A Review of Fabrication and Applications of Bacterial Cellulose Based Nanocomposites

Kaiyan Qiu[a] & Anil N. Netravali[b]

[a] Thayer School of Engineering, Dartmouth College, Hanover, New
Hampshire, USA

[b] Fiber Science Program, Cornell University, Ithaca, New York, USA
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Reviews

A Review of Fabrication and Applications of Bacterial Cellulose Based Nanocomposites

KAIYAN QIU[1] AND ANIL N. NETRAVALI[2]

[1]Thayer School of Engineering, Dartmouth College, Hanover, New Hampshire, USA
[2]Fiber Science Program, Cornell University, Ithaca, New York, USA

Bacterial cellulose (BC) is a unique nanofibrous biomaterial which can have applications in many engineering fields. BC possesses excellent mechanical properties and biocompatibility and can be engineered in various forms from nano to macro scales. BC based nanocomposites can be manipulated to improve their properties and/or functionalities. Such materials can be categorized as high-strength materials as well as materials for plant biomimicking, biomedical, electrically conductive, catalysis, optical, luminescent, proton conductive, separating, antimicrobial, thermo-responsive, and other applications. The review presented here focuses on various fabrication methods used and novel applications of BC based nanocomposites that are expected to be commercialized.

Keywords bacterial cellulose, nanocomposites, mechanical properties, biocompatibility, fabrication methods, BC applications

1. Introduction

Bacterial cellulose (BC) is a promising, sustainable, and biodegradable nanofibrous material that has the same chemical structure (a polysaccharide consisting of a linear chain of $\beta(1{\rightarrow}4)$ linked D-glucose units) and crystalline form (cellulose I) as the plant-based cellulose. However, BC fibers have diameters in the range of a few (40–70) nanometers and display many unique characteristics including high purity, high degree of polymerization, high crystallinity which results in high strength, and modulus.[1–5] Because of their small fiber diameter, resulting in high surface area and highly porous structure, BC membranes have high water-holding capacity. Besides, the membrane thickness and size can be easily controlled. BC also has high thermal stability, excellent environmental biodegradability and strong biocompatibility.[1–5] As a result, BC membranes are already being used in

diverse applications including artificial skin and blood vessel, binding agent for fibers and other materials, loud speaker diaphragms, cosmetics, high quality paper, foods (nata-de-coco), textiles, nanocomposite membranes, etc.[5–10] Because of their excellent properties, research on BC based nanocomposites has accelerated in the past couple of decades.[11, 12] Researchers have used many fabrication methods for developing nanocomposites for a variety of applications. These applications, in general, can be categorized into high-strength materials as well as materials for plant biomimicking as well as biomedical, electrically conductive, catalytic, optical, luminescent, proton conductive, separating, antimicrobial, thermo-responsive applications and many others. This article presents a brief state of the art review of the BC based materials, and especially focus on BC based nanocomposites, their fabrication methods as well as their functionalities and applications.

2. BC and its Applications

As mentioned earlier, BC has many unique and excellent properties.[1–12] BC fabrication pathway used by certain bacteria, with the help of a variety of enzymes, is discussed in detail in the following section.[13–21] BC can be produced in different forms based on different fermentation conditions, including pellicles under static culture condition and fibrils and sphere-like particles under agitated culture condition.[22–26] Many efforts have been made to increase BC yields and lower BC production cost for large scale applications.[22–45] At present the fabricated BC materials are being widely used in many niche applications.[1–52]

2.1 BC Fabrication Pathway

Cellulose is the most abundant natural polymer on Earth.[13–15] It forms the cell wall of eukaryotic plants and algae, and is also found to be the major constituent of the cell wall of fungi. A few bacteria also can secrete cellulose. The genera of these bacteria include *Acetobacter*, *Rhizobium*, *Agrobacterium*, *Sarcina*, *Psedomonas, Achromobacter, Alcaligenes, Aerbacter, and Azotobacter*. Among them, the rod-shaped aerobic gram-negative bacteria genus *Acetobacter (notable example being Acetobacter xylinum)* is the most studied and used to produce BC because of its high-yielding ability.[13–15]

    Acetobacter xylinum is known to secrete cellulose as part of its metabolism of glucose and other carbohydrates.[13–15] A row of pores (extrusion sites) have been found on the longitudinal axis of the outer membrane of the bacterium cells. These pores may contain or be composed of the enzymes involved in cellulose synthesis. In the synthesis process, glucan chains form cellulose nanofibrils via self-assembly and then are secreted through these pores.[13–15] The high degree of organization of the extrusion pores on the surface of the outer membrane in bacterium cells facilitates the coordination of the assembly process. These nanofibrils appear to be about 1.5 nm wide and can aggregate into 3 to 4 nm nanofibrils. Finally, the nanofibrils bind together to form the larger cellulosic nanoribbons of 40 to 70 nm width.[14,15] These ribbons appear to be parallel to the longitudinal axis of the bacterium cells. Although *Acetobacter xylinum* is nonmotile, it can be pushed by the formation of the ribbon of cellulose at a rate of 2 μm/min.[14] Figure 1 shows the scanning electron microscopy (SEM) image of the BC nanoribbons (white fine lines) which are excreted from *Acetobacter* cells (white and rod-like bacteria).[1] BC nanoribbons then interwind with each other and finally form final BC products.

    BC synthesis is mainly tied to oxidative carbohydrate metabolism. However, since cellulose formation in *Acetobacter* can occur independently of protein synthesis, it does not appear to be an indispensable feature of carbohydrate metabolism.[14,15] A group of enzymes
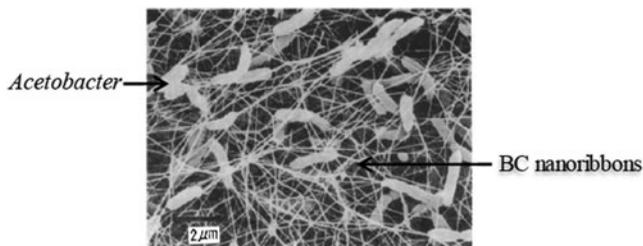
Figure 1. SEM image of freeze-dried surface of BC.[1]

are involved in carbohydrate metabolism. It has been proposed that glucokinase, phosphoglucomutase, and uridine diphosphate (UDP)-glucose pyrophosphorylase are most likely to be involved in the pathway leading to cellulose synthesis.[14,15] The immediate sugar nucleotide precursor of cellulose synthesis in *Acetobacter xylinum* is UDP-glucose pyrophosphorylase. Four enzymatic steps have been characterized in cell extracts of *Acetobacter xylinum* that appear to show the complete pathway from glucose to cellulose.[14,15] Figure 2 shows these four steps of the biochemical pathway leading from glucose to cellulose: these are

1. the phosphorylation of glucose to glucose-6-phosphate (G6P) by glucokinase
2. the generation of glucose-1-phosphate (G1P) from G6P by phosphoglucomutase
3. the synthesis of UDP-glucose from G1P by UDP-glucose pyrophosphorylase, and
4. the final cellulose formation from UDP-glucose by cellulose synthase.[14,15]

Other proper carbohydrates for culture, with the help of enzymes in *Acetobacter xylinum*, will be first transformed into G6P, and then synthesized to cellulose through the remaining three enzymatic steps.[15]

2.2 Properties of BC

BC has many excellent and unique properties.[16–19] The first is its high purity. It has been reported that BC is chemically pure (close to 100% cellulose content), containing no hemicellulose or lignin.[16,17] In contrast, cellulose content in plant tissues and fibers only accounts for 60–70%. The second is its high water-holding capacity and hydrophilicity.[16,17] Water content can be up to 98% in BC pellicle gel, i.e., about 50 times the weight of the fibers, making it more like a hydrogel. The third is its high tensile strength and Young's

Figure 2. The proposed biochemical pathway for cellulose synthesis in *Acetobacter xylinum*.[14]

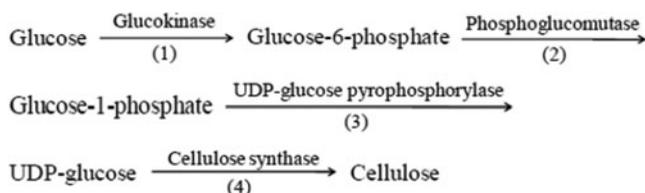modulus resulting from a high degree of polymerization (DP) and the formation of ultrafine nanonetwork architecture.[16,18,19] The degree of polymerization can be up to 20,000 and the Young's modulus of single BC nanofiber is estimated to be up to 114 GPa, close to many high strength synthetic fibers.[18,19] The fourth is its high crystallinity.[16,17] The crystallinity of BC can be up to 70% which is higher than plant cellulose. The fifth is its higher thermal stability resulting from its high purity and crystallinity. As a result, BC can be a good thermal stabilizer when added to resins.[20] The sixth is the highly porous structure of the nanonetwork and controllable shape and thickness.[16–20] While the pore diameters in BC network (membrane) range from several tens to several hundred nanometers, the shape and thickness of BC membranes can be easily controlled by varying reactor shapes and culture time.[20] The seventh is its environmental biodegradability and BC therefore can be utilized as green material.[20] The last but not the least unique characteristic is its excellent biocompatibility.[16–21] An *in vivo* study of subcutaneous BC implantation in rats showed that no fibrotic capsule or giant cells were detectable after 12 weeks which indicated no foreign body reaction.[21] Furthermore, no redness, swelling, or exudate developed around the implantation sites in the study.[21] All these unique properties offer many opportunities for using BC in a variety of applications.

2.3 BC Production Methods

BC can be produced in different forms based on different fermentation conditions.[22–26] Many sugars and sugar alcohols can be utilized as carbon source, the most important fermentation source, for BC production. However, BC production cost is still relatively high at present due to the high cost of the carbon sources used. As a result, BC has not yet been used in large-scale applications. Therefore, many efforts have been made to lower the BC production cost as well as to increase its yield.[22–44]

2.3.1 Regular BC Production. BC production depends heavily on several factors including culture medium and culture conditions.[22–26] The culture medium contains carbon source, nitrogen source, and other nutrients required for bacteria growth. The suitable pH value for the fermentation ranges from 4 to 6. Bacteria are most efficient when supplied with an abundant carbon source and minimal nitrogen source.[22] Qiu and Netravali also found *Acetobacter* prefers to consume small molecule carbon sources (e.g., fructose and glucose) before consuming relatively higher molecule carbon sources (sucrose and other higher sugars such as raffinose and stachyose) during the culture.[20] BC has been produced in a variety of forms, including pellicles, fibrous suspensions (fibrils), and sphere-like particles.[22–26] Figure 3 shows the three different forms of BC: pellicles, fibrils, and sphere-like particles.[25,26] The BC gelatinous pellicles shown in Fig. 3(A) are membrane-like and normally produced at the air-liquid medium interface at 26–30°C under stationary culture conditions.[22] The BC pellicles have been widely used for applications due to their suitable properties.[22] BC fibrous suspensions (fibrils) shown in Fig. 3(B) can be generated at the same culture medium but under agitated culture conditions.[23–26] The BC fibrils have relatively lower cellulose I_α content and hence lower Young's modulus, but higher water holding capacity.[23–25] Recently, BC sphere-like particles shown in Fig. 3(C) have also been reported to form in agitated culture condition and can be potentially utilized for food, healthcare, and materials applications.[26]

2.3.2 Low-Cost Carbon Source for BC Production. Many pure sugars such as glucose, sucrose, fructose, etc., and sugar alcohols such as mannitol, xylitol, sorbitol, etc., have been used as carbon sources for BC culture.[22–27] Among them, glucose, fructose, and mannitol
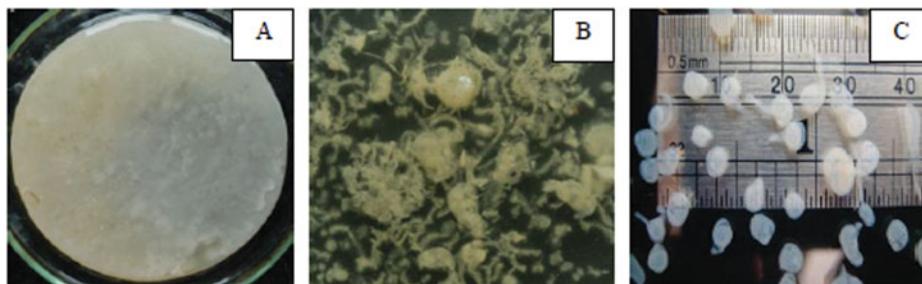
Figure 3. Three different forms of BC: Pellicle (A), Fibrils (B) and Sphere-like particle (C).[25, 26] © Hungund and Gupta; © American Chemical Society. Reproduced by permission of Hungund and Gupta and American Chemical Society. Permission to reuse must be obtained from the rightsholder.

are the most common and have shown excellent results in terms of BC production.[27–33] However, the cost of these sugars or sugar alcohols is high and hence they are not considered to be ideal for large scale, inexpensive BC production. As a result, many researchers have attempted to obtain higher BC yields as well as to reduce the cost of the carbon sources. Some of these efforts have been successful. For example, soy flour extract (SFE),[20] konjac powder hydrolyzate,[27] sugarcane molasses,[34–37] beet molasses,[38] processed rice bark,[39] fruit juice,[40] and tender coconut water,[41] have been found to be useful in BC production. Some of these sources may be used for industrial BC production in the near future to further reduce the cost of BC production by using inexpensive waste products and expand its use in many mass volume applications.

2.3.3 Methods for Improving BC Production and Engineering its Properties. Research for improving BC yields has attracted much attention in the past several decades.[42–44] One of the best ways for high-yield BC production is to use high-yield *Acetobacter* strain during fermentation (culture). Siripong et al. utilized ultraviolet radiation (UV) and/or N-methyl-N'-nitro-N-nitrosoguanidine (NTG) mutagenesis for strain improvement and obtain high-yield strain for BC production.[42] Cheng et al. reported that carboxymethylcellulose (CMC) addition dramatically increases the BC fibril yield in agitated culture condition.[43] Besides these, culture conditions (optimum pH and temperature) and isolation of a pure culture condition are also important factors which can improve the BC production to a certain extent.[44]

Many modification efforts have also been made to engineer the properties of BC needed for broader applications.[44–50] It is worth noting the report presented by Yamanaka et al. where they reported that addition of nalidixic acids and chloramphenicol in culture medium induced elongation of bacteria, resulting in the formation of wider cellulose ribbons and increased Young's modulus of BC sheets.[45] Schlufer et al. recently reported on acetylation, perpropionylation, and carbanilation of BC by using chemical reactions in ionic liquid 1-N-butyl-3-methylimidazolium chloride.[46] Such modifications significantly change the properties of BC, e.g., surface hydrophobicity and mechanical properties, and provide more choices for further BC applications.[46,47] Besides, carboxymethylation, esterification, and other modifications are also able to adjust and/or enhance the properties of BC.[44,48–50]

2.4 Applications of BC

The BC material has been widely used in different applications including artificial skin and blood vessel, binding agent for fibers and other materials, loud speaker diaphragms,
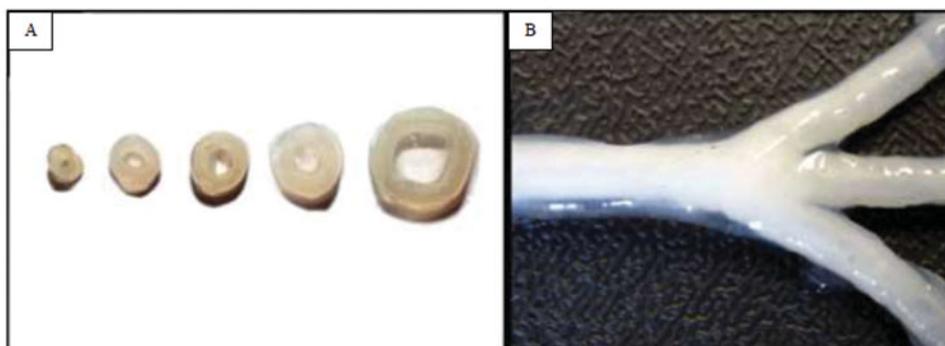
Figure 4. BC tubes with different sizes and shapes for applications: BC tubes with different inner diameters: 1.5 mm, 2.4 mm, 3.0 mm, 4.0 mm, and 6.0 mm (A); Branched BC tube fermented on a branched silicone tube (B).[51]

cosmetics, high quality paper, foods (nata-de-coco), textiles, composite membranes, etc.[5–10] Many interesting and novel medical applications involving BC have emerged in recent years. These include vascular graft, medical tissue scaffolds, matrix for drug and other bioactive compound delivery, wound dressing, cation exchange membrane, and many others.[2,12,51–58]

Bodin et al. first made BC tubes by fermenting *Acetobacter xylinum* on top of silicon tubes.[51] The increase in wall thickness of BC tubes was easily obtained by increasing the oxygen ratio during the fermentation. The fermentation method used by these researchers renders it to produce branched BC tubes with unlimited length and inner diameters. Such BC tubes are shown in Fig. 4.[51] Figure 4(A) shows BC tubes with different inner diameters while Fig. 4(B) shows a branched BC tube fermented on a branched silicon tube. The biocompatible BC tubes showed excellent mechanical properties capable of being utilized as vascular grafts for large animals.[51]

Bäckdahl et al. also developed BC scaffolds with controlled microporosity by placing paraffin wax and starch particles during culture and removing these particles after culture.[2] The BC scaffolds were then seeded with smooth muscle cells for investigating the potential tissue engineered blood vessel application. Several advantages of the BC scaffolds have been cited.[2] Since they are built up of nanofibers, they are visually similar to collagen. Because of their high surface to volume ratio the water-holding capacity is high and there is no observed degradation of the scaffolds. The mechanical properties of BC scaffolds are also higher than other scaffolds with the same solid material content.[2] In addition, Tang et al. reported that post-treatments for BC, including alkali and freeze-drying, can be utilized effectively to control the porosity of BC pellicles for tissue scaffold applications.[52]

Another interesting case for BC application is to use it as a drug (tetracycline) delivery matrix encapsulation as described by Stoica-Guzun et al.[53] They found that electron beam irradiated BC had lower drug release rate. This was shown to be a result of numerous structural changes that occur in BC during irradiation which collectively result in lower diffusion coefficient.[53]

Liebner et al. in their review and Haimer et al. in their study reported that BC aerogels produced by supercritical carbon dioxide-drying retained full accessibility for gases and liquids.[12,54] The porous structure of BC aerogels also resulted in good and reproducible wettability. This renders BC aerogels as attractive matrixes for controlled release applications in cosmetics and medicine. Bioactive compounds such as D-panthenol or L-ascorbic

acid, therefore, can be homogeneously deposited onto the inner surface of the BC with full preservation of pore features. These results also indicated that the bioactive compounds from loaded BC aerogels are able to be released into water in controllable rate.[12,54] The solute concentration hence can be primarily controlled by the combination of thickness of the gel layer and pore structure.[12,54]

Fu et al. have widely reviewed the BC applications in wound dressing and skin repair.[55] Among these applications, Czaja et al. reported novel applications of BC as wound dressing in the treatment of partial thickness burns.[56,57] The BC wound dressing promotes the creation of a favorable environment (conforming to the wound surface, maintaining a moist environment within the wound, etc.) for fast wound cleansing, and consequently for rapid healing.[55–57] Portal et al. further applied BC wound dressing for chronic wounds and found that the mean time for 75% epithelization was reduced to 81 days (with BC) from 315 days without the application of BC.[58] Other researchers also found the BC wound dressing clearly shortened the time to heal or wound closure over standard care when applied to non-healing lower extremity ulcers.[55–58]

Choi et al. modified BC membrane with cation-exchangeable acrylic acid by UV-graft polymerization.[59] The acrylic acid treated BC based membrane showed ion-exchange capacity (IEC: 2.5 meq $\times$ g^{-1}) and greater structural density. In addition, the prepared BC based membrane showed excellent mechanical properties, with tensile strength of 12 MPa and 6.0% elongation.[59]

Beyond these direct uses, BC can be widely and effectively utilized as either functional reinforcements or excellent matrices in nanocomposites for applications in a variety of fields. The following sections provide detailed description of BC application for nanocomposites.

3. Fabrication Methods for BC Based Nanocomposites

BC nanomaterials, with or without modifications, have been used either as direct matrices to be loaded with polymeric or mineral fillers, or as reinforcements in different resins, for fabricating BC based nanocomposites. A variety of methods have been utilized for achieving the purpose. Among them, resin infiltration, *in situ* self-assembly, particle deposition, dispersion and electrospinning, and dispersion and casting can be regarded as most widely-used methods for the purpose.[20,44,60–67]

3.1 Fabrication by Resin Infiltration (BC Pellicle)

Resin infiltration is one of the most common and convenient methods to fabricate BC based nanocomposites. As described earlier, BC is obtained in the form of a nanosized network with a porous structure and hence water-soluble resins can easily penetrate into the BC network structure filling most of the pores. When the wet pellicle is immersed into the resin solution, there is a big concentration difference between water inside of the BC network structure and the resin outside of BC. The mass (resin) transfer is driven by the concentration gradient resulting in resin penetrating into the BC network structure until the equilibrium is reached. Since BC is hydrophilic and the resin is water based, the diffusion is easy and can be assisted by the ultrasonication. The equilibrium is achieved when there is no concentration gradient between the resin inside of BC and outside of BC.[20,60,61] After evaporation of the solvent (water, in this case) in resins and other post-treatment, it was observed that the resins in the fabricated nanocomposites not only covered the surface of BC nanofibers, but also filled most of the pores inside the BC pellicle. The prepregs were
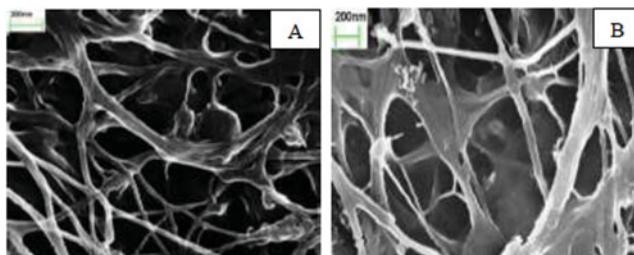
Figure 5. SEM images of freeze dried BC (A) and freeze dried BC-soy protein resin nanocomposite (B).[20]

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then hot pressed into membrane like nanocomposites. In many cases hot pressing may not be needed. Figure 5 shows an SEM image of freeze dried BC (A) and freeze dried BC-soy protein resin nanocomposite (B) before hot pressing.[20] The resin can be seen to have infiltrated into the BC network structure homogenously during the fabrication process. The homogenously fabricated BC-polymer resin nanocomposites can provide excellent tensile, thermal, as well as many functional properties which will be discussed in detail in section 4.[20,60,61]

3.2 In situ *Self-Assembly Fabrication (BC Pellice)*

The bacteria strain *Acetobacter* has been found to grow preferably on the surfaces of natural fiber or certain polymer molecules rather than freely in the medium.[61–63] Natural plant-based fibers or certain polymers (e.g. starch, soy resin, or polyvinyl alcohol (PVA)) provide ideal substrates for the bacteria to grow on. The fermentation process in the presence of natural fibers or polymers, therefore, can lead to the formation of BC based hybrids or nanocomposites. The large number of hydroxyl groups at the surfaces of natural plant-based fibers or certain hydrophilic polymer substrates provides strong hydrogen bonding between them and BC resulting in strong interaction between the two that can result in better composite properties.[61–63] Figure 6 shows BC can grow on the surface of the natural sisal fibers and thus forming a BC-fiber hybrid.[61] Such fibers when used in composites can result in excellent mechanical properties. The *in situ* self-assembly fabrication for preparation of BC based nanocomposites has attracted much attention due to its convenient and unique nature.[61–63]

3.3 Deposition Fabrication Method (BC Pellice)

Deposition of nanoparticles on BC has provided another convenient approach for fabricating BC based nanocomposites.[64] The functional nanoparticles can be homogenously deposited onto BC nanofibers by physical or chemical methods forming nanocomposites that display unique properties depending on the nanoparticle functionality.

3.4 Dispersion and Electrospinning Fabrication (BC Whisker)

Electrospinning is a very commonly employed technique for producing nanofibers and has also been used to produce BC based composite nanofibers. Before putting continuous
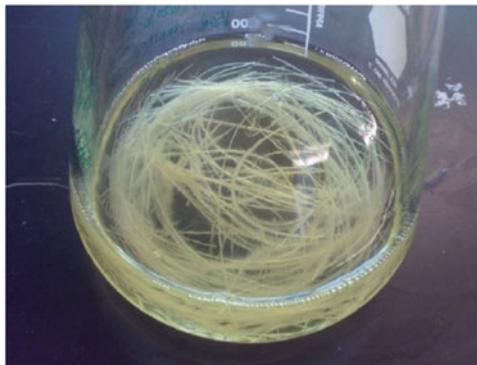
Figure 6. BC-sisal fibers hybrid in culture medium.[61]
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but entangled BC through the electrospinning process, it can be treated by strong acids to form nano-scale whiskers that are much shorter in length.[65,66] The BC whiskers can then be blended into desired polymers to electrospin into composite nanofibers.[64,65] Figure 7 shows transmission electron microscopy (TEM) images of the BC whiskers-imbedded electrospun polyethylene oxide (PEO) nanofibers.[65] It has been found that BC whiskers can be well embedded and aligned inside of the composite nanofibers which can result in high mechanical properties for the electrospun composite nanofibers.[60,61,65,66]

3.5 Dispersion and Casting Fabrication (BC Whisker)

As mentioned in section 3.4, BC can be acid hydrolyzed into whiskers from its pellicle or fibril form and dispersed into resins to form nanocomposites.[64–67] However, BC pellicles may also be ground to obtain shorter lengths, still maintaining high aspect ratio, and dispersed into resins.[67] This is much simpler than the acid hydrolysis process used to obtain whiskers. The ground BC/resin mixture then can be cast instead of electrospinning to form BC based fibrous membrane-like nanocomposites. These nanocomposites offer excellent mechanical properties due to homogenous dispersion of ground BC or whiskers.
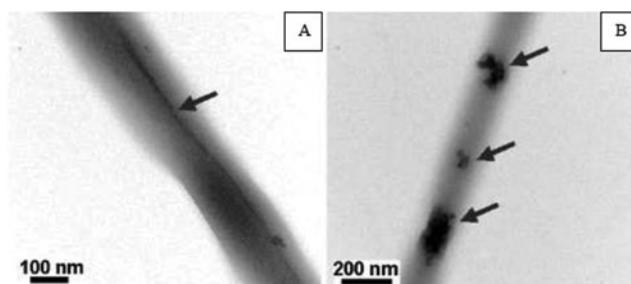
Figure 7. TEM images of the BC whiskers-imbedded electrospun PEO nanofibers: BC whiskers are aligned (A) and entangled (B) in electrospun PEO nanofibers.[65]
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4. Applications of BC Based Nanocomposites

After engineering original BC into BC based nanocomposites, the reinforced materials often obtain better mechanical and thermal properties or additional functionalities and can be useful in many more applications and fields. These fields can be broadly categorized into high-strength materials, plant biomimicking materials, biomedical materials, electrically conductive materials, catalytic materials, optical materials, luminescent materials, proton conductive materials, separating materials, antimicrobial materials, thermo-responsive materials and many others.[20,60–112] These categories are discussed in the following subsections.

4.1 High-Strength Materials

As mentioned earlier BC is an excellent nanofiber for use as direct reinforcement of resins to obtain high-strength nanocomposites because of its high tensile strength and Young's modulus.[20,60,61,65,68–70] Recently, BC based hybrid (such as BC-natural fiber hybrid) reinforced nanocomposites with hierarchical structures and attractive mechanical and physical properties have also been prepared.[61,62,71] These nanocomposites may be used in a wide variety of applications from circuit boards to tennis rackets and from automobile panels to building scaffolds.

4.1.1 BC as Direct Reinforcement. BC can be used as direct reinforcement in the form of either BC pellicle or hydrolyzed BC whiskers as many researchers have done.[20,60,61,65,68–70] However, ground BC, BC fibrils, or BC whiskers can also be used as alternative choice for direct reinforcement applications as discussed earlier. All these options retain high aspect ratio of BC and hence provide excellent opportunity for reinforcement as discussed in the next subsections. This is particularly true for resins with polar groups where significant hydrogen bonding can result in high fiber/resin interfacial bonding. This, in turn, can result in composites with high stiffness (Young's modulus) and strength.

    4.1.1.1 BC Pellicle Reinforcement. The most common and perhaps the easiest way for BC application is to utilize BC pellicles as direct mechanical reinforcement in resins for fabricating high strength nanocomposites. This is simply because BC is most commonly obtained in the pellicle form.

    Qiu and Netravali applied BC pellicles to reinforce PVA, PEO and soy protein resins by resin infiltration method.[20,60,61] The BC percentages in the formed biodegradable BC-PVA, BC-PEO, and BC-Soy resin nanocomposites were easily controlled by varying the resin concentration. Their results indicated that the BC-PVA, BC-PEO, and BC-Soy resin nanocomposites had excellent tensile and thermal properties. These properties are close to or even higher than many traditional petroleum based plastics and could be further enhanced by crosslinking of resins. These nanocomposites, therefore, can be good candidates for many applications due to their high performance and biodegradable nature.[20,60,61]

    In another case Nakagaito et al. prepared high-strength nanocomposites by impregnating BC pellicles in phenolic resin.[68] The fabricated BC-Phenolic resin nanocomposites showed high strength, and in particular the Young's modulus was significantly higher, in the range of 28 GPa. The superior modulus value was attributed to the uniform, continuous and straight nanoscalar network of BC used in their research.[68] Gindl and Keckes also fabricated BC reinforced cellulose acetate butyrate (CAB) nanocomposites by a similar resin infiltration method.[69] It was shown that BC pellicles provided good reinforcement for CAB resin. The tensile properties of BC-CAB nanocomposites were shown to be controllable and could be increased with increasing the BC content.[69]

Grande et al. also used bioinspired process to produce *in situ* self-assembled nanocomposites containing BC and native starch.[63] The BC fibrils grew in the culture medium in the presence of a starch phase. The self-assembled membrane-like BC-starch nanocomposites showed a coherent morphology and provided a novel approach to fabricate BC based nanocomposites.[63]

4.1.1.2 Reinforcement by BC Fibrils and Whiskers. Other forms of BC such as fibrils and whiskers can also be utilized as reinforcement in resins for fabricating BC based nanocomposites.[65,70] While they are not in the continuous form, they have high aspect ratio.

Brown and Laborie fabricated BC fibril-PEO nanocomposites by adding PEO into the BC culture medium during agitated fermentation process.[70] The fine dispersion of BC nanofibers hindered the crystallization of PEO, lowering its melting point and crystallinity. More importantly, BC fibrils reinforced the PEO significantly by increasing its tensile storage modulus. The other advantage of adding BC fibrils was increased thermal stability by increasing the decomposition temperature of PEO.[70]

Park et al. developed BC-PEO composite nanofibers by blending BC whiskers and PEO via electrospinning process.[65] The results showed that the whiskers were uniformly distributed inside of the nanofibers. It was also found that the incorporation of the BC whiskers was an efficient way to enhance the mechanical properties of the electrospun composite nanofibers.[65] Martinez-Sanz et al. also used BC whiskers and ethylene vinyl alcohol copolymer (EVOH) solution to electrospin BC-EVOH composite nanofibers with enhanced mechanical properties.[66]

4.1.2 BC Based Hybrid Reinforcement. BC has been utilized to modify natural fiber surfaces or even as matrices to fabricate hybrids by inserting other materials. In all cases both processes were conducted during *in situ* fermentation process.[61,62,71] The formed BC based hybrids were then capable of being utilized as reinforcements in resins to fabricate advanced nanocomposites. This is because BC modified hybrid fibers have rougher surface with BC fibrils protruding out that get embedded in the resin resulting in better fiber/resin interface. In addition, the BC-fiber hybrids can have more hydroxyl groups and in some cases, for example, BC-microfibrillated cellulose (MFC) hybrids, can have less number of defects as well.

4.1.2.1 In situ Produced BC Modified Natural Fiber. Pommet et al. first utilized *Acetobacter* to deposit nanosized BC to modify the surface of natural hemp and sisal fibers in culture medium during the BC fermentation process.[62] The adhesion between BC nanofibrils and natural fibers is possibly related to a high number of hydrogen bonds formed between the BC and the natural fibers. However, the BC fibers also get entangled with the natural fibers and protrude out. These protruding fibers not only provide roughness to the surface but also get embedded in the resin resulting in strong interfacial adhesion. The BC modified natural fibers (BC-natural fiber hybrids) were then incorporated into renewable polymers, poly(L-lactic acid) (PLLA) and CAB, to obtain a new class of model hierarchical nanocomposites. The single fiber pullout test results indicated that this modification can significantly enhance the interfacial adhesion between natural fibers and the renewable polymers, and therefore greatly improve mechanical performance of the nanocomposites.[62] Juntaro et al. from the same research group as Pommet further investigated the attachment of BC nanofibers to the surface of sisal fibers by *in situ* fermentation.[71] The results indicated that the presence of the BC nanofibers helps to improve the interfacial adhesion between the primary fibers and the resins as mentioned earlier. This leads to the formation of nanocomposites that possess improved mechanical properties and reduced water uptake.

Moreover, the work of BC attachment to natural fiber provides a convenient route to introduce nanoreinforcement with high aspect ratio.[71]

Netravali and Qiu followed the research for BC modified sisal fibers, but investigated the adhesion between BC modified sisal fibers (BC-Sisal hybrid) and soy protein isolate (SPI).[61] The microbond test results showed that the interfacial shear strength (IFSS) for BC-Sisal hybrid to SPI resin is higher than sisal fiber to SPI resin. As explained earlier, the increased IFSS between the BC-Sisal hybrid and SPI is due to rougher surface and more hydrogen bonds on the BC-Sisal hybrid as well as the protruding nanofibers that get embedded in the resin.[61] The higher IFSS values also indicated that the formed BC-Sisal-SPI nanocomposites would be expected to have better tensile properties than Sisal-SPI nanocomposites.

4.1.2.2 In situ *Produced MFC Reinforced BC.* Netravali and Qiu also developed MFC reinforced BC pellicles (BC-MFC hybrid) using *in situ* method via bacterial (*Acetobacter*) fermentation process.[61] MFC fibrils were encompassed by BC nanofibers and filled in nanopores present inside the BC network structure. The test results showed that *in situ* formed BC-MFC hybrids had better reinforcement performance for nanocomposites than BC alone. It was mainly due to the removal of defects in BC network structure by MFC, which also have high aspect ratio as well as excellent mechanical properties.[61] The BC-MFC hybrid was then used to fabricate nanocomposites with soy protein isolate (SPI) resin by solvent (resin) infiltration method. The fabricated BC-MFC-SPI nanocomposites showed excellent Young's modulus, over 1.4 GPa, of the nanocomposites which was higher than BC-SPI nanocomposites (1.3 GPa).[61] The properties can be further improved by increasing the BC-MFC content in these nanocomposites.

4.2 Plant Biomimicking Materials

BC materials have been shown as excellent matrices for fabricating different type of hybrid nanocomposites for plant biomimicking applications, including mimicking natural biomineralization, plant cell walls, and lignin polymerization process.[70,72–75] For example, Maeda et al. produced BC-Silica hybrid nanocomposites by mimicking natural biomineralization in rice plants.[72] BC pellicles were initially immersed in an aqueous solution of silanol which was then converted into silica by polycondensation reaction within the BC hydrogel matrixes. In the leaves of rice plants, large silica bodies (micrometer order) are embedded in the polysaccharide matrix, whereas in the BC-Silica hybrid nanocomposites, nanoscale silica particles were embedded between the fibrils of BC. The fabricated BC-Silica hybrid nanocomposites showed excellent modulus of elasticity (17 GPa) and tensile strength (185 MPa), much stronger than rice plants (3.5 GPa and 25-88 MPa, respectively).[72]

In another interesting case Whitney et al. synthesized BC-Xyloglucan nanocomposites for mimicking the mechanical properties of primary plant cell wall.[73] The fabrication process was conducted in the xyloglucan containing culture medium via *in situ* self-assembly process.[73] Weimer et al. also *in situ* fabricated highly crystalline BC-Xylan nanocomposites in xylan containing culture medium during fermentation.[74] The nanocomposite composition was similar to that of a secondary plant cell wall. The digestion test by ruminal microflora indicated that the intimate association between xylan and cellulose did not inhibit the rate of digestion of the component polysaccharides.[74]

In another novel application, Touzel et al. developed membrane-like BC-Pectin nanocomposites to mimic the lignin polymerization process.[75]A diffusion cell was applied to allow both hydrogen peroxide and coniferyl alcohol to diffuse into the peroxidase impregnated BC-Pectin nanocomposites via dialysis membranes. The results showed that

significant polymerization occurred within the membrane-like BC-Pectin nanocomposites. The presence of pectin led to a better dispersion of the synthetic lignin in the BC network and enhanced the proportion of alky-aryl-ether in the polymer.[75]

4.3 BC Nanocomposites for Biomedical Applications

Plant-based cellulose has long been used in numerous medical applications ranging from cotton for hemostatic wound dressings to sutures and from cotton swabs to renal dialysis membranes.[76] However, the presence of lignin, hemicellulose, and other molecules in plant cellulose requires intensive processes to purify and prepare it for medical applications. In contrast, BC, which is identical to plant cellulose in chemical structure, is produced without any contaminant molecules.[76] In addition BC possesses excellent biocompatibility, water-holding capacity, tensile strength, and chemical and composite morphological controllability. These properties make BC based nanocomposites a natural choice for medical applications, including two main fields, soft tissue engineering and bone and cartilage tissue engineering.[76–88]

4.3.1 Soft Tissue Engineering. BC and polymer resins have been engineered into suitable BC based nanocomposites for soft tissue engineering.[76–79] Millon and Wan utilized BC suspension (fibrils) and PVA, a biocompatible polymer, to fabricate BC-PVA nanocomposites.[77] The results indicated that nanocomposites with a broad range of mechanical properties can be fabricated. Further, their properties can be tuned to match the mechanical properties of cardiovascular tissues, such as aorta and heart valve leaflets. Such nanocomposites were found to perform extremely well in cardiovascular replacement applications.[77] Wang et al. fabricated membrane-like BC-PVA nanocomposites by immersing BC pellicles into optimized PVA solution and treating the prepregs with freeze-thaw cycles that prevented PVA from crystallizing.[78] The resultant nanocomposites exhibited properties suitable for cornea replacement such as high water content, high visible light transmittance and suitable UV absorbance, increased mechanical strength as well as appropriate thermal properties.[78]

Cai and Kim developed BC-Polyethylene glycol (PEG) nanocomposites with desired properties by immersing wet BC pellicles in the PEG aqueous solution followed by freeze-drying process.[79] The biocompatibility of the pure BC and BC-PEG nanocomposite scaffolds were evaluated by cell adhesion studies using 3T3 fibroblast cells. Figure 8 shows the cell attachment results on pure BC (A) and BC-PEG nanocomposite (B).[79] The result suggests that BC-PEG nanocomposite has excellent biocompatibility, even better compared with pure BC in terms of fibroblast cell culture.[79] The prepared BC-PEG scaffolds, therefore, can be suitable for soft tissue engineering applications.

4.3.2 Bone and Cartilage Tissue Engineering. Many BC based nanocomposites with properties suitable for bone and cartilage tissue engineering applications have been developed and reported in recent years.[11,76,80–88]

4.3.2.1 Bone Tissue Engineering. BC-hydroxyapatite (HAp) nanocomposites are one of the most promising biomaterials now for bone tissue engineering study.[11,80–85] Other BC based materials such as BC-Collagen nanocomposites are under development as well for the same applications.

Hong et al. bio-mimetically precipitated HAp from simulated body fluid (SBF) on BC to fabricate BC-HAp nanocomposites for bone tissue engineering.[80] The results revealed that the HAp minerals can be homogeneously precipitated on the BC surface. Figure 9
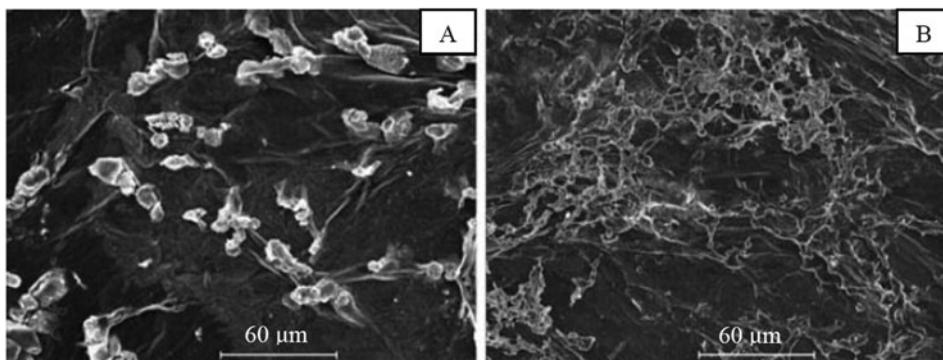
Figure 8. 3T3 fibroblast cell attachments of pure BC (A) and BC-PEG nanocomposite scaffolds (B) of 48 h seeding the cells.[79] (A): Cells attached to pure BC scaffolds after 48 h of incubation and most of the cells remained round; (B): Cells adhered and spread on the surface of BC-PEG scaffolds (with many pseudopodia) forming a layer on the surface indicating cell stretching their morphology and proliferating.

shows SEM images of BC (A) and cross-section views of BC-HAp nanocomposites after 7 days (B) and 14 days (C) immersion in $1.5 \times$ SBF.[80] It indicates that the ions can penetrate the network structure of BC to form HAp particles on the nanofibers throughout the BC.[80] It was also found that HAp minerals were carbonate-containing apatites that had smaller crystallite size as well as low crystallinity, resembling the carbonated HAp found in natural bones.[80]

Wan et al., in their study, chose phosphorylated BC to fabricate BC-HAp nanocomposites.[6,11,81] The BC-HAp nanocomposites were obtained via a biological route by soaking phosphorylated BC in $1.5 \times$ SBF.[6,11,81] Phosphorylation of BC effectively triggered HAp formation on the BC fiber surface. The results also indicated that HAp crystals formed on the phosphorylated BC fibers were carbonate-containing with small nanosized crystallites.
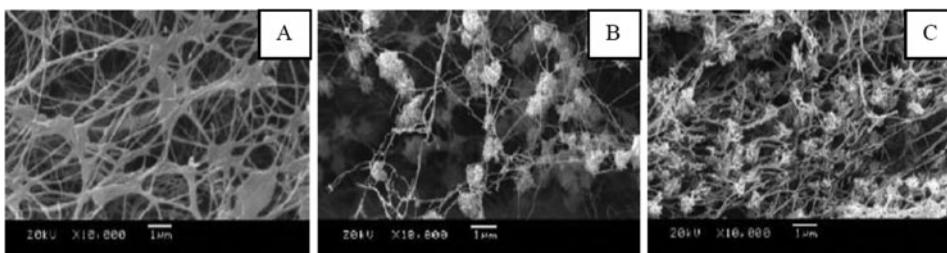

Figure 9. SEM images of BC (A) and BC-HAp nanocomposites after 7 days (B) and 14 days (C) immersion in $1.5\times$ SBF.[80] With increase in time, the HAp particles were well-bonded and distributed more densely and homogeneously.

The crystallinity (of the HAp) in BC-HAp nanocomposites was less than 1%. The phosphorylated BC pellicles, thus, could act as potent substrates for apatite nucleation and the BC-HAp nanocomposites thus formed were capable of being used as artificial bones and scaffolds for tissue engineering.[6,11,81]

Fang et al. prepared BC-HAp nanocomposite based scaffolds utilizing biomimetic technique similar to those conducted by Hong et al. and Wan et al.[6,11,80–83] However, Fang et al. first investigated the proliferation and osteoblastic differentiation of stromal cells derived from human bone marrow (hBMSC) on the nanocomposites even without osteogenic reagents.[83] The results confirmed that the hBMSC seeded on the BC-HAp nanocomposites exhibited better adhesion and showed higher activity than those seeded on pure BC. This is because the fabricated BC-HAp nanocomposites possessed preferred pore sizes as well as improved inorganic component. The study further confirmed that the BC-HAp nanocomposites were biocompatible *in vitro* and suitable for bone tissue engineering.[82]

In another case Grande et al. *in situ* produced BC-HAp nanocomposites exclusively for bone tissue engineering.[84] This was achieved by introducing the HAp in its mineral phase into the bacteria culture medium during the formation of BC nanofibers. During the fabrication, carboxymethylcellulose (CMC) (1% w/v) was used in order to suspend the HAp nanoparticles by controlling the viscosity of the culture medium. The amount of mineral phase reached 23.7% of the total weight of the nanocomposites. These nanocomposites also showed excellent biocompatibility and cell viability which were confirmed by human embryonic kidney (HEK) cell seeding in the test.[84]

Saska et al. developed and evaluated the biological properties of BC-HAp nanocomposites for bone regeneration.[85] The nanocomposites were prepared by incubating BC pellicles sequentially in solutions of calcium chloride ($CaCl_2$) and disodium hydrogen phosphate (Na_2HPO_4). The BC-HAp nanocomposites with 40-50% mineral phase were evaluated for bone regeneration in noncritical bone defects in rat tibiae. Two groups of samples were used in the bone regeneration test for comparison. In the treated group, the left tibia defects were filled with a blood clot and recovered by the BC-HAp barrier nanocomposite membrane, while in the control group, the right tibia defects were filled with a blood clot only. Figure 10 shows histological analysis for the bone regeneration using BC-HAp nanocomposite.[85] The results indicate that BC-HAp nanocomposites do an excellent job of expediting the bone regeneration.[85]

In a recent study, Saska et al. further developed the BC-Collagen nanocomposites for *in vitro* bone regeneration.[86] The production process of the nanocomposites started from modifying BC pellicles by glycine esterification, and followed by immersing the modified BC pellicles into aqueous collagen solution. The collagen solution contained 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide which is used for crosslinking to improve the biostability of the nanocomposites. The obtained nanocomposites were more flexible than BC pellicles even after gamma irradiation, suggesting that BC-Collagen nanocomposites are easier to be manipulated during surgical procedures. The high total protein content and alkaline phosphatase (ALP) activity on day 17 in osteogenic cells cultured on BC-Collagen nanocomposites indicated that these nanocomposites allow the development of the osteoblastic phenotype *in vitro*. As a result, BC-Collagen nanocomposites are also considered as promising BC based biomaterials for bone tissue engineering.[86]

Stoica-Guzun et al. synthesized BC-calcium carbonate ($CaCO_3$) nanocomposites inside of sodium carbonate (Na_2CO_3) and $CaCl_2$ aqueous solution.[87] The crystals of $CaCO_3$ deposited on the BC scaffold were more uniform and relatively bigger when assisted
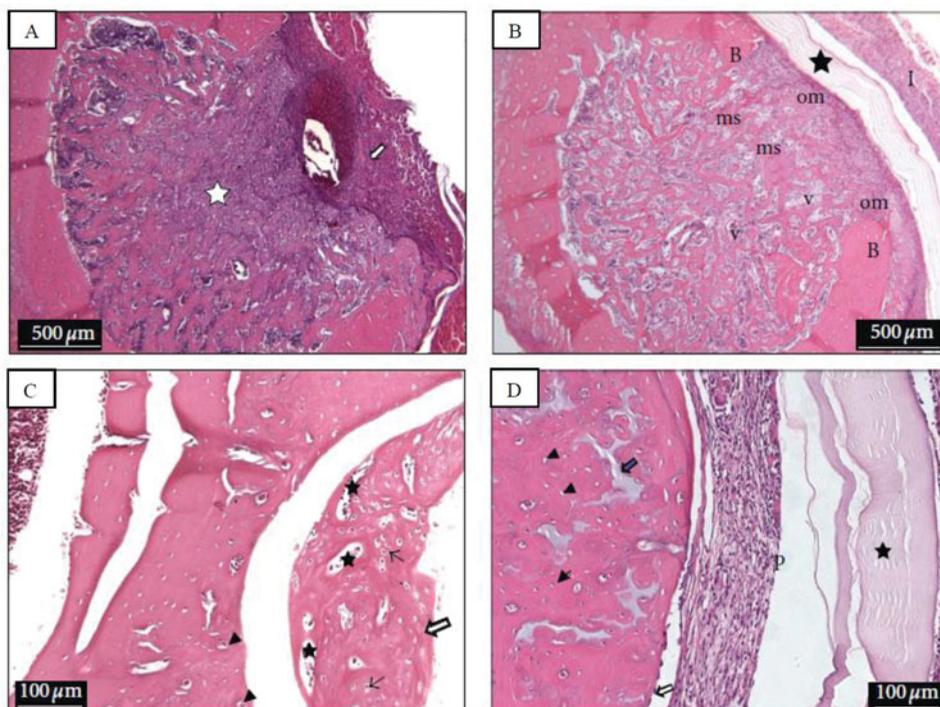
Figure 10. Histological analysis photomicrographs (Hematoxylin-eosin staining) for the bone regeneration using BC-HAp nanocomposite.[85] (A) Control group after 1 week, fibrotic tissue formation was observed within the defect site; (B) Treated group after 1 week, the BC-HAp nanocomposite membrane, osteoblasts, osteoids, newly formed bone, and medullary spaces with mesenchymal cells were observed within the defect site; (C) Control group after 4 weeks, newly formed bone tissue containing medullary spaces with mesenchymal cells, several osteocytes, and blood vessels were observed, but the it was not integrated with tibia bone; (D) Treated groups after 4 week, bone defects were observed to be filled by newly formed bone with several osteocytes, blood vessels, and bone matrix in process of mineralization. Symbols in (A): Bone defects filled by fibrotic tissue (white star), inflammatory infiltrate (white arrow); Symbols in (B): Bone defect filled by newly formed bone, osteoids (om), medullary spaces with mesenchymal cells (ms), several blood vessels (v), mature bone (B), BC-HAp membrane (black star), inflammatory infiltrate (I); Symbols in (C): New formed bone tissue is observed with several osteocytes (black arrows), blood vessels (arrow heads), medullary spaces (stars), bone defect is not filled completely (white star); Symbols in (D): BC-HAp membrane (star), periosteum (P), osteoblasts (white arrow), osteocytes (arrow heads), bone matrix (blue arrow). © Saska, Barud, Caspar, Marchetto, Ribeiro and Messaddeq. Reproduced by permission of Saska, Barud, Caspar, Marchetto, Ribeiro and Messaddeq. Permission to reuse must be obtained from the rightsholder.

with microwave irradiation. In addition, BC-CaCO$_3$ nanocomposites had higher water vapor transmission rate and hardness after microwave irradiation. The nascent BC-CaCO$_3$ nanocomposites prepared with microwave irradiation were expected to have ideal application as scaffolds in the biomedical field for bone regeneration.[87]

4.3.2.2 Cartilage Tissue Engineering. The cartilage tissue engineering by BC based nanocomposites is still in its nascent stage. However, research thus far has been promising. Nakayama et al. developed double-network hydrogel nanocomposites with high mechanical strength using BC and natural polymer gelatin.[88] The fracture strength and elastic
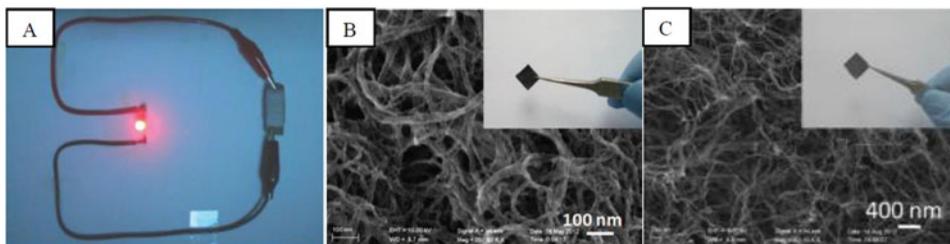
Figure 11. Asymmetric supercapacitor device with *p*-BC@MnO$_2$ anode and *p*-BC@N cathode: Digital image of a red-light-emitting diode (LED) lighted by the supercapacitor device (A), SEM images of the *p*-BC@MnO$_2$ anode (inset: photograph of *p*-BC@MnO$_2$) (B) and the *p*-BC@N cathode (inset: photograph of *p*-BC@N) (C).[90] Both anode and cathode maintained free-standing 3D pellicles with overlapped nanowires and cross-linking pores.

modulus of the BC-Gelatin nanocomposites under compressive stress are on the order of megaPascal (MPa), which is several orders of magnitude higher than those of gelatinous gel. These properties are almost equivalent to those of articular cartilage and therefore the BC-Gelatin nanocomposites are regarded as promising alternatives for articulate (cartilage) tissue engineering.[88]

4.4 Electrically Conductive Nanocomposites

BC can be directly used as an electrically conductive component after pyrolyzing in nanocomposites.[89–92] It is also able to act as excellent matrix for fabricating electrically conductive nanocomposites with other conductive materials.[64,93–95] BC based nanocomposites represent an advance in the field of the electrically conductive materials because the conventional counterparts are normally metals, which are not readily foldable. The BC based nanocomposites can be utilized as conductors, supercapacitors, electronic papers, electrodes, loudspeakers, actuators, and other electronic devices.[44,89–95]

4.4.1 Pyrolyzed BC Based Nancomposites. Liang et al. developed highly conductive and stretchable nanocomposites as conductors by using BC pellicles as starting materials.[89] The pyrolyzed BC (p-BC)-polydimethylsiloxane (PDMS) nanocomposites possessed high electrical conductivity of 0.20-0.41 S/cm, which was much higher than conventional carbon nanotube and graphene based nanocomposites. More importantly, the p-BC-PDMS nanocomposites with high stretching ability and high conductivity also showed great electromechanical stability. Even after 1,000 stretching cycles at the maximum strain of 80%, the resistance of the nanocomposites increased by only 10%.[89]

Chen et al. constructed an asymmetric supercapacitor with a manganese dioxide (MnO$_2$) film coated BC carbon (pyrolyzed) nanofiber (*p*-BC@MnO$_2$) anode and a nitrogen-doped BC carbon (pyrolyzed) nanofiber (*p*-BC@N) cathode.[90] The three-dimensional (3D) BC carbon nanofiber network was obtained by annealing BC pellicles at 1000°C for 2.0 h in nitrogen gas.[90,91] The fabrication process was simple, scalable, cost effective, and green. The optimized device can be reversibly charged and discharged at a voltage of 2.0 V in 1.0 M sodium sulfate (Na$_2$SO$_4$) solution. Figure 11 shows the asymmetric supercapacitor system, including digital image of a red light-emitting diode (LED) lighted by the supercapacitor
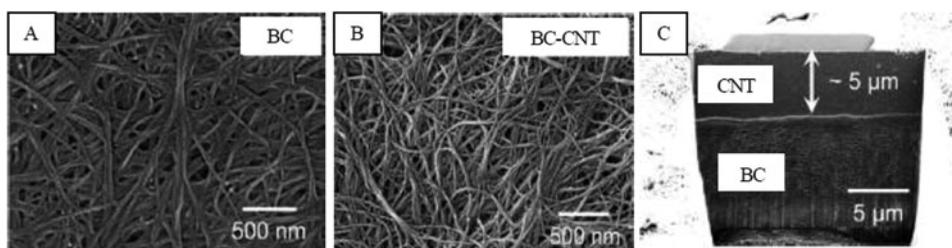
Figure 12. SEM images of BC (A), BC-CNT (B), and cross-section view of BC-CNT (C).[64]
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device (A), SEM images of the *p*-BC@MnO_2 anode (B) and the *p*-BC@N cathode (C).[90] The energy density and maximum power density of the supercapacitor can be considerably high, up to 32.91 Wh/kg and 284.63 kW/kg, respectively. The supercapacitor also exhibited good cycling durability with 95.4% specific capacitance retained after 2000 cycles.[90]

Wang et al. recently demonstrated that the pyrolyzed BC can also be used as a low-cost and green 3D conductive porous scaffold to support nanostructured anode materials for lithium ion batteries.[92] After incorporating tin dioxide (SnO_2) and/or germanium (Ge) nanoparticles into the pyrolyzed BC scaffold, the resulting hybrid (nanocomposite) materials showed high specific capacity and good cycling stability in electrochemical performance. This is mainly because of the structural advantages of the BC scaffolds. The pyrolyzed BC scaffolds with nanoparticles can create efficient conduction pathways at the whole electrode scale, while the interconnected voids in the BC scaffolds can facilitate the diffusion of lithium ions.[92]

4.4.2 Other Conductive Materials Coated BC Based Nanocomposites. In another case Kang et al. developed all-solid-state flexible supercapacitors by using BC pellicles as matrix, and carbon nanotubes (CNT) and triblock-copolymer ion gels (poly(styrene-block-ethylene oxide-block-styrene)) as coating materials.[64] Figure 12 shows the SEM images of BC (A), CNT coated BC (BC-CNT) (B), and cross-section view of BC-CNT (C). The interface of BC and CNT was seamless which ensures good mechanical integration between the two different materials. The high-quality interface may be due to the similar one-dimensional geometry of BC nanofiber and CNT and strong forces between the two layers.[64] After incorporating the triblock-copolymer ion gels between two BC-CNT layers, the fabricated all-solid-state flexible supercapacitors showed high physical flexibility, desirable electrochemical properties, and excellent mechanical integrity. The supercapacitors also showed high tolerance against bending cycles and high capacitance retention over multiple charge/discharge cycles.[64]

Müller et al. developed free-standing membrane-like BC-Polyaniline (PAni) nanocomposites with high electrical conductivity and good mechanical properties.[93] The nanocomposites were prepared through *in situ* oxidative chemical polymerization of aniline on the surface of BC nanofibers by using $FeCl_3 \cdot 6H_2O$ as oxidant. The results showed that the conductive polymer PAni (consisting nanoparticles, around 70 nm mean size) formed a continuous coating which encapsulated the BC nanofibers. Such BC-PAni nanocomposites can be utilized as electrically conductive materials in sensors, electronic devices, flexible electrodes, and intelligent apparel.[93]

The concept of BC based electronic paper has also been proven and attracted special attention.[94] Shah and Brown reported that the electronic paper was capable of being built by impregnating the dried BC pellicles with an electronic dye for coating.[94] The fabricated BC-electronic dye nanocomposite device was based on the ink on paper principle, in which the ink was electronically addressable and dynamically switchable in its light absorption, by applying appropriate voltage. The electronic paper has been found suitable for e-book tablets, e-newspapers, dynamic wall papers, rewritable maps, and learning books.[44,94]

Gutierrez et al. recently synthesized new conductive organic/inorganic materials by using BC (substrate) and titanium dioxide (TiO_2) nanoparticles (coating material).[95] The fabricated BC-TiO_2 nanocomposites showed conductive behavior arising from the electrostatic dipole-dipole interaction generated by hydrogen bonds between the hydroxyl groups of BC and TiO_2.[95]

4.5 Catalytic Materials

Some original developments about BC based nanocomposites for catalytic applications have emerged in recent years.[96–98] Normally BC pellicles are applied as excellent matrixes in these nanocomposites.

Yang et al., for example, developed BC-Cadmium sulfide (CdS) hybrid nanofibers by homogeneously depositing CdS nanoparticles onto the substrate of hydrated BC nanofibers.[96] The BC-CdS hybrid nanofibers showed high-efficiency photocatalysis with 82% methyl orange degradation after 90 min irradiation and good recyclability. The results indicated that the BC-CdS hybrid nanofibers can be easily utilized as visible-light responsive photocatalysts.[96]

In addition, Zhang and Qi fabricated BC-TiO_2 nanocomposites by immersing BC pellicles into a mixed solution of tetra-n-butyl titanium, acetyl acetone and isopropanol.[97] These nanocomposites exhibited enhanced photocatalytic activity which was characterized by measuring the TiO_2-assisted photodegradation of the xanthene dye Rhodamine B.[97]

Zhou et al. first made BC nanofiber-supported-palladium (BC-Pd) nanocomposites as catalyst by facile hydrothermal reduction.[98] The results showed that Pd nanoparticles were deposited onto BC nanofibers via physical coating and, as a result, the crystalline structures of both Pd and BC remained unchanged. The as-prepared catalyst was further explored in Heck coupling reaction between aryl halide and styrene or acrylates, with coupling yields decreased less than 10% for the fifth reaction cycle. This behavior may be attributed to slightly declined quality of BC-Pd catalyst where larger island domains were still observed due to higher aggregation of polydisperse Pd nanoparticles after 5-cycle reaction.[98] Figure 13 shows TEM images of as-prepared BC-Pd catalyst (A) and the catalyst after 5-cycle reaction (B) which can support the above mentioned reason. In addition, no Pd metal was detected in the final coupling product due to the protection from the ordered water layers covering around BC fiber via hydrogen-bonding, indicating the possible Pd loss in workup process.[98] These, BC-Pd nanocomposites, therefore, were regarded as one of the excellent recyclable catalysts for Heck coupling.[98]

4.6 Optical Materials

Nanocomposite materials with components less than one-tenth of a wavelength in size can be free from scattering, making them acceptable for a variety of optical applications.[99] Nanocomposites based on BC nanofibers which range between 40–70 nm in diameters,
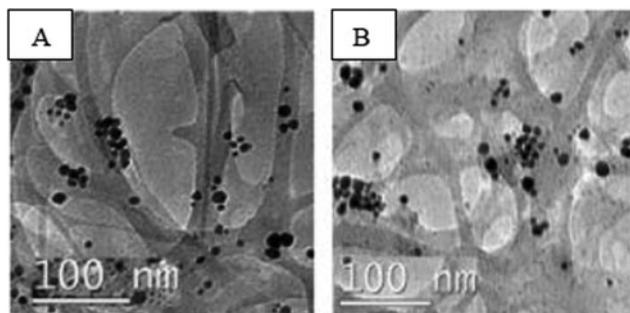
Figure 13. TEM images of as-prepared BC-Pd catalyst (A) and the catalyst after 5-cycle reaction (B).[98]
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possess the excellent optical properties (transparency) as well as good flexibility and dimensional stability. As a result, the BC based nanocomposites can be excellent reinforcements in resins for optical devices.[99–103]

Yano et al. reported the first example of transparent BC based nanocomposites.[99] The nanocomposites were fabricated by BC pellicle sheet and acrylic resin. These nanocomposites were optically transparent at fiber contents as high as 70%. Figure 14 shows the flexibility and transparency of BC-Acrylic resin nanocomposites with 60 wt% BC content.[99] These BC-Acrylic resin nanocomposites also had low coefficient of thermal expansion (CTE) and mechanical strength five times that of engineered plastics. The transparent property of BC-Acrylic resin nanocomposites relied on the nanosized cross sectional area (10×50 nm^2) of BC which was virtually free from light scattering. The significant improvements in the

Figure 14. Flexibility and transparency of a 65 μm thick BC-Acrylic resin nanocomposite sheet (60 wt% BC content).[99]
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thermal and mechanical characteristics of the BC-Acrylic resin nanocomposites were due to the semicrystalline chains of BC nanofibers. The nanocomposites were light, flexible, and easy to mold, thus making them excellent candidates for a variety of applications in the optical field including substrates for flexible displays, components for precision optical devices, and windows for automobiles or trains.[99]

In the research published by the same (Yano) group, Nogi et al. also found that the addition of BC nanofibers linearly decreased the regular transmittance of the BC-Acrylic resin nanocomposites;[100] however, the deterioration of light transmittance was limited due to the nanosized BC stucture. In contrast, the CTE was drastically suppressed by the addition of the BC nanofibers. The addition of just 7.4 wt% of BC nanofibers, which deteriorated light transmittance by only 2.4%, could reduce the CTE of acrylic resin from 86×10^{-6} to $38 \times 10^{-6} \, K^{-1}$.[100] These results suggest that BC could be used as reinforcement that can provide excellent thermal stability to the optical materials besides reinforcing it. In additional experiments, Nogi et al. deposited an electroluminescent layer on these transparent BC-Acrylic resin nanocomposites for electronic device applications.[101] These nanocomposites were also made to be foldable by using low Young's modulus acrylic resin with 5 wt% BC reinforcement.[101]

Ifuku et al. first fabricated BC based transparent nanocomposites by using acetylated BC and acrylic resin.[102] It was found that the acetylation decreased the refractive index of BC and reduced the hygroscopicity and thermal expansion of the nanocomposites. With these enhanced properties, transparent acetylated BC-Acrylic resin nanocomposites could be utilized for different optical applications.[102]

Fernandes et al. developed another kind of transparent nanocomposites for optical applications using BC and chitosan.[103] The fabrication procedure was maintained to be fully green by casting water based suspension of chitosan and BC nanofibrils. The fabricated BC-Chitosan nanocomposites were highly transparent, flexible, and had significantly better mechanical properties than the corresponding unfilled chitosan films. These nanocomposites also showed reasonable thermal stability and low oxygen permeability.[103]

4.7 Other BC Applications

In addition to the above-mentioned applications, BC based nanocomposites have been widely used in other fields as well. These fields include luminescent materials, proton conductive materials, separating materials, antimicrobial materials, thermo-responsive materials and many others.[67,104–112]

4.7.1 Luminescent and Proton Conductive Materials. Yang et al. first fabricated flexible luminescent BC-Cadmium selenide (CdSe) nanocomposite membrane via *in situ* synthesis of CdSe nanoparticles on the BC nanofibers.[104] The nanocomposite membrane showed good photoluminescent properties as well as excellent thermal and mechanical properties. Figure 15 shows the micrographs of BC-CdSe nanocomposite membrane without excitation (A) and with excitation (B).[104] The strong and well-defined green photoluminescence from Fig. 15(B) indicates the nanocomposite membrane is endowed with luminescent properties. This work renders a way for the BC-CdSe nanocomposite membranes to be applied in sensors, security papers, and other luminescent membrane areas.

For proton-conductive application, Yang et al. first develop BC-Platinum (Pt) membrane through liquid phase chemical de-oxidation method.[105] The prepared BC-Pt nanocomposites showed high electrocatalytic activity in hydrogen oxidation reaction. The BC-Pt nanocomposites were further doped with proton acids or inorganic acids to increase their
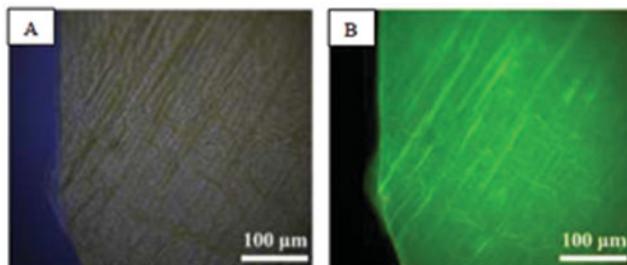
Figure 15. Micrographs of BC-CdSe nanocomposite membrane without excitation (A) and with excitation (B).[104]

proton conductive properties. The obtained nanocomposite membranes were renewable, thermally stable and proton-conductive. These attributes made the BC-Pt nanocomposite membranes good candidates for applications as proton exchange membranes (PEM) in fuel cells.[105]

4.7.2 Separating Materials. Phisalaphong et al. synthesized membrane-like BC-Alginate nanocomposites in an aqueous sodium hydroxide (NaOH)-urea solution for separating applications.[106] The blend solutions of BC slurry and sodium alginate with certain BC-Alginate weight ratios were initially cast onto Teflon® plates. After casting the blend solutions were coagulated in a 5 wt% $CaCl_2$ aqueous solution followed by a 1% hydrochloric acid (HCl) solution treatment. Supercritical carbon dioxide (CO_2) drying was finally applied for the formation of a nanoporous structure. The formed BC-Alginate nanocomposites with 80 wt% BC and 20 wt% alginate displayed a homogeneous structure. The nanocomposites also exhibited a better water adsorption capacity and water vapor transmission rate, though the tensile properties decreased slightly.[106] Dubey et al. also fabricated membrane-like BC-Chitosan nanocomposites as separating membrane materials.[107] The nanocomposites were prepared by the impregnation of BC pellicles into chitosan. The BC-Chitosan nanocomposites were found to be effective for pervaporative separation of ethanol (EtOH)-H_2O azeotrope in the test.[107] This was due to a substantially high pervaporative separation index (PSI) and low energy of activation of the nanocomposites.

4.7.3 Antimicrobial and Thermal Responsive Materials. Barud et al. developed transparent BC based nanocomposites with antimicrobial functions by soaking BC hydrated pellicles into silver triethanolamine (TEA) solutions.[108] This resulted in metallic silver particles with mean diameter of 8 nm that were homogenously adsorbed on to the BC nanofibers. The TEA was used as stabilizer and reducing agent during the process. Such silver-containing BC based nanocomposites could be utilized for antibacterial applications such as wound dressing because of the antimicrobial nature of the nanosilver particles.[108] Dobre et al. fabricated another antimicrobial BC based nanocomposites by dispersing ground BC whiskers into PVA resin and casting the nanocomposites.[67] Sorbic acid was added to the nanocomposites as an antimicrobial agent. The test results indicated that these nanocomposites were suitable for antimicrobial food packaging materials.[67]

Numata et al. were successful in developing nonvolatile and thermo-responsive nanocomposites with shape-memory function using BC and PEG.[109] Around a transition

temperature, the BC-PEG nanocomposites changed their transparency and elastic properties. It was also possible to control the transition temperature of these gels by altering the molecular weight of PEG. Furthermore, the thermo-sensitive change in elastic properties brought the shape-memory nature of the BC-PEG nanocomposites.[109] The shape-memory property of the BC-PEG gels depended on the network structure and mechanical properties of BC as well as the molecular weight of PEG.

4.7.4 Others. Until now, BC based nanocomposites have been applied in the fields of ion and organic solvent absorbent, magnetic aerogel and nanopaper, energy fuel cells, etc.[87,91,110–112] Although most of these applications have still not reached a mature state but are at the research stage, once developed, they will have broad and promising application prospects.

5. Future Opportunities and Challenges

In the future, BC based nanocomposites can be expected to be more widely applied in biomedical fields due to their highly porous structure, excellent biocompatibility, and exceptional mechanical properties. These application areas include drug delivery, wound healing, temporary skin for burn injuries, vascular replacement and many more. In addition, more work is expected on BC based nanocomposites in the high-value-added functional material fields, including electrically conductive, catalytic, optical, luminescent, proton conductive, separating materials and other emerging areas, because of their unique properties. There is also research in the area of energy harvesting using BC nanocomposites. Properties of BC based nanocomposites, however, are still far away from perfection. In addition, the cost of BC itself is still high at present and is reflected in the production cost of BC based nanocomposites for commercial applications with mass production. Improving properties, reducing fabrication cost, and designing proper industrial production line for BC based nanocomposites are three challenges for researchers. Fortunately, research is going on in all these areas and many novel applications can be expected in the future.

6. Conclusions

BC is a renewable and biodegradable material with many unique properties and applications. BC based nanocomposites fabricated by various methods possess excellent mechanical and physical properties and can be easily modified to have additional functionalities. As a result, these nanocomposites can be used in a broad variety of applications. The BC based nanocomposites can be employed in high-strength, plant biomimicking, biomedical, electrically conductive, catalytic, optical, luminescent, proton conductive, separating, antimicrobial, thermo-responsive applications as well as many other fields that are emerging. BC based nanocomposites and their broad range of applications have attracted significant attention of many researchers. These nanocomposites have had significant influence on the development of current functional materials and will continue to do so in the future.

References

1. Iguchi, M.; Yamanaka, S.; Budhiono, A. "Bacterial cellulose: A masterpiece of Nature's arts", *J. Mater. Sci.* **2000**, *35* (2), 261–270.
2. Backdahl, H.; Helenius, G.; Bodin, A.; Nannmark, U.; Johansson, B.R.; Risberg, B.; Gatenholm, P. "Mechanical properties of bacterial cellulose and interactions with smooth muscle cells", *Biomaterials* **2006**, *27* (9), 2141–2149.

3. Klemm, D.; Schumann, D.; Udhardt, U.; Marsch, S. "Bacterial synthesized cellulose: Artificial blood vessels for microsurgery", *Prog. Polym. Sci.* **2001**, *26* (9), 1561–1603.

4. Klemm, D.; Heublein, B.; Fink, H. P.; Bohn, A. "Cellulose: Fascinating biopolymer and sustainable raw material", *Angew. Chem.* Int. Ed. **2005**, *44* (22), 3358–3393.

5. Fink, H. P.; Weigel, P.; Purz, H. J.; Ganster, J. "Structure formation of regenerated cellulose materials from NMMO-solutions", *Prog. Polym. Sci.* **2001**, *26* (9), 1473–1524.

6. Wan, Y.; Hong, L.; Jia, S.; Huang, Y.; Zhu, Y.; Wang, Y.; Jiang, H. "Synthesis and characterization of hydroxyapatite - bacterial cellulose nanocomposites", *Compos. Sci. Technol.* **2006**, *66* (11–12), 1825–1832.

7. Fontana, J. D.; De Souza, A. M.; Fontana, C. K.; Torriani, I. L.; Moreschi, J. C.; Gallotti, B. J.; De Souza, S. J.; Narcisco, G. P.; Bichara, J. A.; Farah, L. F. X. "Acetobacter cellulose pellicle as a temporary skin substitute", *Appl. Biochem. Biotechnol.* **1990**, *24–25*, 253–264.

8. Shibazaki, H.; Kuga, S.; Onabe, F.; Usuda, M. "Bacterial cellulose membrane as separation medium", *J. Appl. Polym. Sci.* **1993**, *50* (6), 965–969.

9. Svensson, A.; Nicklasson, E.; Harrah, T.; Panilaitis, B.; Kaplan, D. L.; Brittberg, M.; Gatenholm, P. "Bacterial cellulose as a potential scaffold for tissue engineering of cartilage", *Biomaterials* **2005**, *26* (4), 419–431.

10. Westland, J. A.; Stephens, S. R.; Johnston, Jr. W. C.; Rosenkrans, H. J. (Weyerhaeuser Company). Bacterial cellulose binding agent. US Patent 5, 207, 826, A, 1993.

11. Wan, W. K.; Hutter, J. L.; Million, L.; Guhados, G. "Bacterial cellulose and its nanocomposites for biomedical applications", In *Cellulose Nanocomposites-Processing, Characterization, and Properties*; Oksman, K.; Sain, M., Eds.; ACS Symposium Series 2006, 938, 221–241.

12. Liebner, F.; Aigner, N.; Schimper, C.; Potthast, A.; Rosenau, T. "Bacterial cellulose aerogels: from lightweight dietary food to functional materials", In *Functional Materials from Renewable Sources*; Liebner, F.; Rosenau, T., Eds.; ACS Symposium Series 2012, 1107, 57–74.

13. Brown Jr., R. M. "The biosynthesis of cellulose", *J. Macromol. Sci. A* **1996**, *33* (10), 1345–1373.

14. Cannon, R. E.; Anderson, S. M. "Biogenesis of bacterial cellulose", *Crit. Rev. Microbiol.* **1991**, *17* (6), 435–447.

15. Ross, P.; Mayer, R.; Benziman, M. "Cellulose biosynthesis and function in bacteria", *Microbiol. Rev.* **1991**, *55* (1), 35–58.

16. Bieleck, S.; Krystynowicz, A.; Turkiewicz, M.; Kalinowska, H. "Bacterial cellulose", In *Biopolymer online*; Vandamme, E. J.; De Baets, S.; Steinbüchel, A., Eds.; John Wiley and Sons, Inc.: Hoboken, NJ; 2004; Vol. 5, pp 37–46.

17. Zhang, H.; Yan, X.; Jiang, Y.; Cong, J. "Development and characteristic of bacterial cellulose for antimicrobial wound dressing", *Adv. Mater. Res.* **2011**, *151–153*, 978–987.

18. Guhado, G.; Wan, W.; Hutter, J. L. "Measurement of the elastic modulus of single bacterial cellulose fiber using atomic force microscopy", *Langmuir* **2005**, *21* (14), 6642–6646.

19. Hsieh, Y.; Yano, H.; Nogi, M.; Eichhorn, S. J. "An estimation of the Young's modulus of bacterial cellulose filaments", *Cellulose* **2008**, *4*, 507–513.

20. Qiu, K.; Netravali, A. N. "'Green' composites based on bacterial cellulose produced using novel low cost carbon source and soy protein resin", In *Recent Advances in Adhesion Science and Technology in Honor of Dr. Kash Mittal*; Gutowski, W.; Dodiuk, H., Eds.; CRC Press: Boca Raton, FL, 2014; pp 193–208.

21. Helenius, G.; Backdahl, H.; Bodin, A.; Nannmark, U.; Gatenholm, P.; Risberg, B. "In vivo biocompatibility of bacterial cellulose", *J. Biomed. Mater. Res. A* **2006**, *76A*, 431–438.

22. Ramana, K. V.; Tomar, A.; Singh, L. "Effect of various carbon and nitrogen sources on cellulose synthesis by Acetobacter xylinum", *World J. Microbio. Biotechnol.* **2000**, *16*, 245–248.

23. Czaja, W.; Romanovicz, D.; Brown Jr., R. M. "Structural investigation of microbial cellulose produced in stationary and agitated culture", *Cellulose* **2004**, *11*, 403–411.

24. Watanabe, K.; Tabuchi, M.; Morinaga, Y.; Yoshinaga, F. "Structural features and properties of bacterial cellulose produced in agitated culture", *Cellulose* **1998**, *5* (3), 187–200.

25. Hungund, B. S.; Gupta, S. G. "Improved production of bacterial cellulose from *Gluconacetobacter persimmonis* GH-2", *J. Microbial. Biochem. Technol.* **2010**, *2*, 127–133.

26. Hu, Y.; Catchmark, J. M. "Formation and characterization of spherelike bacterial cellulose particles produced by *Actobacter xylinum* JCM 9730 strain", *Biomacromolecules* **2010**, *11*, 1727–1734.

27. Hong, F.; Qiu, K. "An alternative carbon source from konjac powder for enhancing production of bacterial cellulose in static cultures by a model strain *Acetobacter aceti subsp. xylinus* ATCC 23770", *Carbohyd. Polym.* **2008**, *72* (3), 545–549.

28. Saddler, J. N.; Gregg, D. J. "Ethanol production from the forest product waste", In *Forest Product Biotechnology*; Bruce, A.; Palfreyman, J. W., Eds.; Taylor & Francis Ltd.: London, 1998; pp 183–195.

29. Tarr, H. L. A.; Hibbert, H. "Studies on reactions relating to carbohydrates and polysaccharides. XXXV. Polysaccharides synthesis by the action of *Acetobacter xylinus* on carbohydrates and related compounds", *Can. J. Res.* **1931**, *4*, 372–388.

30. Kaushal, R.; Walker, T. K. "Formation of cellulose by certain species of *Acetobacter*", *Biochem. J.* **1951**, *48*, 618–621.

31. Keshk, S.; Sameshima, K. "Evaluation of different carbon sources for bacterial cellulose production", *Afr. J. Biotechnol.* **2005**, *4* (6), 478–482.

32. Ishihara, M.; Matsunaga, M.; Hayashi, N.; Tisler, V. "Utilization of d-xylose as carbon source for production of bacterial cellulose", *Enzyme Microb. Technol.* **2002**, *31* (7), 986–991.

33. Hestrin, S.; Schramm, M. "Synthesis of cellulose by *Acetobacter xylinum*", *Biochem. J.* **1954**, *58*, 345–352.

34. Keshk, S.; Sameshima, K. "The utilization of sugar cane molasses with/without the presence of lignosulfonate for the production of bacterial cellulose", *Appl. Microbiol. Biotechnol.* **2006**, *72* (2), 291–296.

35. Premjet, S.; Premjet, D.; Ohtani, Y. "The effect of ingredients of sugar cane molasses on bacterial cellulose production by *Acetobacter xylinum* ATCC 10245", *Sen-I Gakkaishi* **2007**, *63* (8), 193–199.

36. Bae, S.; Shoda, M. "Bacterial cellulose production by fed-batch fermentation in molasses medium", *Biotechnol. Prog.* **2004**, *20*, 1366–1371.

37. Bae, S.; Shoda, M. "Production of bacterial cellulose by Acetobacter xylinum BPR2001 using molasses medium in a jar fermentor", *Appl. Microbiol. Biotechnol.* **2005**, *67*, 45–51.

38. Keshk, S.; Razek, T.; Sameshima, K. "Bacterial cellulose production from beet molasses", *Afr. J. Biotechnol.* **2006**, *5* (17), 1519–1523.

39. Goelzer, F. D. E.; Faria-Tischer, P. C. S.; Vitorino, J. C.; Sierakowski, Maria-R.; Tischer, C. A. "Production and characterization of nanospheres of bacterial cellulose from Acetobacter xylinum from processed rice bark", *Mater. Sci. Eng. C* **2009**, *29* (2), 546–551.

40. Kurosumi, A.; Sasaki, C.; Yamashita, Y.; Nakamura, Y. "Utilization of various fruit juice as carbon source for production of bacterial cellulose by *Acetobacter xylinum* NBRC 13693", *Carbohyd. Polym.* **2009**, *76*, 333–335.

41. Jagannath, A.; Kalaiselvan, A.; Manjunatha, S. S.; Raju, P. S.; Bawa, A. S. "The effect of pH, sucrose and ammonium sulphate concentrations on the production of bacterial cellulose (Nata-de-coco) by *Acetobacter xylinum*", *World J. Microbiol. Biotechnol.* **2008**, *24*, 2593–2599.

42. Siripong, P.; Chuleekorn, S.; Duangporn, P. "Enhanced cellulose production by ultraviolet (UV) irradiation and N-methyl-N'-nitro-N-nitrosoguanidine (NTG) mutagenesis of an *Acetobacter* species isolate", *Afr. J. Biotechnol.* **2012**, *11* (6), 1433–1442.

43. Cheng, K.; Catchmark, J.; Demirci, A. "Effect of different additives on bacterial cellulose production by Acetobacter xylinum and analysis of material property", *Cellulose* **2009**, *16*, 1033–1045.

44. Trovatti, E. "The future of bacterial cellulose and other microbial polysaccharides", *J. Renew Mater.* **2013**, *1* (1), 28–41.

45. Yamanaka, S.; Ishihara, M.; Junji, S. "Structural modification of bacterial cellulose", *Cellulose* **2000**, *7*, 213–225.

46. Schlufer, K.; Schmauder, H.; Dorn, S.; Heinze, T. "Efficient homogeneous chemical modification of bacterial cellulose in the ionic liquid 1-N-butyl-3methylimidatzolium chloride", *Macromol. Rapid Commun.* **2006**, *27*, 1670–1676.

47. Hu, W. L.; Chen, S. Y.; Xu, Q. S.; Wang, H. P. "Solvent free acetylation of bacterial cellulose under moderate conditions", *Carbohyd. Polym.* **2011**, *83* (4), 1575–1581.

48. Schlufer, K.; Heinze, T. "Carboxymethylation of bacterial cellulose", *Macromol. Symp.* **2010**, *294* (4), 117–124.

49. Russler, A.; Wieland, M.; Bacher, M.; Henniges, U.; Miethe, P.; Liebner, F.; Potthast, A.; Rosenau, T. "AKD-modification of bacterial cellulose aerogels in supercritical CO$_2$", *Cellulose* **2012**, *19* (4), 1337–1349.

50. Lee, K. Y.; Quero, F.; Blaker, J. J.; Hill, C. A. S.; Eichhorn, S. J.; Bismarck, A. "Surface only modification of bacterial cellulose nanofibers with organic acids", *Cellulose* **2011**, *18* (3), 595–605.

51. Bodin, A.; Backdahl, H.; Fink, H.; Gustafsson, L.; Risberg, B.; Gatenholm, P. "Influence of cultivation conditions on mechanical and morphological properties of bacterial cellulose tubes", *Biotechnol. Bioeng.* **2007**, *97* (2), 425–434.

52. Tang, W.; Jia, S.; Jia, Y.; Yang, H. "The influence of fermentation conditions and post-treatment methods on porosity of bacterial cellulose", *World J. Microbiol. Biotechnol.* **2010**, *26*, 125–131.

53. Stoica-Guzun, A.; Stroescu, M.; Tache, F.; Zaharescu, T.; Grosu, E. "Effect of electron beam irradiation on bacterial cellulose membranes used as transdermal drug delivery systems", *Nucl. Instrum. Methods Phys. Res. Sect. B* **2007**, *265*, 434–438.

54. Haimer, E.; Wendland, M.; Schlufter, K.; Frankenfeld, K.; Miethe, P.; Potthast, A.; Rosenau, T.; Liebner, F. "Loading of bacterial cellulose aerogels with bioactive compounds by antisolvent precipitation with supercritical carbon dioxide", *Macromo. Symp.* **2010**, *294* (2), 64–74.

55. Fu, L.; Zhang, Y.; Zhang, J.; Yang, G. "Bacterial cellulose for skin repair materials", In *Biomedical Engineering-frontiers and Challenges*; Fazel, R., Ed.; InTech, Rijika: Croatia, 2011; pp. 249–274.

56. Czaja, W.; Young, D. J.; Kawecki, M.; Brown Jr., R. M. "The future prospects of microbial cellulose in biomedical applications", *Biomacromolecules* **2007**, *8* (1), 1–12.

57. Czaja, W.; Krystynowicz, A.; Bielecki, S.; Brown Jr., R. M. "Microbial cellulose-the natural power to heal wounds", *Biomaterials* **2006**, *27*, 145–151.

58. Portal, O.; Clark, W. A.; Levinson, D. J. "Microbial cellulose wound dressing in the treatment of nonhealing lower extremity ulcers", *Wounds* **2009**, *21*(1), 1–3.

59. Choi, Y. J.; Ahn, Y.; Kang, M. S.; Jun, H. K.; Kim, I. S.; Moon, S. H. "Preparation and characterization of acrylic acid-treated bacterial cellulose cation-exchange membrane", *J. Chem. Technol. Biotechnol.* **2004**, *79*, 79–84.

60. Qiu, K.; Netravali, A. N. "Bacterial cellulose-based membrane-like biodegradable composites using cross-linked and noncross-linked polyvinyl alcohol", *J. Mater. Sci.* **2012**, *47* (16), 6066–6075.

61. Netravali, A. N.; Qiu, K. (Cornell University). *Bacterial cellulose based 'green' composites.* US Patent 8, 541, 001, 2013.

62. Pommet, M.; Juntaro, J.; Heng, J. Y. Y.; Mantalaris, A.; Lee, A. F.; Wilson, K.; Kalika, G.; Shaffer, M. S. P.; Bismarck, A. "Surface modification of natural fibers using bacteria: Depositing bacterial cellulose on natural fibers to create hierarchical fiber reinforced nanocomposites", *Biomacromolecules* **2008**, *9*, 1643–1651.

63. Grande, C. J.; Torres, F. G.; Gomez, C. M.; Troncoso, O. P.; Canet-Ferrer, J.; Martínez-Pastor, J. "Development of self-assembled bacterial cellulose-starch nanocomposites", *Mater. Sci. Eng. C* **2009**, *29*, 1098–1104.

64. Kang, Y. J.; Chun, S.; Lee, S.; Kim, B.; Kim, J. H.; Chung, H.; Lee, S.; Kim, W. "All-solid-state flexible supercapacitors fabricated with bacterial cellulose papers, carbon nanotubes, and triblock-copolymer ion gels", *ACS Nano* **2012**, *6* (7), 6400–6406.

65. Park, W.; Kang, M.; Kim, H.; Jin, H. "Electrospinning of poly(ethylene oxide) with bacterial cellulose whiskers", *Macromol. Symp.* **2007**, *249-250*, 289–294.

66. Martinez-Sanz, M.; Olsson, R. T.; Lopez-Rubio, A.; Lagaron, J. M. "Development of electrospun EVOH fibers reinforced with bacterial cellulose nanowhiskers. Part I: Characterization and method optimization", *Cellulose* **2011**, *18*, 335–347.

67. Dobre, L. M.; Stoic-Guzun, A.; Stroescu, M.; Jipa, I. M.; Dobre, T.; Ferdeş, M.; Ciumpiliac, S. "Modeling of sorbic acid diffusion through bacterial cellulose-based antimicrobial films", *Chem. Pap.* **2012**, *66* (2), 144–151.

68. Nakagaito, A. N.; Iwamoto, S.; Yano, H. "Bacterial cellulose: the ultimate nano-scalar cellulose morphology for the production of high-strength composites", *Appl. Phys. A* **2005**, *80*, 93–97.

69. Gindl, W.; Keckes, J. "Tensile properties of cellulose acetate butyrate composites reinforced with bacterial cellulose", *Compos. Sci. Technol.* **2004**, *64*, 2407–2413.

70. Brown, E. E.; Laborie, M. G. "Bioengineering bacterial cellulose/poly(ethylene oxide) nanocomposites", *Biomacromolecules* **2007**, *8*, 3074–3081.

71. Juntaro, J.; Pommet, M.; Kalinka, G.; Mantalaris, A.; Shaffer, M. S. P.; Bismarck, A. "Creating hierarchical structures in renewable composites by attaching bacterial cellulose onto sisal fibers", *Adv. Mater.* **2008**, *20*, 3122–3126.

72. Maeda, H.; Nakajima, M.; Hagiwara, T.; Sawaguchi, T.; Yano, S. "Bacterial cellulose/silica hybrid fabricated by mimicking biocomposites", *J. Mater. Sci.* **2006**, *41*, 5646–5656.

73. Whitney, S. E. C.; Wilson, E.; Webster, J.; Bacic, A.; Reid, J. S.; Gidley, M. J. "Effects of structural variation in xyloglucan polymers on interactions with bacterial cellulose", *Am. J. Bot.* **2006**, *93* (10), 1402–1414.

74. Weimer, P. J.; Hackney, J. M.; Jung, H. G.; Hatfield, R. D. "Fermentation of a bacterial cellulose/xylan composite by mixed ruminal microflora: Implications for the role of polysaccharide matrix interactions in plant cell wall biodegradability", *J. Agric. Food Chem.* **2000**, *48*, 1727–1733.

75. Touzel, J.; Chabbert, B.; Monties, B.; Debeire, P.; Cathala, B. "Synthesis and characterization of dehydrogenation polymers in *gluconacetobacter xylinus* cellulose and cellulose/pectin composite", *J. Agric. Food Chem.* **2003**, *51*, 981–986.

76. Petersen, N.; Gatenholm, P. "Bacterial cellulose-based materials and medical devices: current state and perspectives", *Appl. Microbiol. Biotechnol.* **2011**, *91*, 1277–1286.

77. Millon, L. E.; Wan, W. K. "The polyvinyl alcohol-bacterial cellulose system as a new nanocomposite for biomedical applications", *J. Biomed. Mater. Res. B* **2006**, *79* (2), 245–253.

78. Wang, J.; Cao, C.; Zhang, Y.; Wan, Y. "Preparation and in vitro characterization of BC/PVA hydrogel composite for tis potential use as artificial cornea biomaterials", *Mater. Sci. Mater. C* **2010**, *30*, 214–218.

79. Cai, Z.; Kim, J. "Bacterial cellulose/poly(ethylene glycol) composite: characterization and first evaluation of biocompatibility", *Cellulose* **2010**, *17*, 83–91.

80. Hong, L.; Wang, Y. L.; Jia, S. R.; Huang, Y.; Cao, C.; Wan, Y. Z. "Hydroxyapatite/bacterial cellulose composite synthesized via a biomimetic route", *Mater. Lett.* **2006**, *60*, 1710–1713.

81. Wan, Y.Z.; Huang, Y.; Yuan, C. D.; Raman, S.; Zhu, Y.; Jiang, H. J.; He, F.; Gao, C. "Biomimetic synthesis of hydroxyapatite/bacterial cellulose nanocomposites for biomedical applications", *Mater. Sic. Eng. C* **2007**, *27*, 855–864.

82. Fang, B.; Wan, Y. Z.; Tang, T. T.; Gao, C.; Dai, K. R. "Proliferation and osteoblastic differentiation of human bone marrow stromal cells on hydroxyapatite/bacterial cellulose nanocomposite scaffolds", *Tissue Eng. A* **2009**, *15* (5), 1091–1098.

83. Lin, S.; Calvar, I. L.; Catchmark, J. M.; Liu, J.; Demirci, A.; Cheng, K. "Biosyntheiss, production and applications of bacterial cellulose", *Cellulose* **2013**, *20*, 2191–2219.

84. Grande, C. J.; Torres, F. G.; Gomez, C. M.; Bano, M. C. "Nanocomposites of bacterial cellulose/hydroxyapatite for biomedical applications", *Acta Biomater.* **2009**, *5*, 1605–1615.

85. Saska, S.; Barud, H. S.; Caspar, A. M. M.; Marchetto, R.; Ribeiro, S. J. L.; Messaddeq, Y. "Bacterial cellulose-hydroxyapatite nanocomposites for bone regeneration", *Int. J. Biomater.* **2011**, Article ID: 175362.

86. Saska, S.; Teixeira, L. N.; De Oliveira, P. T.; Gaspar, A. M. M.; Ribeiro, S. J. L.; Messaddeq, Y.; Marchetto, R. "Bacterial cellulose-collagen nanocomposite for bone tissue engineering", *J. Mater. Chem.* **2012**, *22*, 22102–22112.

87. Stoica-Guzun, A.; Stroescu, M.; Jinga, S. I.; Jipa, I. M.; Dobre, T. "Microwave assisted synthesis of bacterial cellulose-calcium carbonate composites", *Ind. Crop Prod.* **2013**, *50*, 414–422.

88. Nakayama, A.; Kakugo, A.; Gong, J. P.; Osada, Y.; Takai, M.; Erata, T.; Kawano, S. "High mechanical strength double-network hydrogel with bacterial cellulose", *Adv. Funct. Mater.* **2004**, *14* (11), 1124–1128.

89. Liang, H. W.; Guan, Q. F.; Zhu, Z.; Song, L. T.; Yao, H. B.; Lei, X.; Yu, S. H. "Highly conductive and stretchable conductors fabricated from bacterial cellulose", *NPG Asia Mater.* **2012**, *4*, e19, DOI:10.1038/am.2012.34.

90. Chen, L.; Huang, Z.; Liang, H.; Guan, Q.; Yu, S. "Bacterial-cellulose-dervied carbon nanofiber@MnO2 and nitrogen-doped carbon nanofiber electrode materials: An asymmetric supercapacitor with high energy and power density", *Adv. Mater.* **2013**, *25* (34), 4746–4752.

91. Wu, Z.; Li, C.; Liang, H.; Chen, J.; Yu, S. "Ultralight, flexible, and fire-resistant carbon nanofiber aerogels from bacterial cellulose", *Angew. Chem. Int. Ed.* **2013**, *52* (10), 2925–2929.

92. Wang, B.; Li, X.; Luo, B.; Yang, J.; Wang, X.; Song, Q.; Chen, S.; Zhi, L. "Pyrolyzed bacterial cellulose: A versatile support for lithium ion battery anode materials", *Small* **2013**, *9* (14), 2399–2404.

93. Müller, D.; Mandelli, J. S.; Marins, J. A.; Soares, B. G.; Porto, L. M.; Rambo, C. R.; Barra, G. M. O. "Electrically conducting nanocomposites: preparation and properties of polyaniline (PAni)-coated bacterial cellulose nanofibers (BC)", *Cellulose* **2012**, *19*, 1645–1654.

94. Shah, J.; Brown Jr., R. M. "Towards electronic paper displays made from microbial cellulose", *Appl. Micribiol. Biot.* **2005**, *66* (4), 352–355.

95. Gutierrez, J.; Tercjak, A.; Algar, I.; Retegi, A.; Mondragon, I. "Conductive properties of TiO2/bacterial cellulose hybrid fibres", *J. Colloid Interf. Sci.* **2012**, *377* (1), 88–93.

96. Yang, J.; Yu, J.; Fan, J.; Sun, D.; Tang, W.; Yang, X. "Biotemplated preparation of CdS nanoparticles/bacterial cellulose hybrid nanofibers for photocatalysis application", *J. Hazard Mater.* **2011**, *189* (1–2), 377–383.

97. Zhang, D.; Qi, L. "Synthesis of mesoporous titania networks consisting of anatase nanowires by templating of bacterial cellulose membranes", *Chem. Commun.* **2005**, *21*, 2735–2737.

98. Zhou, P.; Wang, H.; Yang, J.; Tang, J.; Sun, D.; Tang, W. "Bacterial cellulose nanofibers supported palladium (0) nanocomposite and its catalysis evaluation Heck reaction", *Ind. Eng. Chem. Res.* **2012**, *51*, 5743–5748.

99. Yano, H.; Sugiyama, J.; Nakagaito, A. N.; Nogi, M.; Matsuura, T.; Hikita, M.; Handa, K. "Optically transparent composites reinforced with networks of bacterial nanofibers", *Adv. Mater.* **2005**, *17* (2), 153–155.

100. Nogi, M.; Ifuku, S.; Abe, K.; Handa, K.; Nakagaito, A. N.; Yano, H. "Fiber-content dependency of the optical transparency and thermal expansion of bacterial nanofiber reinforced composites", *Appl. Phys. Lett.* **2006**, *88* (13), 133124–133124-3.

101. Nogi, M.; Yano, H. "Transparent nanocomposites based on cellulose produced by bacteria offer potential innovation in the electronics industry", *Adv. Mater.* **2008**, *20*, 1849–1852.

102. Ifuku, S.; Nogi, M.; Abe, K.; Handa, K.; Nakatsubo, F.; Yano, H. "Surface modification of bacterial cellulose nanofibers for property enhancement of optically transparent composites: dependence on acetyl-group DS", *Biomacromolecules* **2007**, *8*, 1973–1978.

103. Fernandes, S. C. M.; Oliveira, L.; Freire, C. S. R.; Silvestre, A. J. D.; Neto, C. P.; Gandini, A.; Desbriéres, J. "Novel transparent nanocomposite films based on chitosan and bacterial cellulose", *Green Chem* **2009**, *11*, 2023–2029.

104. Yang, Z. H.; Chen, S. Y.; Hu, W. L.; Yin, N.; Zhang, W.; Xiang, C.; Wang, H. P. "Flexible luminescent CdSe/bacterial cellulose nanocomposite membranes", *Carbohyd. Polym.* **2012**, *88* (1), 173–178.

105. Yang, J.; Sun, D.; Li, J.; Yang, X.; Yu, J.; Hao, Q.; Liu, W.; Liu, J.; Zou, Z.; Gu, J. "*In situ* deposition of platinum nanoparticles on bacterial cellulose membranes and evaluation of PEM fuel cell performance", *Electrochim Acta* **2009**, *54*, 6300–6305.
106. Phisalaphong, M.; Suwanmajo, T.; Tammarate, P. "Synthesis and characterization of bacterial cellulose/alginate blend membranes", *J. Appl. Polym. Sci.* **2008**, *107* (5), 3419–3424.
107. Dubey, V.; Pandey, L. K.; Saxena, C. "Pervaporative speration of ethanol/water azeotrope using a novel chitosan-impregnated bacterial cellulose membrane and chitosan-poly(vinyl alcohol) blends", *J. Membr. Sci.* **2005**, *251*, 131–136.
108. Barud, H. S.; Barrios, C.; Regiani, T.; Marques, R. F. C; Verelst, M.; Dexpert-Ghys, J.; Messaddeq, Y.; Ribeiro, S. J. L. "Self-supported silver nanoparticles containing bacterial cellulose membranes", *Mater. Sci. Eng.* **2008**, *28*, 515–518.
109. Numata, Y.; Nuromoto, K.; Furukawa, H.; Gong, J. P.; Tajima, K.; Munekata, M. "Nonvolatile and shape-memorized bacterial cellulose gels swollen by poly(ethylene glycol)", *Polym. J.* **2009**, *41* (7), 524–525.
110. Olsson, R. T.; Azizi Samir, M. A. S.; Salazar-Alvarez, G.; Belova, L.; Strom, V.; Berglund, L. A.; Ikkala, O.; Nogues, J.; Gedde, U. W. "Making flexible magnetic aerogels and stiff magnetic nanopaer using cellulose nanofibrils as templates", *Nat. Nanotechnol.* **2010**, *5*, 584–588.
111. Katepetch, C.; Rujiravanit, R. "Synthesis of magnetic nanoparticle into bacterial cellulose matrix by ammonia gas-enhancing in situ co-precipitation method", *Carbohyd. Polym.* **2011**, *86* (1), 162–170.
112. Evans, B. R.; O'Neill, H. M.; Malyvanh, V. P.; Lee, I.; Woodward, J. "Palladium-bacterial cellulose membranes for fuel cells", *Biosens. Bioelectron.* **2003**, *18* (7), 917–923.