was shown that man-made cellulose-based fibers and textile, such as cotton, viscose, cupro, and lyocell, were able to be modified with CPs. This type modification is sought after in the applications of technical apparel, such as antistatic fabrics for work clothing, sportswear, heating, and cooling equipment [14]. Another method of coating the fabric with CPs besides the bulk in situ technique is the vapor phase polymerization. The cellulose fabric is impregnated with aqueous solution of oxidant and dopant, and followed by exposure to monomer in order to start the polymerization. The method revealed a partial penetration of PPY into the amorphous zones of fiber bulk [15]. Coating of CPs on protein fibers such as wool and silk has also been reported [16, 17]. Dip coating of PEDOT:PSS on wood-based microcrystalline celluloses showed that PEDOT was preferentially adsorbed rather than PSS. A strong interaction between the PEDOT:PSS and the cellulose was observed, implying a broad molecular distribution of the CP. As the pH of the solution increased, the amount of adsorbed PEDOT:PSS decreased due to the higher repulsive forces existing at higher pH levels [18].

5. CPs on bacterial cellulose

Bacterial cellulose (BC) is a straight chain polysaccharide with an ultrafine nanosized 3D fibrous network structure and is produced by certain microorganism (bacteria). The fibril diameter ranges between 10 and 100 nm with crystallinity up to 90%. It is highly hydrophilic due to neat hydroxyl groups of cellulose on the surface. These fibers are stronger than those of conventional natural fibers [19].

In situ coating of PANI on BC template showed high conductivity (10^{-2} S/cm) when doped with organic acids such as HCl. The PANI forms a continuous nanosheath surrounding the BC due to the attraction force between the amine of aniline and abundant available hydroxyl of BC during the polymerization. The twisting-induced conductivity of the BC/PANI was reported to be activated at twisting angle of 200° [19]. Coating of BC with PANI doped with dodecylbenzene sulfonic acid (DBSA) depends on the amount of DBSA used. The highest conductivity (10^{-5} S/cm) was at DBSA to aniline molar ratio of 1.5. Excess of DBSA dopant for the BC/PANI might avoid the penetration of PANI into the bulk BC with more preferable PANI formation at the surface of the BC that lead to the lowering of the conductivity [20]. It was later

on reported that FeCl_3 oxidant can yield a better conductivity (10^{-1} S/cm) to the BC/PANI [21]. A higher doping level was achieved by using p-toluene sulfonic acid dopant with good thermodynamic stability [22]. A further optimized reaction protocol was able to produce BC/PANI with conductivity of 5.1 S/cm and specific capacitance of 273 F/g. This was achieved due to the flake-shaped morphology of the BC/PANI facilitated by DMF (dimethylformamide) during the in situ polymerization [23]. Good redox properties were also observed for BC coated PPY [24].

6. CPs/cellulosic fiber as filler in polymer composites

These CP-coated cellulosic fibers have been explored as fillers in polymer composites. Incorporating fibers modified with CPs into insulating polymer matrices could induce some degree of electrical conductivity to the load-bearing host mainly for antistatic, electromagnetic, and pressure-sensing applications.

Curauá fiber modified with PANI was reported to be blended with polyamide-6 thermoplastic in a twin-screw extruder to form composites. The conductivity of composites was at 10^{-7} S/cm with a good polymer-fiber interface. The fibers provide easy conductive path (avoiding recombination of charge transport) for the PANI compared to PANI alone in the polymer matrix [25]. It was reported that epoxy resin could be cured with a PANI-coated kenaf fiber to form composites. The composite achieved conductivity in the range of antistatic applications. Mechanical properties of the composite could be improved by using suitable doping agent [26]. Similar approach was demonstrated using PANI-coated coconut fiber blended in polyurethane derived from castor oil. An increase in conductivity was observed when stress was applied to the composite [27].

7. CPs on paper and pulp fibers

Paper is a porous sheet made up of cellulosic fibers. The sheet usually has many pores generated by the fiber texture, depending on paper grades and manufacturing processes. Cellulose-based paper is intrinsically hydrophilic and contains strong hydrogen bonds after being dried. The main advantages of paper substrate are their lightweight, low cost, and environmental friendly characteristics which have potential to be modified with CPs.

Most of the earlier reports focus on the in situ polymerization of the CPs during the pulping stage or at the interface of the paper. The interest in conductive paper was initiated by a report by [28]. It was shown that the individual cellulose fiber of a filter paper was coated with 50–150 nm of PPY spheres. The spheres were fused together forming an integral layer of CPs with approximate thickness of one sphere. The pores within the paper matrix were not filled with PPY, indicating there is a significant bonding between the cellulose surface and the PPY. Furthermore, these pores open up for further modifications for new grades of paper. The sonication process for removal of impurities after the in situ polymerization did not remove

any bounded PPY. The strong interaction was suggested to be an H bond between the free available OH groups of the cellulose and the amide groups of the PPY. Similar structure was observed by using PANI as the CP but with a slight reduction in the available pores. Low temperatures (0–25°C) during the in situ polymerization of PANI coating on filter paper yielded better electrical conductivity (10^{-5} S/cm) compared to that of high temperature condition (50°C) (10^{-8} S/cm) [29].

In situ coating of PPY on bleached kraft soft wood pulp indicated there is a concentration threshold of pyrrole monomer for the composite paper to achieve a certain degree of surface conductivity. It was reported that the monomer concentration should be more than $1.8 \text{ g}\cdot\text{L}^{-1}$ in order to achieve a stable conductive paper [30]. PPYs have low oxidation potential; the redox reaction of PPY is more sensitive to oxygen, thus making the resulting conductive paper composites less stable in air or oxygen-rich environment. Conductive PPY paper composite is electrically unstable when stored in air at an ambient temperature. The electrical conductivity decays with an increase in storage temperature. On the contrary, the decay was inhibited when stored in a nitrogen environment. This signified that the conductivity of the paper composite was related to the oxidation of PPY which in turn relates to the temperature. PPY particles were observed to become larger when aged at 100°C in air due to the thermal oxidation accompanied by a huge increase in resistivity [31]. Doping of PPY with amphiphilic cationic polyacrylates resulted in a more stable coating on the cellulose substrate. High-charge dopant induces easier PPY entrance into the fiber lumen and easier formation of bipolaron charge carriers. The mechanical strength of the paper was enhanced due to the good interfiber bonding induced by the polymeric dopant that was able to build connections between the fibers. The bonding between PPY-coated fibers (doping other than polyacrylate) is much weaker than H bond between cellulose fibers [32].

PEDOT coating on bleached softwood kraft pulp showed that the polymerization temperature and time is optimum at 60°C and 4 h, respectively, with good environmental stability due to the higher oxidation potential of PEDOT compared to other CPs. The volume resistivity was achieved at $5.9 \Omega/\text{cm}$ with monomer concentration of $3 \text{ g}\cdot\text{L}^{-1}$ [33]. PEDOT in situ coating on a filter paper revealed a significant increase in tensile strength due to the interlocking between PEDOT and cellulose fibers. Furthermore, the PEDOT layer fixes and covers the fibrils tightly [34].

It was describe by X-ray photoelectron spectroscopy that the bond between PANI and cellulose in pulp paper existed in the form of H bonding and the lowering of mechanical properties is due to the coverage of hydroxyl groups of the fibers by PANI. p-toluene sulfonic acid doping of PANI achieved a conducting network and lowest resistivity at 30% of coated PANI [35]. PANI-coated commercial paper pulp has been described to be rigid and flexible enough to be used as paper folding artwork or origami. The electrical conductivity increased with a bend angle of 250°. The twisting process induced high contact between fibers in the sheet, resulting in the increase of electrical conductivity [36]. Pulping conditions of the paper played a significant role in PANI deposition and yield. It was shown that chemical pulping had higher amount of coated PANI and higher conductivity than those prepared from high-yield pulp. Furthermore, bleached chemical pulp had better paper properties. It was proposed that the

increasing content of sulfonic group of the chemical pulp had a positive linear effect to the amount of coated PANI. Sulfonic groups in the pulp fibers could be dissociate and promote the adsorption of the positively charged PANI onto the fibers [37]. Interfacial polymerization was suggested to be the better method in protecting the fiber strength to some degree. The aniline polymerization reactions take place at the paper interface and not across the whole sample. Thus, multiple steps of polymerization are required. Polyamideamine-epichlorohydrin (PAE), a commercial wet strength agent in papermaking showed to be beneficial in improving the mechanical properties of multiple interfacials of cellulose paper in situ coated with PANI [38].

Other types of cellulosic paper sources have shown potential to be deposited with CPs. Coating of PANI on rice straw and bagasse pulp paper has shown potential for packaging applications. The main drawback of such paper substrate is that their mechanical properties such as breaking length, burst factor, and tear factor decreased with increasing PANI amount. A total of 10 wt % of PANI is needed to impart electrical conductivity to the paper composite [39]. Pineapple leaf fiber paper pulp was coated with PANI using the in situ polymerization method. The addition of PANI showed a marginal drop in mechanical properties (burst strength and tear index) and a reduction in moisture absorption with increasing PANI amount. The DC conductivity was achieved around 10^{-5} S/cm at the concentration threshold of PANI [40]. It was shown that the mechanical and electrical conductivity of PANI-coated kenaf paper could be optimized by controlling the PANI amount and dopant concentration [41]. Further studies have shown that PANI-coated kenaf fibers were able to blend with kenaf pulp during the pulping stage. The composite paper revealed enhancement in the electrical conductivity with improved mechanical properties [42]. Another effort is by coating pulp of wasted egg holder tray by PPY. The raw pulp was bleached and in situ coated with PPY, giving conductivity value of 10^{-4} S/cm in the frequency-independent region [43].

Paper is usually extremely rough, with peak-to-valley roughness values of up to hundreds of micrometers. The packing density of fibers also limits its overall mechanical properties. Nanosized fiber papers or nanopapers can provide excellent mechanical properties, provide smooth surface, and be optically transparent. Modification of nanopapers with CPs will open up many opportunities in electronic/optoelectronic devices [44]. It was displayed that at the percolation threshold, nanofibrillated cellulose/PANI composite paper had mechanical properties similar to its unmodified counterpart. The percolation was achieved at 4.57 vol% of PANI with conductivity of 10^{-5} S/cm. The nanosize of the cellulose opened more available OH for the in situ polymerization, thus increasing the PANI coating [45]. PEDOT:PSS can also be spin coated on nanofibrillar cellulose film [46].

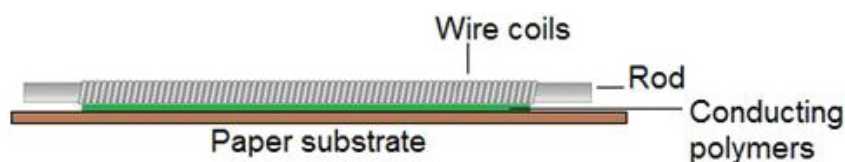


Figure 2. Mayer rod coating of CP on paper.

Mayer rod coating (**Figure 2**) is one of the most popular coating methods on a paper substrate. A Mayer rod is a stainless steel rod that is wound tightly with stainless wire of varying diameter. The grooves between the wire coils determine the precise amount of coating materials that will pass through as it moved along the web. Coating technology can avoid the complication faced with in situ polymerization technique and is a very feasible process for coating a layer of any material over paper substrate. Nevertheless, the viscosity of the CP solution should be low enough to allow easy flow between the wire windings.

Physical coating of PEDOT:PSS using a Mayer rod was achieved by using organic solvents such as dimethyl sulfoxide and N-methylpyrrolidone. The solvents induced plasticizing effect and conformation changes to the PEDOT molecules that lead to higher conductivity compared to PEDOT:PSS coating without any solvents. The paper conductivity level was at 10^{-3} S/cm with a slight increase in tensile strength [47]. It was reported that multiwalled carbon nanotubes could be dispersed in PEDOT:PSS solution without the use of any added surfactant. This mixtures were coated onto the paper substrate using a Mayer rod coater and heated using a specially design unidirectional ceramic heating board. The heating method revealed better conductivity compared to those dried using conventional drying. This was due to the good bonding between the solution mixture and the paper fiber during the drying stage [48]. Clay has been suggested to act as carrier for the CP for conductive paper. Though the reasons are unclear, the nanosize of clay minerals can provide good dispersion of the CP for the physical rod coating process [49].

8. Electroactive papers, supercapacitors, and adsorbents

Due to the interesting redox properties of CPs, they are being explored as electroactive polymers and actuators. They can create a mechanical response from an electrical stimulation. The response can be either a transverse bending or an axial expansion/contraction. Papers that are modified with CPs for their actuation properties can be classified as an electroactive paper. Electroactive paper has the advantages of low cost, lightweight, biodegradability, large displacement output, and low actuation voltages. Drawbacks of this material are that it suffers performance degradation over time and produces a low displacement output at a low humidity.

It was shown that PANI-cellophane actuator had better performance than PPY-cellophane in terms of bending displacement and ruggedness to humidity. This was described due to the relatively high conductivity of PANI and the crystalline nature of PANI which changes to amorphous structure after the actuation [50]. Electroactive paper of regenerated cellulose and PPY with dispersed hydrophobic ionic liquid resulted in reduced resistance and better durability under ambient humidity conditions. The movement of anions in the conducting system resulted in bending displacement [51]. In situ coating of PANI on cellulose solution using p-toluenesulfonic acid showed that the resulting paper had low Young's modulus and reduced thermal stability. The cellulose-PANI electroactive paper was fabricated by depositing very thin gold electrodes on both surfaces of the paper. A large bending displacement and long actuation stability was reported at ambient humidity and temperature [52].

The key technology that underlies the performance of supercapacitor materials has turned it into a research hotspot is the electrode material. Electrode materials mainly include carbon material, metal oxide, and CPs. Flexible electrode-based paper is very promising for low cost and lightweight energy storage applications. The rough and porous paper surface is advantageous when electrochemical active materials were coated onto cellulose fibers.

Cellulose extracted from green polluting *Cladophora* algae was in situ coated with PPY and revealed excellent ion-exchange capacity and cycling stability when used as a working electrode in a chloride-containing solution [53]. The group later on developed the *Cladophora*/PPY as aqueous batteries that can exhibit charge capacities 25 and 33 mAh g⁻¹. This was suggested to be due to the thin 50 nm coating layer of PPY on the individual cellulose fiber [54]. A sandwich of PPY/A4 paper and PVA/H₃PO₄ showed electrical conductivity of 15 S/cm and an energy density of 1.0 mWh cm⁻³ [55]. Similar energy storage potential was shown by PEDOT:PSS dispersed with multiwalled carbon nanotubes coated on paper substrate [56]. It was shown that a regenerated cellulose film coated with PPY achieved conductivity of 0.59 S/cm at nearly 30 wt% of PPY. The specific capacitance was reported at 392–308 F/g [57].

Anion-exchange properties of PPY on wood saw dust have shown potential use as adsorbent for the uptake of Cr(VI) in wastewater solution [58]. Another study later on improved the uptake findings using industrially favorable hydrogen peroxide as the oxidant to minimize the cost of using ammonium peroxydisulfate oxidant [59]. Layers of copper metals were reported to be deposited electrochemically onto the outer surface of lightweight balsa wood coated with PPY and reduction of silver by suspending the coated samples in hydrazine hydrate solution. The conductivity was comparable to that of the metal alone [60]. Similarly, redox-active surface of CPs on kraft paper pulp was utilized for the reduction of silver metals [61].

9. Inkjet printing of CPs on cellulose paper

Recent research interest has been directed toward inkjet printing of CPs. The precision and flexibility of inkjet printer is ideal for printed electronics compared to the high cost and labor-intensive method of photolithography and vapor deposition. The main challenges of inkjet printing of CPs on paper substrate are their film homogeneity, wetting behavior, and nozzle clogging during printing.

Suspension of DBSA-doped PANI has been successfully printed using a commercial piezoelectric desktop inkjet printer. The surface tension was reported to be in a range suitable for inkjet printing with bulk conductivity as same magnitude as those of drop-coated film [62]. PANI has also been identified for printing conductive wires on paper substrates for the fabrication of transistors with a low operating voltage. It was shown that the resistance of the printed paper has linear correlation with the short length scale roughness of the print substrate [63]. PEDOT:PSS have been explored as inks for printing on paper substrates. Roughness of the paper substrate, additives, and the ink formulation itself play a role in the conductivity.

A more stable conductivity was reported to be achieved by adding single-walled carbon nanotubes into the PEDOT:PSS ink. Retention aids and fixation agents of the paper seem to interact with the PSS ions thus lowering the conductivity of the printed films [64]. Another interesting method of patterning CPs on to paper is the “pen-writing” method. Patterns or drawing of FeCl_3 oxidant were drawn on the paper substrate using an iridium nib pen and followed by exposure to pyrrole vapor that leads to quick interfacial polymerization. The paper can be served as sensors for ammonia gas, thermal heat, and NIR (near-infrared) irradiation [65].

10. Layer-by-layer assembly of CPs on paper

Cellulosic substrate or paper can be deposited by CPs using a layer-by-layer (LbL) multilayering technique. Surface properties of the paper substrate can be controlled according to electrostatic or hydrophobic interaction. It was described earlier that LbL polyelectrolyte coating can modify the surface charge to make the resulting paper stronger [66]. An LbL of wood microfibers, PEDOT:PSS, and small amount of multiwalled carbon nanotubes (0.2%) have shown conductivity up to 20 S/cm^{-1} and electrical capacitance of 10^{-11} F/in^2 [67]. It was reported that unbeaten eucalyptus-bleached kraft pulp were coated with cationic polyelectrolyte polyethyleneimine and PEDOT:PSS. The conductivity of the resultant paper was in the range of 10^{-5} – 10^{-4} S/cm without loss of paper strength. Increased contact between PEDOT:PSS, low salt concentration, and the calendering process contributed to the improved conductivity [68]. Multilayering of conductive paper sheets made of carboxymethylated fibers displayed a much higher conductivity than those made of non-carboxymethylated fibers when both pulps were coated with PEDOT:PSS and poly(allyl amine) polyelectrolyte [69].

11. Flame retardancy

CPs are good flame retardant agents. Flame retardant agents are added in textile or plastics to inhibit or delay the flaming process. Coating of CPs on to papers would open up many potential applications in functional papers by enhancing the thermal stability. It was reported that both forms of PANI, base and protonated (hydrochloride), give the flame-retardant performance to cellulose filter paper. The PANI-coated cellulose retains the original fibrillar morphology after burning. This was suggested due to the protection of the solid carbonaceous PANI that restricts the access of oxygen to cellulose [70]. Similar heat protection was reported by coating of PANI onto wood scantlings [71]. It has been investigated that the flame retardancy increased with the amount of PANI deposited in the paper pulp and the doping agent played a major role in the flame retardancy. It was suggested that organic sulfonic acids (p-toluenesulfonic acid and sulfosalicylic acid) were more suitable than inorganic acids (sulfuric acid and hydrochloric acid). This was due to the easy dedoping and low doping level of the latter dopants [72, 73]. A further study reported that phytic acid greatly enhanced the flame retardancy of the composite paper but the conductivity level was lowered [74].

12. Conclusion

Coating of CPs on cellulosic fibers show promise in wide variety of applications from conductive papers to smart actuating materials. The utilization of natural-based and low-cost resource for high-end applications is feasible by modifying the cellulosic fibers with CPs. CPs have been shown to impart their unique features to many types of cellulosic fibers such as pure cellulose, commercial grade papers, kenaf, bamboo, vegetal fibers, rice straw, and BC. In general, further investigation should be focused on producing more mechanically reliable and electrically stable CP-coated cellulosic fibers. Polyaniline, polypyrrole, poly(3,4-ethylenedioxythiophene);poly(styrenesulfonate), and their derivatives are currently being explored extensively for their applications with cellulosic fibers. The coating method of CPs such as in situ during pulping, physical deposition using a Mayer rod, spin coating, layer-by-layer assembly, or inkjet printing plays a major role in determining the targeted properties. It envisioned that the combination of CPs and cellulosic fibers could promote more sustainable electrically functional materials for the future.

Acknowledgements

The authors would like to express their gratitude to Universiti Teknologi Malaysia for the financial assistance through research grants.

Author details

Saiful Izwan Abd Razak^{1,2*}, Nor Syuhada Azmi², Khalida Fakhruddin²,
Farah Nuruljannah Dahli³, Izzati Fatimah Wahab², Noor Fadzliana Ahmad Sharif³,
Abdul Halim Mohd Yusof³ and Nadirul Hasraf Mat Nayan⁴

*Address all correspondence to: saifulizwan@utm.my

1 IJN-UTM Cardiovascular Engineering Centre, Universiti Teknologi Malaysia, Skudai, Johor, Malaysia

2 Faculty of Biosciences and Medical Engineering, Universiti Teknologi Malaysia, Skudai, Johor, Malaysia

3 Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, Skudai, Johor, Malaysia

4 Faculty of Engineering Technology, Universiti Tun Hussein Onn Malaysia, Batu Pahat, Johor, Malaysia

References

- [1] Park, S., Baker, J. O., Himmel, M. E., Parilla, P. A., Johnson, D. K. (2010). Cellulose crystallinity index: measurement techniques and their impact on interpreting cellulase performance. *Biotechnology for Biofuels*, 3, 10–20.
- [2] Mohanty, A. K., Misra, M., Hinrichsen, G. (2000). Biofibres, biodegradable polymers and biocomposites: an overview. *Macromolecular Materials and Engineering*, 276(277), 1–24.
- [3] Bhadra, S., Khastgir, D., Singha, N. K., & Lee, J. H. (2009). Progress in preparation, processing and applications of polyaniline. *Progress in Polymer Science*, 34(8), 783–810.
- [4] Khomenko, V., Frackowiak, E., & Beguin, F. (2005). Determination of the specific capacitance of conducting polymer/nanotubes composite electrodes using different cell configurations. *Electrochimica Acta*, 50(12), 2499–2506.
- [5] Groenendaal, L., Jonas, F., Freitag, D., Pielartzik, H., & Reynolds, J. R. (2000). Poly (3, 4-ethylenedioxythiophene) and its derivatives: past, present, and future. *Advanced Materials*, 12(7), 481–494.
- [6] Stöcker, T., Köhler, A., & Moos, R. (2012). Why does the electrical conductivity in PEDOT: PSS decrease with PSS content? A study combining thermoelectric measurements with impedance spectroscopy. *Journal of Polymer Science Part B: Polymer Physics*, 50(14), 976–983.
- [7] Yin, W., Li, J., Li, Y., Wu, J., & Gu, T. (2001). Conducting composite film based on polypyrrole and crosslinked cellulose. *Journal of Applied Polymer Science*, 80(9), 1368–1373.
- [8] Hassel, B. I., Trey, S. M., Leijonmarck, S., & Johansson, M. (2014). A study on the morphology, mechanical, and electrical performance of polyaniline-modified Wood-A semiconducting composite material. *BioResources*, 9(3), 5007–5023.
- [9] Rodrigues, P. C., Muraro, M., Garcia, C. M., Souza, G. P., Abbate, M., Schreiner, W. H., & Gomes, M. A. (2001). Polyaniline/lignin blends: thermal analysis and XPS. *European Polymer Journal*, 37(11), 2217–2223.
- [10] Rodrigues, P. C., Cantão, M. P., Janissek, P., Scarpa, P. C., Mathias, A. L., Ramos, L. P., & Gomes, M. A. (2002). Polyaniline/lignin blends: FTIR, MEV and electrochemical characterization. *European Polymer Journal*, 38(11), 2213–2217.
- [11] He, W., Zhang, X., Yu, C., Huang, D., & Li, Y. (2015). Synthesis of bamboo/polyaniline composites by in situ polymerization and their characteristics. *BioResources*, 10(2), 2969–2981.

- [12] Souza, F. G., Oliveira, G. E., Rodrigues, C. H., Soares, B. G., Nele, M., & Pinto, J. C. (2009). Natural Brazilian amazonic (Curauá) fibers modified with polyaniline nanoparticles. *Macromolecular Materials and Engineering*, 294(8), 484–491.
- [13] Souza, F. G., da Silva, A. M., de Oliveira, G. E., Costa, R. M., Fernandes, E. R., & Pereira, E. D. (2015). Conducting and magnetic mango fibers. *Industrial Crops and Products*, 68, 97–104.
- [14] Dall'Acqua, L., Tonin, C., Peila, R., Ferrero, F., & Catellani, M. (2004). Performances and properties of intrinsic conductive cellulose–polypyrrole textiles. *Synthetic Metals*, 146(2), 213–221.
- [15] Dall'Acqua, L., Tonin, C., Varesano, A., Canetti, M., Porzio, W., & Catellani, M. (2006). Vapour phase polymerisation of pyrrole on cellulose-based textile substrates. *Synthetic Metals*, 156(5), 379–386.
- [16] Hosseini, S. H., & Pairovi, A. (2005). Preparation of conducting fibres from cellulose and silk by polypyrrole coating. *Iranian Polymer Journal*, 14(11), 934.
- [17] Johnston, J. H., Kelly, F. M., Moraes, J., Borrmann, T., & Flynn, D. (2006). Conducting polymer composites with cellulose and protein fibres. *Current Applied Physics*, 6(3), 587–590.
- [18] Montibon, E., Järnström, L., & Lestelius, M. (2009). Characterization of poly (3, 4-ethylenedioxythiophene)/poly (styrene sulfonate)(PEDOT: PSS) adsorption on cellulosic materials. *Cellulose*, 16(5), 807–815.
- [19] Hu, W., Chen, S., Xu, Q., & Wang, H. (2011). Solvent-free acetylation of bacterial cellulose under moderate conditions. *Carbohydrate Polymers*, 83(4), 1575–1581.
- [20] Marins, J. A., Soares, B. G., Dahmouche, K., Ribeiro, S. J., Barud, H., & Bonemer, D. (2011). Structure and properties of conducting bacterial cellulose-polyaniline nanocomposites. *Cellulose*, 18(5), 1285–1294.
- [21] Müller, D., Mandelli, J. S., Marins, J. A., Soares, B. G., Porto, L. M., Rambo, C. R., & Barra, G. M. O. (2012). Electrically conducting nanocomposites: preparation and properties of polyaniline (PAni)-coated bacterial cellulose nanofibers (BC). *Cellulose*, 19(5), 1645–1654.
- [22] Lee, B. H., Kim, H. J., & Yang, H. S. (2012). Polymerization of aniline on bacterial cellulose and characterization of bacterial cellulose/polyaniline nanocomposite films. *Current Applied Physics*, 12(1), 75–80.
- [23] Wang, H., Zhu, E., Yang, J., Zhou, P., Sun, D., & Tang, W. (2012). Bacterial cellulose nanofiber supported polyaniline nanocomposites with flake-shaped morphology as supercapacitor electrodes. *Journal of Physical Chemistry*, 116(24), 13013–13019.

- [24] Müller, D., Rambo, C. R., Recouvreux, D. O. S., Porto, L. M., & Barra, G. M. O. (2011). Chemical in situ polymerization of polypyrrole on bacterial cellulose nanofibers. *Synthetic Metals*, 161(1), 106–111.
- [25] Araujo, J. R., Adamo, C. B., & De Paoli, M. A. (2011). Conductive composites of polyamide-6 with polyaniline coated vegetal fiber. *Chemical Engineering Journal*, 174(1), 425–431.
- [26] Razak, S. I. A., Rahman, W. A. W. A., Sharif, N. F. A., Nayan, N. H. M., Saidi, M. A. A., & Yahya, M. Y. (2013). Polyaniline coated kenaf core and its effect on the mechanical and electrical properties of epoxy resin. *Composite Interfaces*, 20, 611–622.
- [27] Merlini, C., Barra, G. M., Schmitz, D. P., Ramôa, S. D., Silveira, A., Araujo, T. M., & Pegoretti, A. (2014). Polyaniline-coated coconut fibers: structure, properties and their use as conductive additives in matrix of polyurethane derived from castor oil. *Polymer Testing*, 38, 18–25.
- [28] Johnston, J. H., Moraes, J., & Borrmann, T. (2005). Conducting polymers on paper fibres. *Synthetic Metals*, 153(1), 65–68.
- [29] Youssef, A. M., El-Samahy, M. A., & Rehim, M. H. A. (2012). Preparation of conductive paper composites based on natural cellulosic fibers for packaging applications. *Carbohydrate Polymers*, 89(4), 1027–1032.
- [30] Ding, C., Qian, X., Shen, J., & An, X. (2010). Preparation and characterization of conductive paper via in-situ polymerization of pyrrole. *BioResources*, 5(1), 303–315.
- [31] Li, J., Qian, X. R., Chen, J. H., Ding, C. Y., & An, X. H. (2010). Conductivity decay of cellulose–polypyrrole conductive paper composite prepared by in situ polymerization method. *Carbohydrate Polymers*, 82(2), 504–509.
- [32] Wang, H., Hu, M., Fei, G., Wang, L., & Fan, J. (2015). Preparation and characterization of polypyrrole/cellulose fiber conductive composites doped with cationic polyacrylate of different charge density. *Cellulose*, 22(5), 3305–3319.
- [33] Chen, Y., Qian, X., & An, X. (2011). Preparation and characterization of conductive paper via in situ polymerization of 3, 4-ethylenedioxythiophene. *BioResources*, 6(3), 3410–3423.
- [34] Kawashima, H., Shinotsuka, M., Nakano, M., & Goto, H. (2012). Fabrication of conductive paper coated with PEDOT: preparation and characterization. *Journal Of Coatings Technology and Research*, 9(4), 467–474.
- [35] Li, J., Qian, X., Wang, L., & An, X. (2010). XPS characterization and percolation behavior of polyaniline-coated conductive paper. *BioResources*, 5(2), 712–726.
- [36] Goto, H. (2011). Electrically conducting paper from a polyaniline/pulp composite and paper folding art work for a 3D object. *Textile Research Journal*, 81(2), 122–127.

- [37] Qian, X., Shen, J., Yu, G., & An, X. (2010). Influence of pulp fiber substrate on conductivity of polyaniline-coated conductive paper prepared by in-situ polymerization. *BioResources*, 5(2), 899–907.
- [38] Yan, J., & Xu, R. (2015). Reinforced conductive polyaniline-paper composites. *BioResources*, 10(3), 4065–4076.
- [39] Youssef, A. M., Kamel, S., El-Sakhawy, M., & El Samahy, M. A. (2012). Structural and electrical properties of paper–polyaniline composite. *Carbohydrate Polymers*, 90(2), 1003–1007.
- [40] Razak, S. I. A., Sharif, N. F. A., & Nayan, N. H. M. (2014). Electrically conductive paper of polyaniline modified pineapple leaf fiber. *Fibers and Polymers*, 15(6), 1107–1111.
- [41] Razak, S. I. A., & Sharif, N. F. A. (2015). Concurrent optimization of the mechanical and electrical properties of polyaniline modified kenaf paper. *Cellulose Chemistry And Technology*, 49(2), 195–202.
- [42] Hisham, N. S. A., Razak, S. I. A., Nayan, N. H. M., & Rahman, W. A. W. A. (2015). Influence of Polyaniline coated kenaf fiber on kenaf paper sheet. 4th International Conference on Engineering and Innovative Materials (ICEIM 2015). 3–4 September. Penang, Malaysia, (27), 01002.
- [43] Razaq, A., Idrees, M., Malik, A., Mushtaq, N., Nadeem, M., Hussain, I., & Yar, M. (2015). Dielectric studies of composite paper reinforced with polypyrrole coated pulp fibers from wasted egg holders. *Journal of Applied Polymer Science*, 132(33), 42422.
- [44] Hu, L., Zheng, G., Yao, J., Liu, N., Weil, B., Eskilsson, M., & McGehee, M. D. (2013). Transparent and conductive paper from nanocellulose fibers. *Energy & Environmental Science*, 6(2), 513–518.
- [45] Luong, N. D., Korhonen, J. T., Soininen, A. J., Ruokolainen, J., Johansson, L. S., & Seppälä, J. (2013). Processable polyaniline suspensions through in situ polymerization onto nanocellulose. *European Polymer Journal*, 49(2), 335–344.
- [46] Valtakari, D., Liu, J., Kumar, V., Xu, C., Toivakka, M., & Saarinen, J. J. (2015). Conductivity of PEDOT: PSS on Spin-Coated and Drop Cast Nanofibrillar Cellulose Thin Films. *Nanoscale Research Letters*, 10(1), 1–10.
- [47] Montibon, E., Lestelius, M., & Järnström, L. (2010). Electroconductive paper prepared by coating with blends of poly (3, 4-ethylenedioxythiophene)/poly (4-styrenesulfonate) and organic solvents. *Journal of Applied Polymer Science*, 117(6), 3524–3532.
- [48] Huang, L., Chen, K., Peng, C., & Gerhardt, R. A. (2011). Highly conductive paper fabricated with multiwalled carbon nanotubes and poly (3, 4-ethylenedioxythiophene)-poly (styrenesulfonate) by unidirectional drying. *Journal of Materials Science*, 46(20), 6648–6655.

- [49] Saravanan, C., He, Z., & Ni, Y. (2014). Application of polyaniline/clay combination to cellulosic paper as an approach to conductivity development. *BioResources*, 9(2), 1886–1897.
- [50] Kim, J., Deshpande, S. D., Yun, S., & Li, Q. (2006). A comparative study of conductive polypyrrole and polyaniline coatings on electro-active papers. *Polymer Journal*, 38(7), 659–668.
- [51] Mahadeva, S. K., & Kim, J. (2010). Nanocoating of ionic liquid and polypyrrole for durable electro-active paper actuators working under ambient conditions. *Journal of Physics D: Applied Physics*, 43(20), 205502.
- [52] John, A., Mahadeva, S. K., & Kim, J. (2010). The preparation, characterization and actuation behavior of polyaniline and cellulose blended electro-active paper. *Smart Materials and Structures*, 19(4), 045011.
- [53] Mihranyan, A., Nyholm, L., Bennett, A. E. G., & Strømme, M. (2008). A novel high specific surface area conducting paper material composed of polypyrrole and Cladophora cellulose. *The Journal of Physical Chemistry B*, 112(39), 12249–12255.
- [54] Nyström, G., Razaq, A., Strømme, M., Nyholm, L., & Mihranyan, A. (2009). Ultrafast all-polymer paper-based batteries. *Nano Letters*, 9(10), 3635–3639.
- [55] Yuan, L., Yao, B., Hu, B., Huo, K., Chen, W., & Zhou, J. (2013). Polypyrrole-coated paper for flexible solid-state energy storage. *Energy & Environmental Science*, 6(2), 470–476.
- [56] Montibon, E., Lestelius, M., & Järnström, L. (2012). Conductivity of paper containing poly (3, 4-ethylenedioxythiophene)/poly (4-styrenesulfonate) and multiwall carbon nanotubes. *Journal of Applied Polymer Science*, 125(S1), E34–E40.
- [57] Liu, S., He, K., Wu, X., Luo, X., & Li, B. (2015). Surface modification of cellulose scaffold with polypyrrole for the fabrication of flexible supercapacitor electrode with enhanced capacitance. *RSC Advances*, 5(106), 87266–87276.
- [58] Ansari, R., & Fahim, N. K. (2007). Application of polypyrrole coated on wood sawdust for removal of Cr (VI) ion from aqueous solutions. *Reactive and Functional Polymers*, 67(4), 367–374.
- [59] Liu, X., Qian, X., Shen, J., Zhou, W., & An, X. (2012). An integrated approach for Cr (VI)-detoxification with polyaniline/cellulose fiber composite prepared using hydrogen peroxide as oxidant. *Bioresource Technology*, 124, 516–519.
- [60] Richardson, M. J., Johnston, J. H., & Borrmann, T. (2006). Electronic properties of intrinsically conducting polymer-cellulose based composites. *Current Applied Physics*, 6(3), 462–465.
- [61] Kelly, F. M., Johnston, J. H., Borrmann, T., & Richardson, M. J. (2007). Functionalised hybrid materials of conducting polymers with individual fibres of cellulose. *European Journal of Inorganic Chemistry*, 2007(35), 5571–5577.

- [62] Ngamna, O., Morrin, A., Killard, A. J., Moulton, S. E., Smyth, M. R., & Wallace, G. G. (2007). Inkjet printable polyaniline nanoformulations. *Langmuir*, 23(16), 8569–8574.
- [63] Ihalainen, P., Määttänen, A., Järnström, J., Tobjörk, D., Österbacka, R., & Peltonen, J. (2012). Influence of surface properties of coated papers on printed electronics. *Industrial & Engineering Chemistry Research*, 51(17), 6025–6036.
- [64] Angelo, P. D., Cole, G. B., Sodhi, R. N., & Farnood, R. R. (2012). Conductivity of inkjet-printed PEDOT: PSS-SWCNTs on uncoated papers. *Nordic Pulp and Paper Research Journal*, 27(2), 486.
- [65] Jia, H., Wang, J., Zhang, X., & Wang, Y. (2013). Pen-writing polypyrrole arrays on paper for versatile cheap sensors. *ACS Macro Letters*, 3(1), 86–90.
- [66] Eriksson, M., Notley, S. M., & Wågberg, L. (2005). The influence on paper strength properties when building multilayers of weak polyelectrolytes onto wood fibres. *Journal of Colloid and Interface Science*, 292(1), 38–45.
- [67] Agarwal, M., Xing, Q., Shim, B. S., Kotov, N., Varahramyan, K., & Lvov, Y. (2009). Conductive paper from lignocellulose wood microfibers coated with a nanocomposite of carbon nanotubes and conductive polymers. *Nanotechnology*, 20(21), 215602.
- [68] Lee, J., Ryu, J., & Youn, H. J. (2012). Conductive paper through LbL multilayering with conductive polymer: dominant factors to increase electrical conductivity. *Cellulose*, 19(6), 2153–2164.
- [69] Wistrand, I., Lingström, R., & Wågberg, L. (2007). Preparation of electrically conducting cellulose fibres utilizing polyelectrolyte multilayers of poly (3, 4-ethylenedioxythiophene): poly (styrene sulphonate) and poly (allyl amine). *European Polymer Journal*, 43(10), 4075–4091.
- [70] Stejskal, J., Trchová, M., & Sapurina, I. (2005). Flame-retardant effect of polyaniline coating deposited on cellulose fibers. *Journal of Applied Polymer Science*, 98(6), 2347–2354.
- [71] Stejskal, J., Trchová, M., Brodinová, J., & Sapurina, I. (2007). Flame retardancy afforded by polyaniline deposited on wood. *Journal of Applied Polymer Science*, 103(1), 24–30.
- [72] Wu, X., Qian, X., & An, X. (2013). Flame retardancy of polyaniline-deposited paper composites prepared via in situ polymerization. *Carbohydrate Polymers*, 92(1), 435–440.
- [73] Mao, H., Wu, X., Qian, X., & An, X. (2014). Conductivity and flame retardancy of polyaniline-deposited functional cellulosic paper doped with organic sulfonic acids. *Cellulose*, 21(1), 697–704.
- [74] Zhou, Y., Ding, C., Qian, X., & An, X. (2015). Further improvement of flame retardancy of polyaniline-deposited paper composite through using phytic acid as dopant or co-dopant. *Carbohydrate Polymers*, 115, 670–676.

