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Nanocellulose electroconductive composites

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Cellulose-based electroconductive composites can be prepared by combining conducting electroactive materials with hydrophilic biocompatible cellulose. Inorganic nanoparticles, such as metal ions and oxides, carbon nanotubes, graphene and graphene oxide, conducting polymers, and ionic liquids (through doping, blending or coating) can be introduced into the cellulose matrix. Such composites can form a biocompatible interface for microelectronic devices, and provide a biocompatible matrix or scaffold for electrically stimulated drug release devices, implantable biosensors, and neuronal prostheses. Here the benefits of combining conventional and bacterial cellulose with these electroactive composites are described and future applications are considered.

Introduction

Cellulose is an important natural material which is biocompatible and hydrophobic and which can be extensively derivatized and so form strong and stable stiff-chain homomolecular structures with film- and hydrogel-forming properties. It is, therefore, complementary to other conducting optical materials and has the potential to be a stable and robust carrier, matrix or scaffold component for the fabrication of new functional materials.[1]

Inorganic nanoparticles, metal ions and oxides, carbon nanotubes, graphene and graphene oxide, conducting polymers, and ionic liquids can associate with cellulose to form such materials. In this way their specific conducting properties can be combined with the characteristic properties of cellulose such as high hydration, swellability, *in vitro* and *in vivo* biocompatibility and allow small molecules to diffuse into the matrix.

Due to the wide range of morphological forms of cellulose the composites provide opportunities to produce materials with high electrical conductivity, ON–OFF electrical and optical

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switching and electrochemical redox properties. These can form stimuli responsive materials with viable sensory and actuation applications and can be fabricated into biorecognition membrane layers within biosensors, neural prosthetics, and devices for electrostimulated drug release, and flexible biocompatible energy harvesting.

This paper reviews the current status of electroconductive cellulose composites to include their synthesis, characterization and key applications.

Fabrication of electroconductive cellulose composites

Cellulose and conducting materials can be combined by blending, forming a co-network, or by doping the conductor with cellulose. Fig. 1 illustrates such synthetic routes. The cellulose can be a solid matrix, with the electroconductive material dispersed on the surface or within the matrix. Cellulose can also be dissolved in solvents such as dimethylacetamide (DMAc)/LiCl, aqueous NaOH/urea, *N*-methylmorpholine-*N*-oxide (NMMO) or the ionic liquid 1-butyl-3-methylimidazolium acetate (BMIM-OAc),[2–5] and after mixing in solution cast or electrospun with the conductor to form microspheres, fibers or membranes.

Combination with conducting polymers

Conducting polymers, developed since the 1970s, are a family of highly conjugated polymers with spatially extended π-bonding which provide unique electrical, electrochemical and optical properties. Most derive from just a few basic polymer structures, such as polyacetylene, polypyrrole, polyfuran, polyaniline and polythiophene (Table 1). They find applications as diverse as electrical conductors, nonlinear optical devices, polymeric light emitting diodes (LEDs), anti-static and corrosion protective coatings, chemical and biological sensors, electrodes of batteries, electromagnetic shielding materials, solar cells, microwave absorbing materials, and valves in micro-electromechanical systems (MEMs) devices.[6–9]

It is difficult to form films when cast and dried from such dispersions because their H-bond forming ability is low or even absent. However, cellulosic hydrogels or solutions provide sufficient H-bonding to cast films from heterogenic mixtures of cellulose and conducting polymers and so form microspheres, spun as fibers or applied to electrodes and to other solid-state electronic devices. A conducting nanocomposite film was cast from aqueous slurries using doped polypyrrole (PPy) particles, and carboxymethyl cellulose (CMC) and nanofibrillar cellulose (NFC) as the conducting and reinforcing phase, respectively.[13] PPy–cellulose composites were prepared by *in situ* polymerization of pyrrole in cellulose pulp suspensions.[14] PPy coating of individual fibers of wood-based nanocellulose was carried out *in situ* by chemical polymerization to give an electrically conducting continuous high-surface-area composite.[15] The conducting polymer, polyaniline (PANI), was synthesized by polymerisation in the presence of dispersed pulp fibers to yield PANI–pulp composite fibers, which were then formed into a conducting paper sheet.[16]

Cellulose can also provide a stabilizing and film-forming matrix that can adhere to a supporting substrate. This can be either within the cellulose network or on the surface through chemical oxidative polymerization or electrochemical polymerization. Li *et al.* thus prepared PANI–cotton composites by *in situ* polymerization of aniline on grafted cotton.[17] Another study, by Castillo-Ortega *et al.*, looked at the adsorption and desorption of a gold–iodide complex on a cellulose acetate membrane coated with PANI or PPy.[18] PANI could also be deposited onto the surface and insides of the pores of microporous mixed cellulose ester membranes using various chemical oxidative polymerization techniques.[19] In this way the charge transport processes of PANI composite membranes could be identified and correlated with the PANI deposition site and the extent of PANI surface layering on the microporous membranes. Li *et al.*[20] used cotton as a template to synthesise PANI microbelts. Zhou *et al.*[21] described the anisotropic actuation of electroactive papers with a poly(3,4-ethylenedioxythiophene)/poly(4-styrene sulfonate) (PEDOT/PSS) coating on cellulose-based paper. The electroactive papers displayed a contractile stress when an external voltage was applied, the magnitude and direction of the stress depending on the relative orientation of the paper fibers and the loading direction of the coating.

Combination with carbon nanotubes

Discovered in 1991, carbon nanotubes (CNTs) form unique structures with unexpected physical (mechanical, thermal and electronic) properties which offer promising applications in both the physical and life sciences. These can be classified into two main types: single-walled carbon nanotubes (SWNTs), which consist of one single layer of graphene sheet seamlessly rolled into a cylindrical tube; and multi-walled carbon nanotubes (MWNTs), which are made up of several concentric graphene layers.

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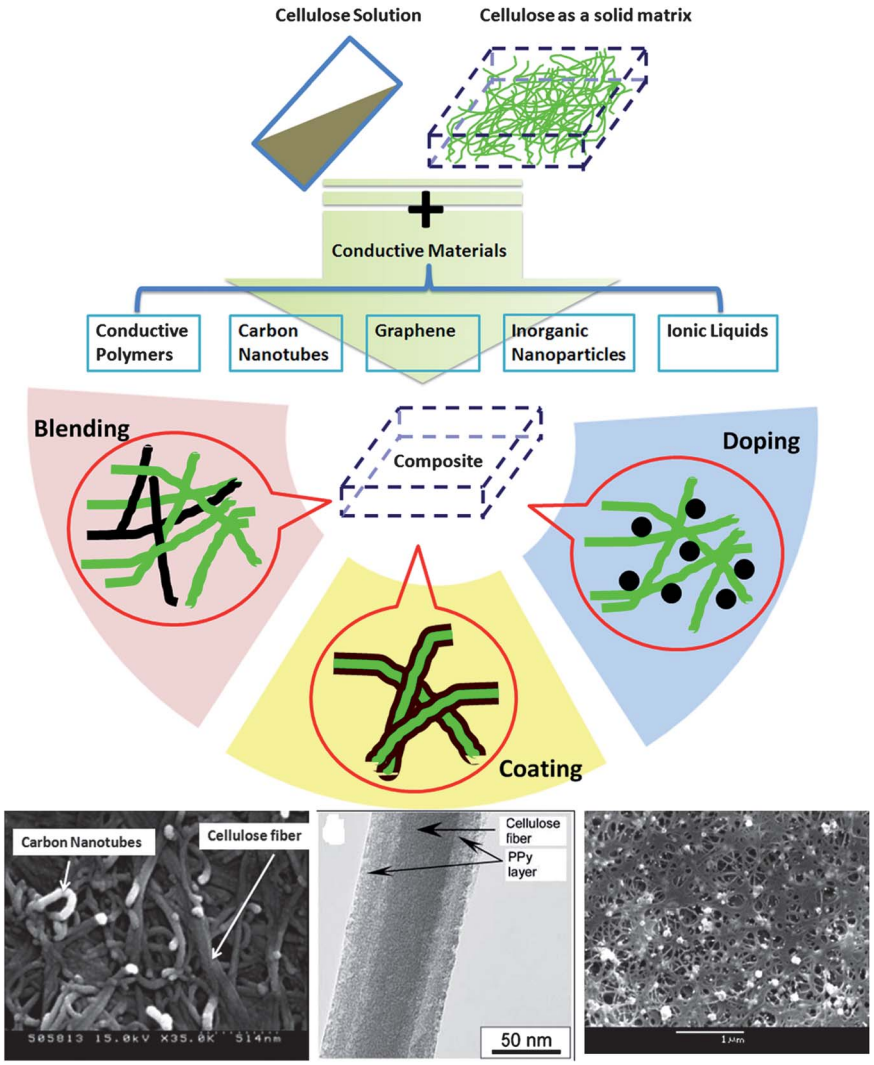

Fig. 1 Schematic illustration of the generalized synthetic routes to electroconductive cellulose composites.[10–12] Copyright 2005 Royal Society of Chemistry. Copyright 2006 American Chemical Society. Copyright 2009 Elsevier.

Table 1 Structures of some conductive polymers

Polyacetylene (PA)	Polyaniline (PANI)	Polythiophene (PTh)
Poly(*para*-phenylene) (PP)	Polypyrrole (PPy)	Poly(*para*-phenylene vinylene) (PPV)
Poly(*para*-phenylene sulfide) (PPs)	Polyazulene	Poly(3,4-ethylenedioxythiophene) (PEDOT)

Many biomolecules (including cellulose) combine with CNTs *via* non-covalent interactions. After solubilization CNTs can attach to chemical or biological molecules without affecting the electronic network of the nanotubes or their non-covalent functionalisation. Applications have been found in biomedical technologies. Tanaka *et al.*[22] fabricated MWCNT–cellulose composite papers and measured the temperature dependence of their electrical conductivity. Basavaraja *et al.*[23] used different weight percentages of MWNTs dispersed in cellulose triacetate (CTA) solution to prepare CTA–MWNTs. Such composite films can be used for electromagnetic interference shielding. CNT–cellulose composite materials can also be used to decrease electromagnetic wave interference, control undesired reflections, prevent cross-talk, and suppress noise in circuits.[24,25] Lu and Hsieh[26] recently reported MWCNTs reinforced with cellulose fibers prepared by electrospinning MWCNT-loaded cellulose acetate (CA) solutions. Miyauchi *et al.*[27] also used electrospinning technology to combine cellulose and MWCNTs, to fabricate core–sheath MWNT-cellulose fibers having a cable structure with a conductive core and an insulating sheath.

Cellulose has also been shown to combine with SWNTs, and Oya and Ogino[28] reported the preparation of an electrically conductive SWNT–cellulose nanocomposite simply using the "washi" process by adding the SWNTs into a pulp suspension. Kim *et al.*[29] used *N*-methylmorpholine-*N*-oxide (NMMO) monohydrate as a dispersing agent for acid-treated SWNTs (A-SWNTs) as well as a cellulose solvent. A cellulose–SWNT composite has been shown to be homogenous, hydrophilic, conductive and biocompatible, and was used to immobilize leukemia K562 cells on a gold electrode in a cell impedance sensor.[30] SWCNTs wrapped with cellulose have been prepared by the treatment of SWCNTs with a cellulose solution in the ionic liquid 1-butyl-3-methylimidazolium bromide. This cellulose–SWCNT scaffolds could promote the growth of HeLa cells.[31]

Combination with graphene

Graphene has attracted considerable interest as a potential new electronic material. It is a two-dimensional carbon material with atomic thickness and versatile electrochemical properties, because graphene-based assemblies combine high electrical conductivity, electroactivity, and strength. Thus, assemblies of graphene, graphene oxide, or related polymer composites have been used as soft electrodes for flexible batteries, super-capacitors, *etc.*

Highly ordered graphene paper can be prepared by directional flow-induced assembly of graphene sheets which have been well dispersed in solution. Moderate thermal annealing can enhance the mechanical stiffness, strength and electrical conductivity. In this way graphene paper can become biocompatible and suitable for biomedical applications.[32] Kim *et al.*[33] used *N*-methylmorpholine-*N*-oxide (NMMO) monohydrate as solvent to prepare graphene oxide (GO)–cellulose composite films. The products had improved thermal and electrical properties, and were strong but brittle. It is also possible to fabricate mechanically robust and electrically conductive materials based on amine functionalized cellulose nanofibrils and chemically reduced grapheme oxide sheets. These composites not only exhibit good electrical properties (1.8 S m^{-1}) but also have excellent mechanical properties (tensile strength of 273 MPa).[34] Graphene–cellulose paper (GCP) membranes have advantages as free standing binder-free electrodes for flexible super-capacitors. Their electrical conductivity is highly stable and decreases only 6% after being bent 1000 times. Flexible GCP electrodes have a high capacitance per geometric area of 81 mF cm^{-2}, which is equivalent to a gravimetric capacitance of 120 F g^{-1} of graphene, and retain >99% capacitance over 5000 cycles.[35]

Combination with inorganic nanoparticles

Hybrid inorganic–organic nanocomposites are a new class of functional nanomaterials that show improved conductive, optical, thermal and mechanical properties because of the synergistic effect of the combined physical or chemical interactions between the inorganic and organic components.

Mineral nanoparticle-reinforced, metal nanoparticle-reinforced and nanofiber-reinforced polymer matrix nanocomposites and hybrid nanocomposites have been based on natural cellulose. A conductivity of 0.15 S cm^{-1} has been reported for cellulose-based composites containing copper which had been introduced by electrolysis plating.[36] Sol–gel indium tin oxide films on cellulose have shown a conductivity as high as 16 S cm^{-1} after annealing at 450 °C for 6 h.[37] Nylon fibers electrolytically coated with silver showed an effective conductivity up to 1950 S cm^{-1}. Cotton fibers and paper coated with ZnO by atomic layer deposition (ALD) showed an effective conductivity of up to 24 S cm^{-1}.[38] The electrical transport and photoconductivity of pure and iodine-doped cellulose fibers showed significant enhancements of more than four orders of magnitude when compared with undoped samples.[39] TiO_2–cellulose composite films were fabricated by *in situ* synthesis of TiO_2 nanoparticles in the regenerated cellulose matrix having a micronanoporous structure *via* a sol–gel method. This composite had good high photocatalytic activity and was useful for waste water treatment. Free-standing, nanotubular indium tin oxide (ITO) sheets with different In/Sn ratios were fabricated by the surface sol–gel process using cellulose filter paper as a template. When prepared by this template synthesis the product exhibited a high electrical conductivity of 0.53 S cm^{-1}.[40]

Combination with ionic liquids

At room-temperature ionic liquids are frequently colorless, fluid, and easy to handle but at high temperatures can be corrosive and viscous.[41] Nevertheless, they have widely been promoted as "green solvents" for chemical applications due to their chemical and thermal stabilities, low vapor pressure and high ionic conductivity.[42] They have been used in several types of polymerization processes, and also investigated as components for polymeric matrices (such as polymer gels), as templates for porous polymers and as novel electrolytes for electrochemical polymerizations.[43]

Ionic liquids have excellent ionic conductivity up to their decomposition temperature and so can play an important role

Table 2 Cellulose combined with several conductive materials

Conductive material	Methods	Properties	Applications	References
Conducting polymers (PPy, PANI, PEDOT/PSS, PEDOT, *etc.*)	Casting conducting polymers/cellulose dispersions; *in situ* chemical polymerization; coating on the cellulose fiber	Conductivity 10^{-5} to 10^{2} S cm^{-1}; enhanced mechanical properties; electromechanical properties; biocompatible	Conductors; biosensors; electromechanical devices; organic electronics	18,19,47–49
Carbon nanotubes (SWNTs and MWNTs)	Solution evaporation technique; solvent casting after blending; electrospinning; blending in the cellulose matrix	Conductivity 10^{-4} to 10^{2} S cm^{-1}; enhanced mechanical properties; electromagnetic interference shielding efficiency; thermal stimulated conductivity; anti-static; biocompatible	Wearable electronics; energy storage; decrease electromagnetic wave interference; cell impedance sensors	22,23,25,50
Graphene	Solvent casting after blending; filtering a graphene nanosheet suspension through a sheet of filter paper	Conductivity 10^{-4} to 10^{2} S cm^{-1}; mechanically strong; biocompatible	Flexible supercapacitors; energy-storage devices; biocompatible materials; transparent and flexible electrodes	35,51–53
Inorganic nanoparticles (ZnO, SnO_2, TiO_2, I, Au, Ag, Cu)	Atomic layer deposition; compression molding after internal mixing; liquid-phase deposition; LbL deposition; doping	Conductivity 10^{-6} to 10^{3} S cm^{-1}; antimicrobial activity; biodegradable; enhanced mechanical properties	Antimicrobials; functional chemical sensing; biosensors	38,54–56
Ionic liquids	Casting IL/cellulose dispersions	Conductivity 10^{-8} to 10^{-4} S cm^{-1}	Gel electrolytes	45

in forming electrolyte matrixes. Varying amounts of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (BMITFSI), for example, have been loaded into a cellulose film during its regeneration process by utilizing a traditional solution blending technique. Such BMITFSI–cellulose had very high conductivity under ambient conditions.[44] Cellulose triacetate (CTA), *N*-methyl-N0-propylpyrrolidinium bis(trifluoromethanesulfonyl)imide (Pyr1,3TFSI), and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) were used to obtain new composite polymer gels. The ionic conductivities of these polymer gels were significantly enhanced by the presence of LiTFSI, and could be used as electrolytes.[45] Another group[46] synthesized a grafted cellulose gel electrolyte in an ionic liquid 1-butyl-3-methylimidazolium iodide ([Bmim]I) for preparing dye-sensitized solar cells. The cellulose was grafted homogeneously with acrylic acid by *in situ* polymerization in an ionic liquid [Bmim]I as reaction medium. Using the grafted cellulose gel as polymer host, and KI and I_2 as ionic conductors, an ionic conductivity of 7.33 mS cm^{-1} of the gel polymer electrolyte was produced (Table 2).

Bacterial cellulose electroconductive composites

The biosynthesis of cellulose takes place not only in plants, but also in bacteria, algae, and fungi. Bacterial cellulose (BC) is produced by many microorganisms (such as *Acetobacter*, *Agrobacterium*, *Achromobacter*, *Aerobacter*, *Azotobacter*, *Sarcina ventriculi*, *Salmonella*, *Escherichia* and *Rhizobium*). Sharing the same structural unit, BC does not only have the properties of conventional cellulose produced by plants, but it also has special properties such as high chemical purity and crystallinity, a high degree of polymerization, excellent biocompatibility and biodegradability. These properties have already led to its successful commercialization in a variety of niche markets, including health foods, high-end audio components, speciality papers, and wound care, and even for gene detection. Significantly, BC is a natural polymer hydrogel, which has three-dimensional polymeric networks and adsorbs large amounts of water. BC hydrogels are flexible and have good mechanical properties, and they can accordingly easily change their size and shape in response to environmental stimuli. Moreover, BC can also contain other monomeric, reactive and potentially polymerizable monomers within its networks, occupying its void volume and interacting with BC fiber chains. These properties can be used to combine with inorganic nanoparticles, metal ions and oxides, carbon nanotubes, graphene and graphene oxide, conducting polymers, and ionic liquids to thus change or improve the characteristics of BC, and in particular to improve its electrical conductivity. Yoon *et al.*[11] incorporated multiwalled carbon nanotubes (MWCNTs) into bacterial cellulose pellicles produced by *Gluconacetobacter xylinum*, and so increased the conductivity up to 1.4×10^{-1} S cm^{-1}. Jung *et al.*[57] used an aqueous silk fibroin solution to improve the light transmittance of bacterial cellulose membranes, then incorporated these with MWCNTs to enhance the electrical conductivity, transparency and electrical properties. A light transmittance of 70.3% at 550 nm and electrical conductivity of 2.1×10^{-3} S cm^{-1} was achieved. Bacterial cellulose productivity can be improved by adding conducting materials to the culture medium. The structure of cellulose microfibrils has been investigated in a static culture medium containing acid-treated MWCNTs.[58] Bacterial

celluloses have been synthesized in MWCNT-dispersed medium and it was found that a substantial number of MWCNTs were attached to the surfaces of the bacterial cellulose fibrils.[59]

Recently, we have fabricated a BC–polyaniline (PANI) composite. PANI was polymerized and deposited as an adhering layer on the surfaces of the cellulose fibers. This forms a relatively uniform thin-film conductive material, and its electrical conductivity can reach 10^{-1} S cm^{-1}. By varying the reaction time and controlling the proton acid doping/dedoping it is possible to obtain materials having a range of conductivities.[47] BC can also be combined with polyaniline[60,61] and polypyrrole,[62] which can be polymerized through chemical or electrochemical polymerization.

Metal nanoparticles (such as Au, Ag) have also been applied as the film forming material to produce various types of films (including BC) because of their good biocompatibility and conductivity. Silver metal and its compounds have strong inhibitory and bactericidal effects as well as a broad spectrum of antimicrobial activities. As a result there have been many investigations of silver combined with BC for antimicrobial applications.[63–65]

Medical applications of bacterial cellulose electroconductive hydrogels

Bacterial cellulose is a natural hydrogel, with a stable nanofiber network, high water content, shape-ability during biosynthesis, and biocompatibility.[66] Such nanofibers are neither cytotoxic nor genotoxic. BC is also a 3D template for *in vitro* and *in vivo* tissue growth, which can be used for medical implants ranging from bone and cartilage repair to tubular prototype grafts for vascular surgery.[67]

Electroconductive hydrogels provide good small molecule transport, high hydration levels and biocompatibility. Cross-linked hydrogels can then provide redox switching and electrical properties of inherently conductive polymers. When based on bacterial cellulose these have three-dimensional polymeric networks, imbibe large amounts of water, and are flexible with good mechanical properties. They can change their size and shape in response to environmental stimuli. Cellulose–SWNT composites have proved to be homogenous, hydrophilic, conductive and biocompatible, and have been used to immobilize leukemia K562 cells on a gold electrode in a cell impedance sensor.[30] Using BC hydrogels as natural biotemplates, mesoporous titania networks consisting of interconnected anatase nanowires have been synthesized. These BC–TiO_2 hydrogels may find potential applications in areas including photocatalysis, photovoltaics, and bone-tissue engineering.[68] Gold nanoparticles (AuNPs) and BC nanocomposites have been used for the immobilization of heme proteins. Horseradish peroxidase (HRP), hemoglobin (Hb) and myoglobin (Mb) immobilized in a Au–BC film showed high biocatalytic activity with good sensitivity, low detection limit and fast response toward hydrogen peroxide.[69]

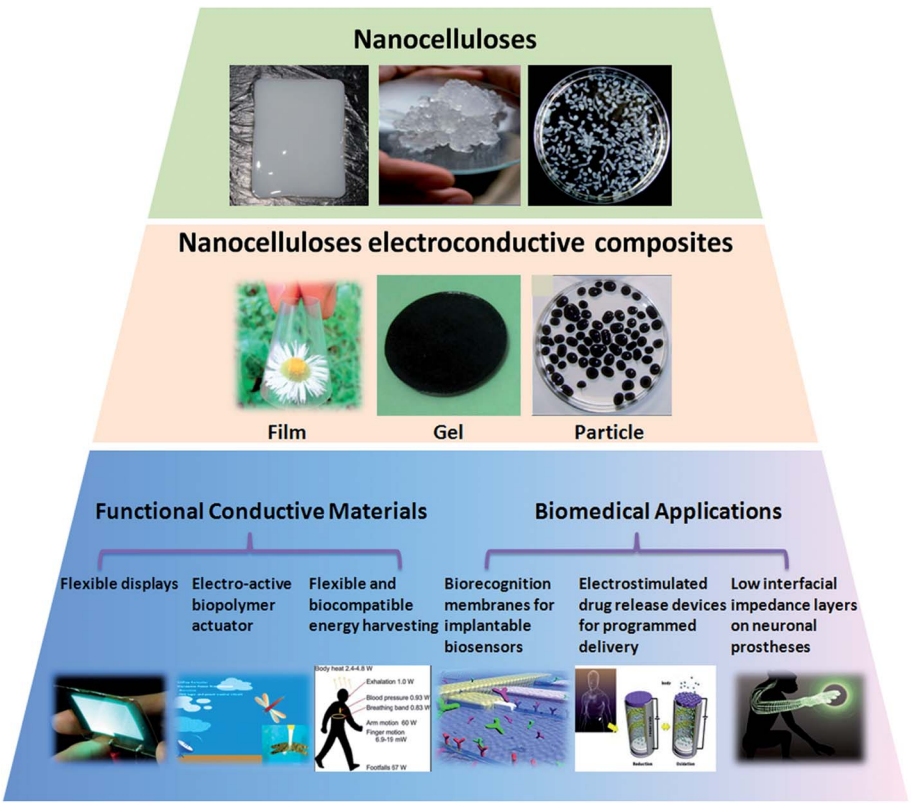

Fig. 2 Applications of nanocellulose electroconductive composites.[47,59,66,73–75,77] Copyright 2010 and 2011 Royal Society of Chemistry. Copyright 2009 Elsevier. Copyright 2005, 2008 and 2011 John Wiley and Sons. Copyright 2006 American Chemical Society.

Flexible displays

Flexible displays have been produced by using bacterial cellulose as the substrate or the basic optical film to improve their electronic properties.[70] Legnani *et al.*[71] used BC as the flexible substrate for the fabrication of organic light emitting diodes (OLEDs). Indium tin oxide (ITO) thin films were deposited onto the membrane at room temperature using radio frequency magnetron sputtering. The average transmittance of BC membrane substrates at 550 nm is only 40%. Clarity is the most important property for bottom emissive displays, and a total light transmission of >85% over 400–800 nm coupled with a haze of less than 0.7% are typical of what is required.[72] Thus many groups have made efforts to improve the light transmittance of BC.[73] Nogi *et al.*[74] fabricated transparent composites with bacterial cellulose (BC) nanofibers which have low thermal expansion, and even an electroluminescent layer could be deposited onto these transparent BC nanocomposites. However, this final nanocomposite material is not flexible enough and therefore cannot achieve the bending radius required for roll-to-roll processing.

Electro-active biopolymer actuators

Cellulose-based electro-active paper is light in weight, is biodegradable, and has a large displacement output and low actuation voltage when dry.[75] Jeon *et al.* developed such an electro-active biopolymer actuator based on bacterial cellulose. They showed that the LiCl treated bacterial cellulose can be adjusted to achieve a better actuation performance by controlling the crystallinity and stiffness of the pristine BC.[76] Piezoelectric materials are smart materials which can convert mechanical energy (such as from breathing, or walking) into more useful electrical energy. However, traditional piezoelectrics are hard, inflexible crystals which can also be toxic. BC-based piezoelectric materials could lead to nanopiezoelectric devices that combine the key qualities of flexibility, energy efficiency, and biocompatibility. The target is to use piezoelectric nanogenerators for continuously self-powering portable electronics and biomedical implants.

Conclusions

We have indicated that the combination of cellulose and conductive electroactive materials allows both materials to retain their unique responsive properties. Cellulose as a matrix of cellulose-based conductive composites, gives the composites rich and colorful forms. Hydrogels were the first biomaterials to be specifically designed for use in humans. Cellulose hydrogels, especially bacterial cellulose hydrogels, have an especially stable nanofiber network, high water content, shape-ability during biosynthesis, and biocompatibility. These natural polymers open up the important and rapidly expanding fields of personal care, medicine, and life sciences. When cellulose is combined with conductive materials, it has the potential to introduce novel properties into flexible electrodes, flexible displays, biocompatible energy scavenging, electrically stimulated drug release devices, implantable biosensors and neural prosthetics (Fig. 2).

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