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Review

Functionalized bacterial cellulose derivatives and nanocomposites

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ABSTRACT

Bacterial cellulose (BC) is a fascinating and renewable natural nanomaterial characterized by favorable properties such as remarkable mechanical properties, porosity, water absorbency, moldability, biodegradability and excellent biological affinity. Intensive research and exploration in the past few decades on BC nanomaterials mainly focused on their biosynthetic process to achieve the low-cost preparation and application in medical, food, advanced acoustic diaphragms, and other fields. These investigations have led to the emergence of more diverse potential applications exploiting the functionality of BC nanomaterials. This review gives a summary of construction strategies including biosynthetic modification, chemical modification, and different in situ and ex situ patterns of functionalization for the preparation of advanced BC-based functional nanomaterials. The major studies being directed toward elaborate designs of highly functionalized material systems for many-faceted prospective applications. Simple biosynthetic or chemical modification on BC surface can improve its compatibility with different matrix and expand its utilization in nano-related applications. Moreover, based on the construction strategies of functional nanomaterial system, different guest substrates including small molecules, inorganic nanoparticles or nanowires, and polymers can be incorporated onto the surfaces of BC nanofibers to prepare various functional nanocomposites with outstanding properties, or significantly improved physicochemical, catalytic, optoelectronic, as well as magnetic properties. We focus on the preparation methods, formation mechanisms, and unique performances of the different BC derivatives or BC-based nanocomposites. The special applications of the advanced BC-based functional nanomaterials, such as sensors, photocatalytic nanomaterials, optoelectronic devices, and magnetically responsive membranes are also critically and comprehensively reviewed.

Contents

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1. Introduction

It is well known that cellulose is a very important and fascinating biopolymer and an almost inexhaustible and sustainable natural polymeric raw material, which is of special importance both in industries and in daily lives. In the past decade, the design and development of renewable resources and innovative products for science, medicine and technology have led to a global revival of interdisciplinary research and utilization of this abundant natural polymer. Formed by repeated connection of glucose building blocks, cellulose possesses abundant surface hydroxyl groups forming plentiful inter- and intra-molecular hydrogen bonds, characterized by its hydrophilicity, chirality, biodegradability, and broad chemical-modifying capacity (Klemm, Heublein, Fink, & Bohn, 2005). The properties of cellulose largely depend on the specific assembling and supramolecular order controlled by the origin and treatment of cellulose (Eichhorn et al., 2010). Bacterial cellulose (BC) has the same molecular formula as plant cellulose, but with unique and sophisticated three-dimensional porous network structures. Intrinsically originated from the unique structure, BC demonstrates a serious of distinguished structural features and properties such as high purity, high degree of polymerization (up to 8000), high crystallinity (of 70–80%), high water content to 99%, and high mechanical stability, which is quite different from the natural cellulose (Barud et al., 2011). These specific parameters are determined by the biofabrication approach of BC (Fig. 1) and the controllable shape and supramolecular structure through the alteration of cultivation conditions during fermentation. These amazing physicochemical properties have attracted significant interest from both research scientists and industrialists. So far, BC has wide application in various fields including medical, food, advanced acoustic diaphragms, and so on (Klemm et al., 2011). These research and exploration have led to the emergence of more diverse potential applications exploiting the functionality of BC nanomaterials.

In view of expanding the scope of BC applications, it is important to take full advantage of the unique structure and properties of BC nanomaterials to develop novel BC-based nanomaterials with ground-breaking new features. Various modification methods have been explored to open up possibilities for endowing BC with new functionalities (Klemm et al., 2011). Simple biosynthetic or chemical modification on BC surface can improve its compatibility with different matrixes and expand its utilization in nano-related applications. Another notable feature of BC is its high aspect ratio and abundant active functional hydroxyl groups, which makes it suitable for combination with different nanostructures by providing powerful interaction of BC with surrounding species, such as inorganic and polymeric nanoparticles and nanowires (Huang & Gu, 2011). This novel concept breaks new ground to make optimum use of the specific chemical properties of the guest substrates, in association with the unique features of renewable BC resources. As a promising template in the synthesis of a great variety of nanostructures with designed properties and functionalities, BC can play the role of reducing agent, structure-directing agent and stabilizer (Yang, Xie, Deng, Bian, & Hong, 2012). The polymeric or inorganic ingredients can be incorporated and cooperatively interact with BC nanofibers to attain some functional products. Such new high-value materials are the subject of continuing research and are commercially interesting in terms of new products from the inexhaustible and sustainable natural polymeric raw material.

In the last few years, growing worldwide activity can be observed regarding extensive scientific investigation and increasing efforts for the practical use of the BC materials. There is an increasing annual publication activity on BC (also known as microbial cellulose or bacterial nanocellulose) since 2000 as presented in Fig. 2. In recent years, the investigation and utilization of BC in functional materials have been the focus of research, and a growing number of works have been included in this field. Functional BC-based nanomaterials are especially an attractive topic because they enable the creation of materials with improved or new properties by mixing multiple constituents and exploiting synergistic effects, such as electronic, optical, magnetic, catalytic properties and bioactivity. With a special property or several remarkable functions, functional BC-based nanomaterials are a type of high value-added materials possessing potential applications in specific fields. In this review, recent developments on BC-based advanced functional nanomaterials including modified BC nanomaterials, functional BC-based nanocomposites and their applications will be discussed and reviewed. A variety of surface functionalization through biosynthetic or chemical modification will be considered, which can improve the functionality of BC nanomaterials and expand its

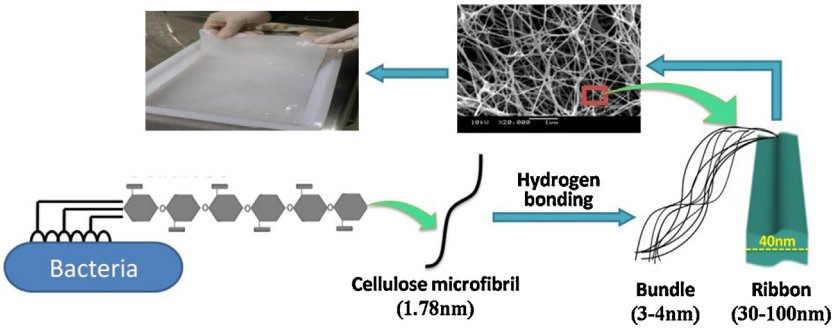

Fig. 1. The illustration of biofabrication process of BC.

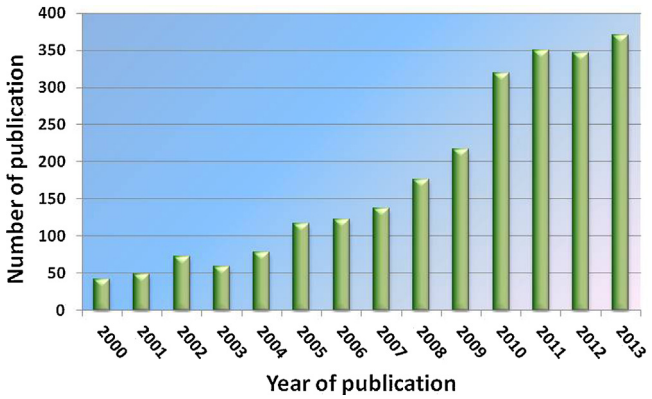

Fig. 2. The illustration of the annual number of publications on BC since 2000 (SciFinder Scholar search system, search term "bacterial cellulose").

potential application fields. Various approaches to the preparation of functional BC-based nanocomposites by incorporating different guest substrates including small molecules, inorganic nanoparticles or nanowires, and polymers on the surfaces of BC nanofibers are summarized, which mainly focus on the preparation methods, performances and some formation mechanisms of specific functional nanomaterials.

2. Construction strategies of BC-based functional nanomaterials

Although BC nanomaterial has unique physical and chemical characteristics, its high degree of crystallinity and sole functional group lead to its poor dissolubility and processability, thereby limiting the application fields. BC possesses an abundance of hydroxyl groups on the surface, where modification can be easily achieved. It can be modified to achieve alternative functional groups and patterns of functionalization using in situ and ex situ modification methods as shown in Fig. 3. The properties of BC derivatives are primarily determined by the type of the functional groups. In particular, modified BC with more than one functional group possessing different surface characteristics such as lipophilic–hydrophilic properties, magnetic and optical properties combined with a controlled pre-set functionalization pattern is in the center of interest.

2.1. Biosynthetic modification

The shape and supramolecular structure of BC can be controlled by the change of cultivation conditions such as the type of strain, carbon source, and additives (Heßler & Klemm, 2009; Klemm et al., 2006). Studies have demonstrated the potential for manipulating the biogenesis of BC in order to produce modified BC nanofibers with a controlled composition, morphology, and properties. The inclusion of additives in the nutrient media components during biosynthesis can influence the assembly and microstructure of BC including the crystallinity, crystalline polymorphism, crystallite size and ribbon width. The presence of additives in the media may interfere with the bacterial cells or bind directly to the cellulose during production, thereby affecting the yield, structure, morphology and physical properties of BC. The in situ generation of composites can also be effectively regulated during biosynthesis by the inclusion of additives and dispersed particles.

2.1.1. Altered BC structure

As a remarkable benefit of BC, the ultrastructure and morphology of BC can be altered by introducing additives not specifically required for bacterial cell growth in the media. The effects of the water-soluble agents in culture media on the aggregation and crystallization of BC microfibrils were intensively studied. Adding various water-soluble chemical reagents can modify the microfibrillar features of the cellulosic ribbons. Adding nalidixic acid or chloramphenicol produced ribbons with an apparently larger width, probably because several ribbons from a cluster of cells whose dividing process was inhibited, combined or intertwined. While adding dithiothreitol produced ribbons with only 45% width of the control ribbons on average (Yamanaka & Sugiyama, 2000).

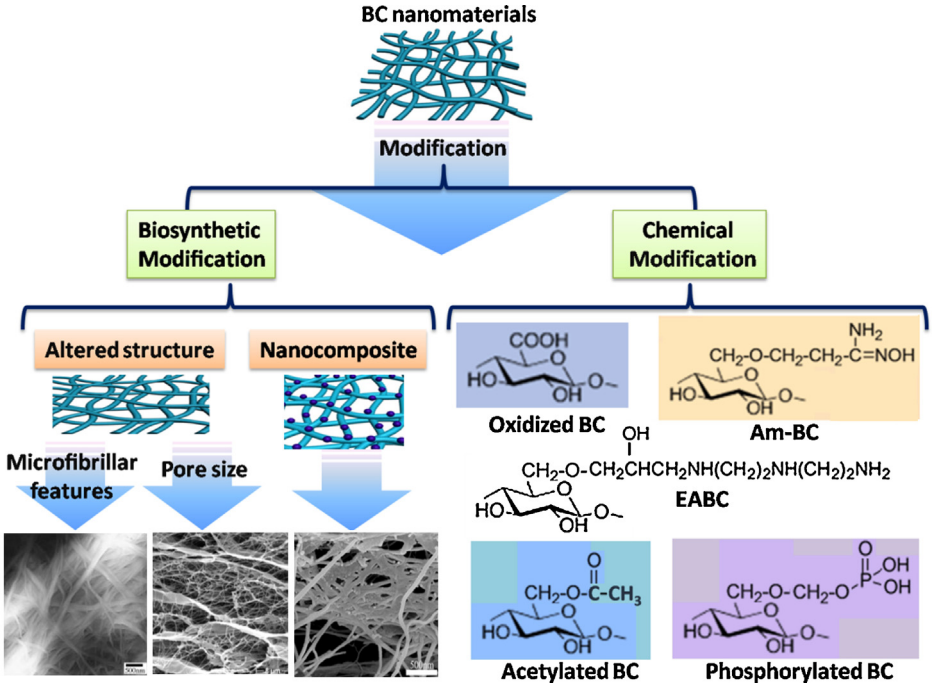

Fig. 3. Schematic illustration of the generalized synthetic routes to modified BC nanomaterials (Chen et al., 2010; Geng et al., 2011; Heßler & Klemm, 2009; Hu, Chen, Xu, et al., 2011; Ifuku et al., 2009; Oshima et al., 2008; Shen et al., 2009; Yamanaka & Sugiyama, 2000).

The pore system and water content of BC can be controlled in situ by the incorporation of water soluble polymers such as carboxymethylcellulose (CMC), hydroxypropylmethyl cellulose (HPMC), methylcellulose (MC), poly(vinyl alcohol) (PVA) and polyethylene glycol (PEG) to the culture medium (Seifert, Hesse, Kabrelian, & Klemm, 2004). In the presence of these additives, the pore system and elasticity of BC, as well as the water adsorption and water holding capacity can be controlled. It has been claimed the addition of HPMC, CMC and MC can cause decreased crystallinity and crystal size, as well as greater thermal stability and pore size (Chen, Chen, Huang, & Lin, 2011). Along with the formation of porelike network structure, the water retention ability and the ion absorption capacity increase. The functionalized BC produced with CMC also showed good adsorption performances for copper and lead ions (Chen et al., 2009). Nevertheless the presence of PVA in the culture medium results in a reduced water absorption ability and a slightly higher copper ion capacity in comparison with original BC. The addition of β-cyclodextrin or PEG 400 causes a remarkable pore size increase (Heßler & Klemm, 2009). Surprisingly, these co-substrates act as removable auxiliaries not incorporated in the BC samples.

Other polymers such as Tween 80, urea, fluorescent brightener and sodium alginate (NaAlg) have also been incorporated into the BC fermentation medium, with the observed differences in pore size, degree of polymerization, crystallinity, fiber widths and mechanical strength (Huang, Chen, Lin, Hsu, & Chen, 2010; Ruka, Simon, & Dean, 2013; Zhou, Sun, Hu, Li, & Yang, 2007). The results revealed that the addition of urea can increase the mechanical strength. The bundle widths of BC produced with fluorescent brightener increased and the cellulose network void grew. BC produced with NaAlg added has a lower crystallinity, a smaller crystalline size and an enhanced yield.

2.1.2. Nanocomposites

In particular, the additives can be in situ incorporated into the growing BC fibrils to create a novel type of nanocomposites, which represents a very specific and important modification method of BC. This in situ technique can combine the properties of altered supramolecular structure of BC with those of the incorporated components. So far, researchers have put different efforts to obtain BC nanocomposites by applying various additives such as organic compounds, polymers and inorganic substances (Klemm et al., 2011).

The biological fermentation of BC in presence of cationic starch leads to the formation of double-network BC composites by incorporation of the starch derivative in the BC network (Heßler & Klemm, 2009). This double-stage structure consists of an opaque upper and a transparent under part. As shown in Fig. 4a, in case of the upper layer, the additive adsorbs at the cellulose fibers and causes an irregular distribution of the pore sizes. The under layer indicates the incorporation of the starch into the solvate shells of the BC prepolymer, forming an exciting skinny film structure (Fig. 4b). Other characteristic examples include the additives of poly(ethylene oxide) (Brown & Laborie, 2008), PVA (Gea, Bilotti, Reynolds, Soykeabkeaw, & Peijs, 2010) and starch (Grande et al., 2009) in the media for the formation of nanocomposites with the incorporation of these additives into the network of BC. Along with the increase of the additive content, the cellulose crystallized into smaller nanofibers, which further bonded together into bundles. The BC nanofibers were well dispersed in the composites and the nanocomposites typically show significantly improved mechanical properties.

The inorganic additives can drastically modify the performance of BC. BC/multiwalled carbon nanotubes (MWCNTs) composites can be obtained in the presence of MWCNTs in an agitated culture (Park, Kim, Kwon, Hong, & Jin, 2009; Yan, Chen, Wang, Wang, & Jiang, 2008). Interestingly, a core–shell structure model was demonstrated, with the packed MWNTs attached nascent sub-elementary fibrils as the core of the cellulose assemblies as shown in Fig. 4c. While in the static culture method, band-like assemblies with sharp bends and rigidness were produced in the presence of MWCNTs. Similarly, the crystallinity index, crystallite size, and cellulose I_α content also changed, which may be attributed to the interaction between the hydroxyl groups of treated MWCNTs and the sub-elementary BC fibrils, interfering with the aggregation and crystallization of BC microfibrils. By adding silica or titanium precursor into the static growth medium, the SiO_2 and TiO_2 nanoparticles about several tens of nanometers in size can be incorporated onto BC microfibrils (Geng et al., 2011; Yano, Maeda, Nakajima, Hagiwara, & Sawaguchi, 2008) (Fig. 4d). It is inferred that the basic proteins in the outer membrane of bacterium cell act as the catalyst for the hydrolysis and condensation of inorganic precursor, the surface of both outer membrane and BC nanofibers renders the nucleation and growth sites for inorganic nanoparticles. The space-temporal effect endows bacteria the delicate control ability over formation of the nanocomposites.

2.2. Chemical surface modification

Although the biosynthetic modification of BC is a kind of green sustainable technology, the strict microbial fermentation environment restricts the introduction of some additives. Other questions involving the interaction mechanism between the additives and microfibrils growth, as well as the structure control of BC nanofibers still need to be addressed. While chemically modified methods are not limited by the required types of additives. Compared to the biosynthesis method, its more clearly defined objectives and principles make it a feasible modified method for BC material. Since the chemical composition of BC is similar to plant fibers, it can also be carboxymethylated, acetylated, phosphorylated, and modified by other graft copolymerization and crosslinking reaction to obtain a series of BC derivatives. The introduction of new functional groups to the BC structure can endow BC with various features such as hydrophobicity, ions adsorption capacity and optical properties while maintaining the unique three-dimensional nano network and excellent mechanical properties of BC.

In most cases, the modification of BC focuses on the improvement of its applicability and performance in different application fields. Several methods have been employed to achieve BC derivatives with improved metal ions absorption capacity. The functionalized diethylenetriamine-BC (EABC), amidoximated BC (Am-BC) and phosphorylated BC have been prepared as new adsorbents for metal ions (Chen, Shen, Yu, Hu, & Wang, 2010; Oshima, Kondo, Ohto, Inoue, & Baba, 2008; Shen et al., 2009). The experimental data showed that the microporous network structure of BC was maintained after the modification and these novel adsorbent showed good adsorption performances for different metal ions. To anchor metallic ions on BC nanofibers, the carboxylate groups have been introduced onto the BC nanofiber surface using the 2,2,6,6-tetramethylpiperidine-1-oxyradical (TEMPO)-mediated oxidation system (Ifuku, Tsuji, Morimoto, Saimoto, & Yano, 2009). The oxidation can proceed under mild aqueous conditions maintaining the crystallinity and crystal size of BC nanofibers.

In order to improve the dispersability and compatibility in different solvents or matrices that are suitable in the production of nanocomposites, the acetylation of BC based on a non-swelling reaction mechanism was reported recently. BC could be partially acetylated by the fibrous acetylation method to modify its physical properties, while preserving the microfibrillar morphology (Kim, Nishiyama, & Kuga, 2002). The hydrophobicity of the acetylated surface is advantageous for maintaining a large surface area on drying from water and would make the microfibrils compatible with other hydrophobic materials. While most of the chemically

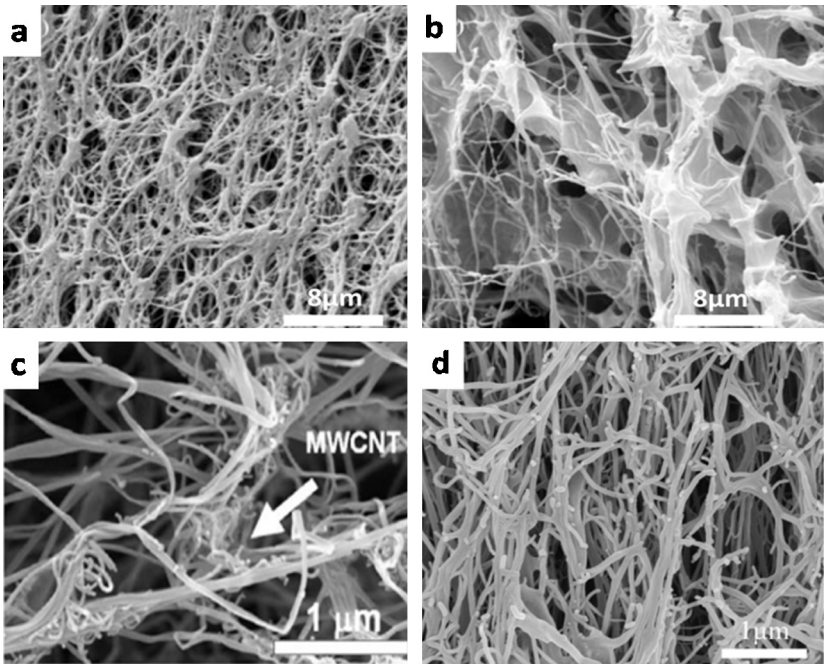

Fig. 4. SEM images of freeze-dried upper part of BC/starch composite (a), under part of BC/starch composite (b), middle layer of BC/MWCNTs composites (c), and BC/SiO_2 nanocomposites (d) (Geng et al., 2011; Heßler & Klemm, 2009; Park et al., 2009).

modified techniques require tedious solvent exchanges that strongly diminish the environmental benefit of the use of BC. A major thrust of recent BC modification research focused on the design of more economical and environmentally friendly method to obtain novel BC derivatives. Thus, a solvent-free derivatization system appears as an important goal to get BC derivative products with hydrophobic surfaces with a minimum environment impact. In line with the solvent-free BC derivatization concept, BC preserving the microfibrillar morphology has been partially acetylated using acetic anhydride in the presence of iodine as a catalyst (Hu, Chen, Xu, & Wang, 2011). Another example is the reported vapor-phase technique which has been applied recently for the surface esterification of BC microfibrils with the help of gaseous trifluoroacetic acid mixed with acetylating agents (Berlioz, Molina-Boisseau, Nishiyama, & Heux, 2009). Experimental results have shown the acetylation proceeded from the surface to the interior crystalline core of BC nanfibers. Hence, for moderate degree of substitution, the surface was fully grafted whereas the cellulose core remained unmodified and the original fibrous morphology was maintained. The obtained acetylated BC membrane shows more hydrophobic surface and good mechanical properties as shown in Fig. 5, which is in favor of enhancing the hydrophobic non-polar polymeric matrix.

2.3. In situ formation of nanostructures

BC has unique micro-nano porous three-dimensional network, which can facilitate the penetration of various metal ions into the interior. It also possesses a great deal of hydroxyl and ether bonds, forming the effective reactive sites to anchor metallic ions on the surface of the nanofibers. Then a variety of inorganic nanoparticles or nanowires can be formed through precipitation, oxidation–reduction and sol–gel reaction as shown in Fig. 6. Different from the doped nanoparticles into BC matrix, the size and morphology of the nanoparticles can be regulated by adjusting the structure of BC template and the in situ preparation conditions. At the same time, the nanospace in the BC fibers can behave as an effective nanoreactor to prevent the unwanted agglomeration phenomenon, ensuring the effective dispersion of the formed nanoparticles in the BC matrix.

In the process of in situ preparation of BC-based nanocomposites, the second components such as metal and polymer in the form of particles or fibers can be introduced into the BC matrix, while retaining the unique three-dimensional nanoporous network of BC. BC can be viewed as a soft template to control the synthesis of desired nano-materials or nano-structure with specific size and shape. This can obtain a variety of novel functional materials with

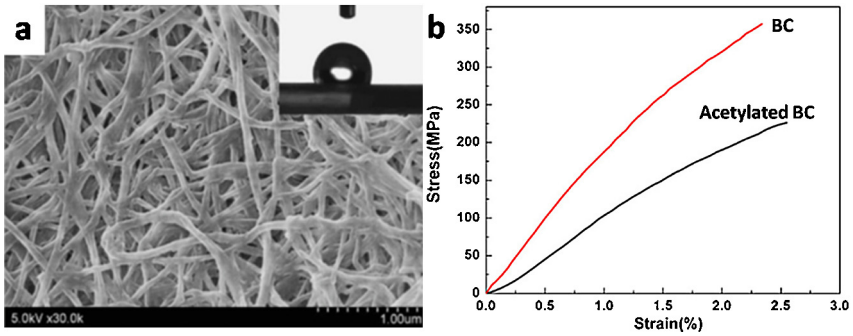

Fig. 5. (a) FE-SEM image of vacuum-dried acetylated BC, and the inset shows the profile of water droplets on the membrane surface. (b) Tensile stress–strain behaviors of air dried BC and acetylated BC (Hu, Chen, Xu, et al., 2011).

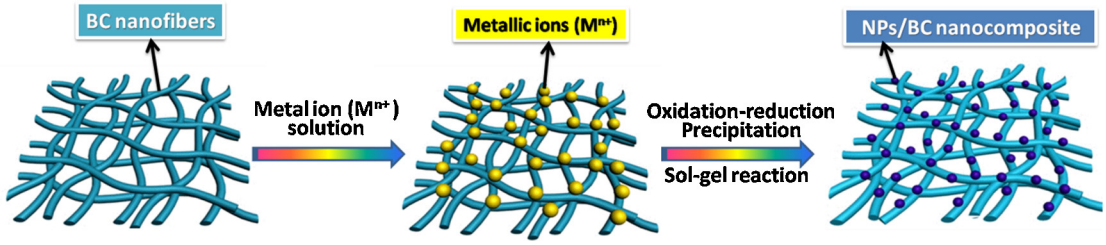

Fig. 6. Schematic diagram of the in situ preparation of nanoparticles/BC nanocomposites.

unique features and outstanding performances. Using BC as a template in the in situ synthesis of nano-materials has the following advantages: BC is a kind of environment-friendly and renewable material which can be produced from a wide range of raw materials. The shape, structure and properties can be easily adjusted during the biosynthesis, pretreatment and chemical modification process. Furthermore, the BC matrix can be removed by calcination to obtain the pure inorganic nanoparticles and nanowires structure.

Therefore, BC with controllable structure and pore size can provide restrictive environment to ensure a variety of nanostructures effectively embedded in the matrix. The method does not require severe conditions, and is simple and easy to implement, which can obtain the nano-particles with narrow size distribution. So far, this method has been applied to synthesize different nanomaterials such as metal, semiconductor and electrically conducting polymers through different preparation methods.

2.3.1. *In situ formation of nanostructures through reduction reaction*

There have been some reports regarding the application of BC as a soft template to in situ form different metal nanoparticles by the reduction reaction as shown in Table 1. The size and morphology of the formed nanoparticles can be controlled by using different reducing agents including sodium borohydride ($NaBH_4$), triethanolamine, hydrazine (NH_2NH_2), hydroxylamine (NH_2OH), ascorbic acid, polyethylenimine (PEI) and so on (Barud et al., 2008; Yang, Xie, Hong, Cao, & Yang, 2012; Zhang et al., 2010). These reducing agents can serve as an assistant material for stabilizing nanoparticles, preventing their aggregation. In addition, BC itself can be used as a reductant to produce metal nanoparticles (Yang, Xie, Deng, et al., 2012), without introducing additional reducing agent or stabilizing agent, thus avoiding the secondary pollutants and guaranteeing the feasibility of its applications in medical and catalytic field.

2.3.2. *In situ formation of nanostructures through precipitation reaction*

Well-separated nanofibrils of BC create an extensive surface area forming active sites for metal ion adsorption, and the subsequent introduction of precipitating agent will react with the immobilized metal ions to generate the initial nuclei of metal or oxide. Then the nuclei continue to grow, thereby further forming functional inorganic nanoparticles as shown in Fig. 7. The growth of the nanoparticles was readily controlled by repeated alternating dipping of BC membranes in the metal ion and precipitating agent solution followed by a rinse step. So it is feasible for BC to serve as an excellent matrix in the synthesis of nanoparticles through the in situ precipitation reaction.

CdS and CdSe nanoparticles have been synthesized and stabilized on BC nanofibers using in situ precipitation method (Li et al., 2009a; Yang et al., 2012a). At first, hydroxyl and ether groups of BC anchored Cd^{2+} or thioglycolic acid capped Cd^{2+}, then the anchored Cd^{2+} reacted with S^{2-} or Se^{2-} to generate CdS or CdSe nanoparticles on the BC nanofibers as shown in Fig. 8. The results indicated that nanoparticles with the diameter of 20–30 nm deposited on BC nanofibres are well-dispersed in the BC nanofibre-network. AgCl nanoparticles with a size of several tenths of nanometers have been in situ synthesized in the three-dimensional non-woven network of BC nanofibrils (Hu et al., 2009). The growth of the nanoparticles was readily obtained by repeated alternating dipping of BC membranes in the solution of silver nitrate or sodium chloride followed by a rinse step. The nanopore is essential for introduction of silver ions and reaction with Cl^- to form AgCl particles into BC fibers and removal of the excess chemicals from BC fibers.

BC can serve as an excellent matrix in the in situ synthesis of the Fe_3O_4 nanoparticles through the coprecipitation reaction (Zhang et al., 2011). The ultrafine network architecture of BC gives a good tunnel for Fe^{2+}/Fe^{3+} adsorption and ensures the effective anchoring of absorbed ions onto the BC nanofibers through ion–dipole interactions. After being rinsed with distilled water to remove the unanchored ions, the obtained ions/BC complexes were immersed into the excessive NaOH solution. The interaction between Fe^{2+}/Fe^{3+} and OH^- can induce the formation of Fe_3O_4 nanoparticles with the diameter of 80–100 nm as shown in Fig. 9.

During the in situ formation process of different nanostructures, the size and size distribution of the formed nanoparticles are controllable by adjusting synthetic parameters such as the concentration of metal ions. When the concentration of metal ions is too high, the BC nanofibers fails to fully immoblize and disperse the large number of metal ions due to the limited hydroxyl reactive sites shown in Fig. 10. Meanwhile, the presence of excess metal ions would result in the agglomeration of the nanoparticles due to the higher aggregation speed than the orientation speed in the particle growth process. Therefore the concentration of the reaction solution needs to be reduced appropriately to ensure the metal ions and nanoparticles effectively dispersed and fixed onto the surface of the nanofibers. However, when the concentration is too low, the loading amount of the nanoparticles will be significantly reduced, which would degrade the performance of the final products. The exploration of optimal reaction conditions would be particularly important to achieve the effective dispersion of nanoparticles with sufficient loading amount, thereby obtaining the functional nanocomposite materials with excellent optical, electrical, magnetic and antibacterial properties.

2.3.3. *In situ formation of nanostructures through sol-gel reaction*

Taking advantage of the ultrafine nanofibrous structure, as well as abundant porous channels inside the network, BC nanomaterials can be used as the templates to in situ prepare metal oxides through the sol–gel reaction. The schematic diagram of the in situ preparation process is described in Fig. 11. When immersing BC into the precursor solution, the inorganic ions can be immobilized onto the BC nanofibers. Then it can be solidified to form the gel through hydrolysis and condensation, and subsequently heated to form the desired oxides. BC template can stabilize and disperse the formed oxides nanoparticles through van der Waals forces and hydrogen bonding interaction, prompting generated nanoparticles distributed along the surface of nanofibers. The BC template can

Table 1
The in situ preparation of metal nanoparticles using BC as the template through reduction reaction.

Reducing agent	Reference	Metal NPs	Particle size (nm)	Content (%, w/w)	Application
BC	Yang, Xie, Deng, et al. (2012)	Ag	17.1 ± 5.9	1.78	Artificial skin; wound dressings; food packaging; water treatment; anti-counterfeiting; bio-sensing; catalysis; textiles
$NaBH_4$	Yang, Xie, Hong, et al. (2012)		5–14	0.86–1.60	
Ascorbic acid +Gelatin	Maria et al. (2009)		70–100	50–70	25.0	19.6	
+PVP				20–50		6.0	
NH_2NH_2 +Gelatin			>100	40–60	22.4	4.9	
+PVP				80–100		4.9	
NH_2 OH +Gelatin			>100	30–50	–	7.8	
+PVP				70–100		8.0	
Oxidized BC	Ifuku et al. (2009)		10–20		–		
triethanolamine	Barud et al. (2008)		~8.5		21		
PEI	Zhang et al. (2010)	Au	~9		65.4		Biosensing; catalytic; electronic devices; drugs and protein release; smart clothing
$NaBH_4$	Cai, Kimura, Wada, and Kuga (2009)		7.0 ± 3.2		–		
$NaBH_4$	Cai et al. (2009)	Pt	5.6 ± 2.3		19.2		Catalytic
HCHO	Yang, Sun, Li, Yang, and Yu (2009)		~3.9		14.4%		
$NaBH_4$	Pinto, Neves, Neto, and Trindade (2012)	Cu	~36		–		Antibacterial; catalytic
KBH_4	Zhou et al. (2012)	Pd	~20		8.15%		Catalytic

also be removed by calcination to obtain hollow nanofibers with a three-dimensional network structure.

TiO_2/BC hybrid composites were prepared using BC as a hydrophilic substrate for synthesizing TiO_2 nanoparticles via sol–gel (Gutierrez, Tercjak, Algar, Retegi, & Mondragon, 2012) as shown in Fig. 12. The spherical TiO_2 nanoparticles with an average size of 25 nm in diameter were located on the surface of the nanofibers due to hydrogen bonding interactions. The BC template could also be removed in order to change or optimize the properties of the in situ formed nanomaterial. The process also can make use of the synergy between the BC template and inorganic materials to synthesize a variety of nanoscale metal oxides with the hollow network. Mesoporous titania networks consisting of interconnected anatase nanowires typically 20–30 nm in diameter have been synthesized by using BC as natural biotemplates through the sol–gel titania coating (Zhang & Qi, 2005). The titania networks exhibit enhanced photocatalytic activity due to the larger accessible surface areas.

2.4. Ex situ introduction of components

The functional BC-based nanocomposites can also be formed through the ex situ introduction of different components by the solution impregnation method. BC nanocomposites loaded with nano-scale silica nanoparticles have been prepared by immersing BC hydrogel into different concentrations of silica sols, allowing nano scale silica to be trapped and fixed in the spaces between the ribbon-shaped fibrils in the BC hydro-gel matrix (Fig. 13) (Ashori, Sheykhnazari, Tabarsa, Shakeri, & Golalipour, 2012; Maeda, Nakajima, Hagiwara, Sawaguchi, & Yano, 2006; Yano et al., 2008). This method improved the modulus and strength compared to the pure BC matrix, but it was difficult to load the BC with more than 10% silica in this way.

This strategy also can utilize the nanoeffect of the ribbon-shaped fibrils of BC to prepare optically transparent materials. Transparent poly(L-lactic acid) (PLLA)/BC nanocomposites was prepared by incorporating microbial nanofibrils into PLLA matrix (Kim, Jung, Kim, & Jin, 2009). The nanocomposite retained the transparency of the pure PLLA film due to the nanofibrillar structure of the BC, which is smaller than the wavelength of visible rays. An increase in the mechanical properties was observed by incorporating BC as reinforcement into the PLLA matrix. The highly translucent bionanocomposites have been prepared by simply incorporating BC into the pullulan or poly(3-hydroxybutyrate) (PHB) matrix (Trovatti et al., 2012; Zhijiang & Guang, 2011; Zhijiang, Guang, & Kim, 2011) (Fig. 14a and b), which have improved the mechanical performance and thermal stability of the nanocomposite films. Novel nanocomposite films based on chitosan and BC were prepared by a fully green procedure by casting a water based suspension of chitosan and BC nanofibrils (Fernandes et al., 2009). They were highly transparent, flexible and displayed better mechanical properties than the corresponding unfilled chitosan films (Fig. 14c). These new renewable nanocomposite materials also presented reasonable thermal stability and low O_2 permeability.

2.5. Other combined strategies

In most cases, we can adopt the combined strategies mentioned above to obtain the nanocomposites with designed structures and required performance. The hydrophobic BC-based nanocomposite sheets can be produced by the in situ synthesis of BC/CNTs nanocomposite by biosynthetic modification and the subsequent heterogeneous acetylated surface modification (Adnan & Radiah Awang Biak, 2012). The epoxidized soybean oil (ESO)/BC nanofibers have been prepared through the acetylated modification and the following solution impregnation in the ESO resin (Retegi et al.,

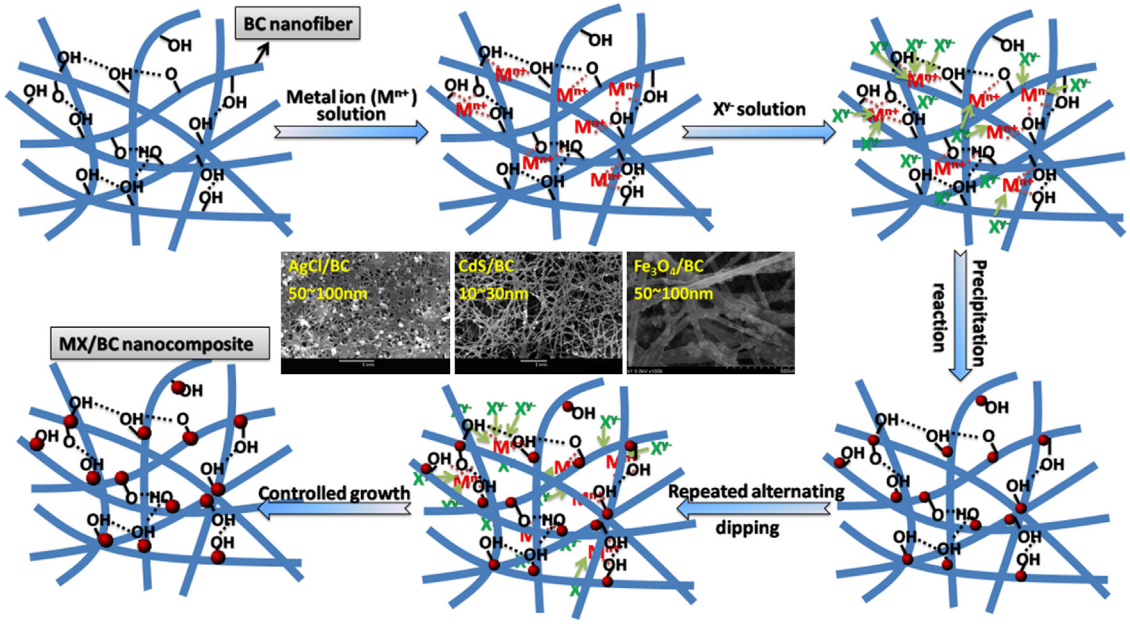

Fig. 7. Schematic diagram of the in situ preparation of nanoparticles onto the BC nanofibers through the precipitation reaction (Hu et al., 2009; Li et al., 2009a; Zhang et al., 2011).

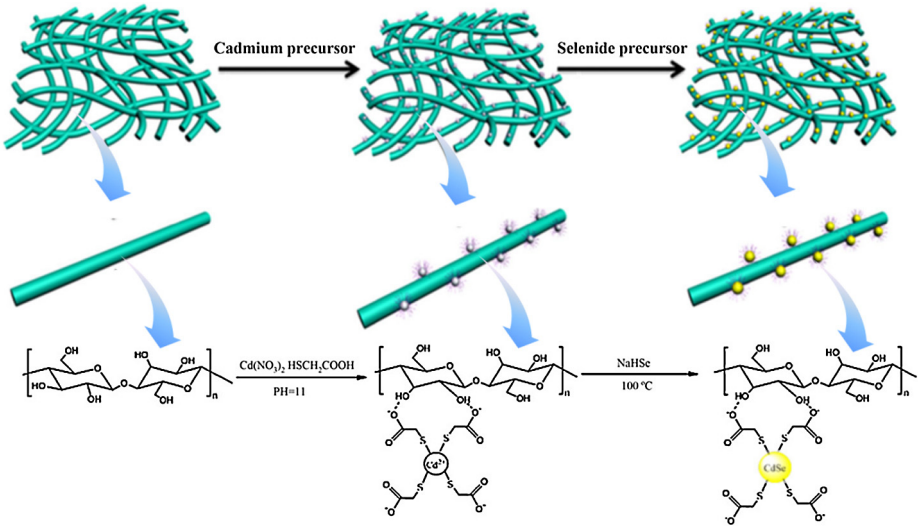

Fig. 8. Schematic diagram of the formation of CdSe/BC nanocomposite (Yang et al., 2012a).

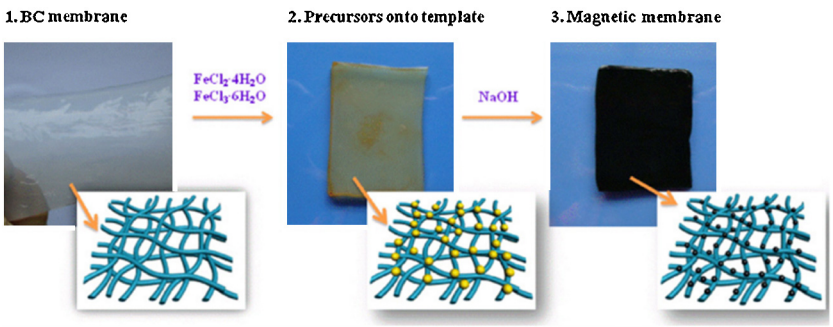

Fig. 9. Schematic illustration for the flexible magnetic nanohybrid membrane (Zhang et al., 2011).

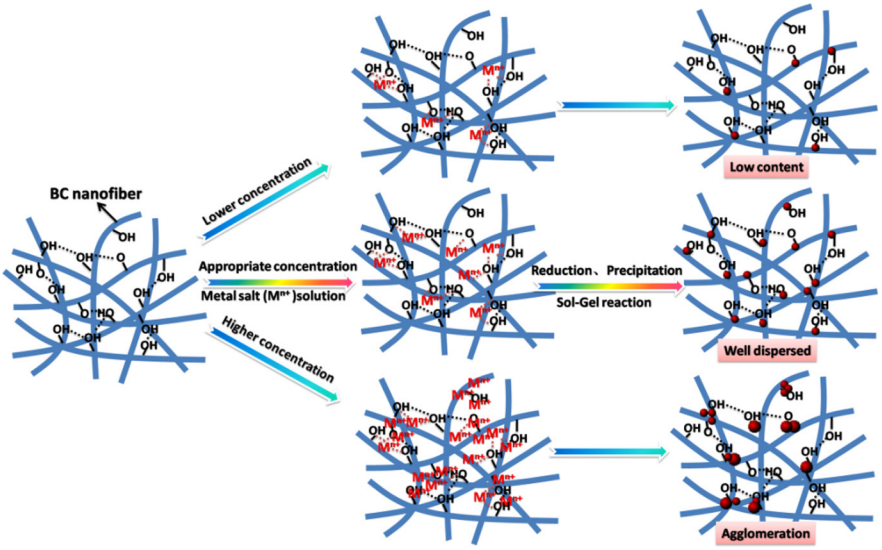

Fig. 10. Schematic diagram of the effect of different concentrations of metallic ions on the size and size distribution of the in situ formed nanoparticles.

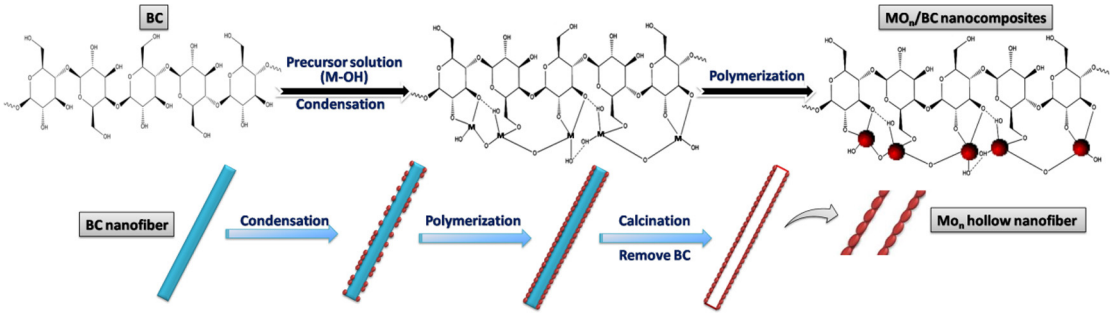

Fig. 11. Schematic diagram of the in situ preparation of inorganic hollow nanofibers using BC as a template through the sol–gel reaction (Hu et al., 2009; Li et al., 2009a; Zhang et al., 2011).

2012). An electromagnetic composite of BC has been synthesized by culturing *Gluconacetobacter xylinus* in a medium containing magnetite nanoclusters (MNP) and the subsequently in situ formation of PANI on the magnetic BC fibers by chemical oxidative polymerization with ammonium persulfate (APS) as the oxidant (Fig. 15) (Park, Cheng, Choi, Kim, & Hyun, 2013).

For BC to be suitable as a more effective nanoreactor to control the formation of nanomaterials, the chemical functionalization should be employed to modify the BC fibers for imparting BC membranes with new functionalities and producing BC nanocomposites with tailored characteristics. The Am-BC as host matrix can stably anchor numerous zinc ions and then as nanoreactors to fabricate ZnO nanoparticles by hydrolysis of zinc acetate in a polyol medium to form the ZnO/Am-BC nanocomposites as shown in Fig. 16. The TEMPO-mediated oxidized BC nanofibers has been applied as reaction templates to prepare fine silver nanoparticles with a controlled size distribution (Ifuku et al., 2009). The amidoximation and oxidation of BC can provide more reactive sites to immobilize the formed nanoparticles with high density, which are important factors for electronic, catalytic, and biomedical applications.

Thus, the functional nanostructures can be achieved by in situ formation of nanoparticles or ex situ introduction of components into the biosynthetically or chemically modified BC matrix. At the same time, the fabrication steps can be adjusted or even reversed to construct the BC-based functional nanomaterials with controllable structures and designed functional performance.

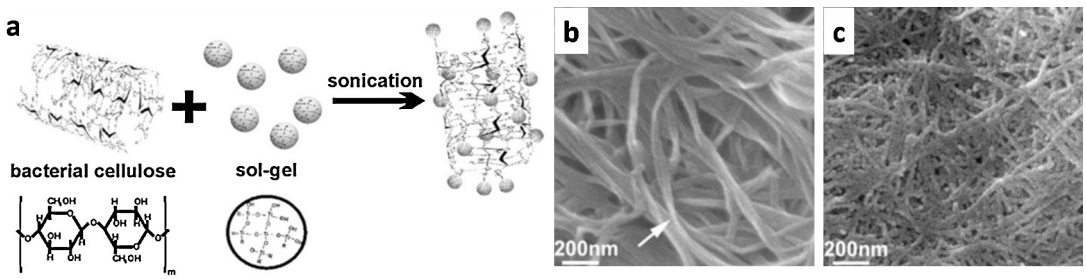

Fig. 12. (a) Illustration of the synthesis of TiO_2/BC composites (Gutierrez, Tercjak, et al., 2012). (b) SEM images of BC-titania hybrid membranes, and (c) titania networks templated by BC membranes (Zhang & Qi, 2005). The arrow indicates the twisted structure of ribbon-like nanofibers.

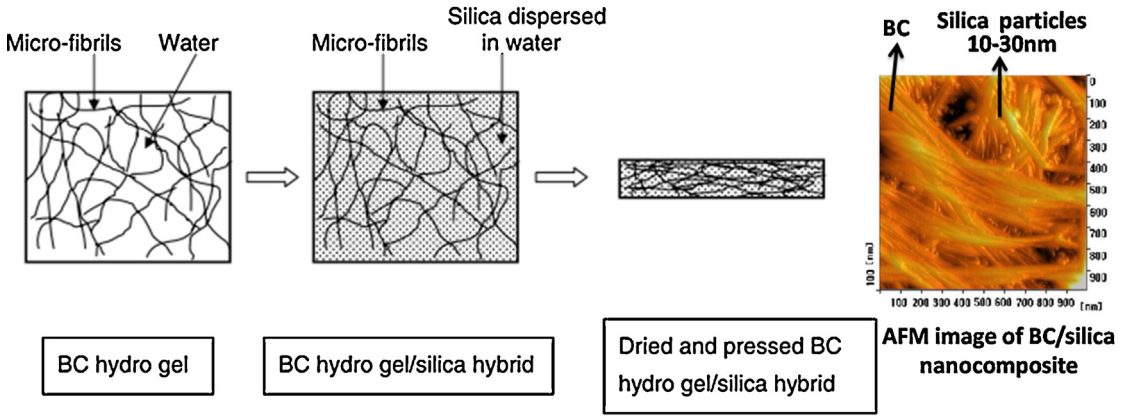

Fig. 13. Preparation process and AFM image of BC/silica composites by the solution impregnation method (Ashori et al., 2012; Yano et al., 2008).

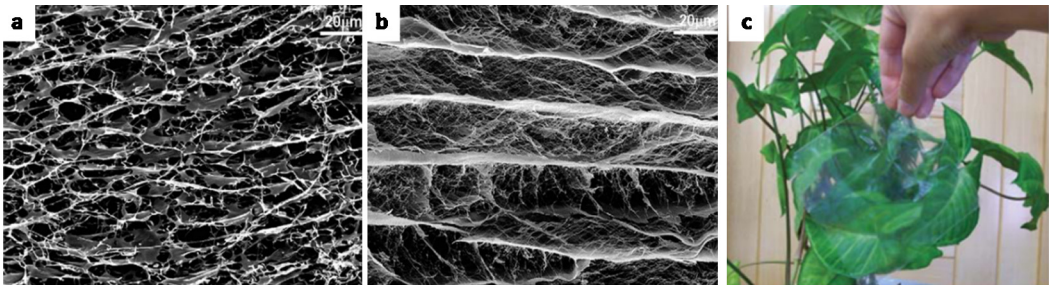

Fig. 14. FESEM images of PHB/BC nanocomposite: (a) surface morphology, and (b) cross-section morphology. (c) Image of chitosan and BC nanocomposite films placed in front of a green plant (Trovatti et al., 2012; Zhijiang & Guang, 2011; Zhijiang et al., 2011).

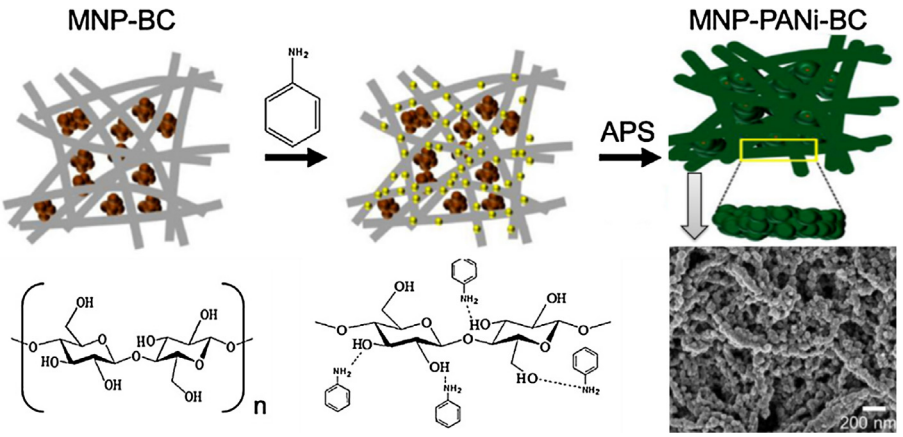

Fig. 15. Schematic diagram of the preparation of electromagnetic BC nanocomposites (Park et al., 2013).

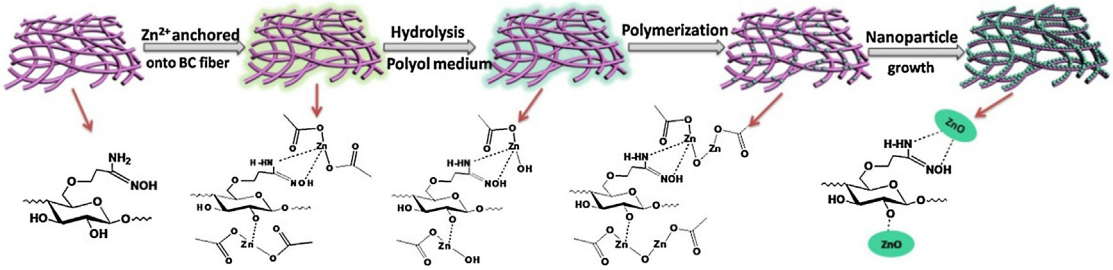

Fig. 16. Schematic diagram of the formation of ZnO nanoparticles onto nanofibers of Am-BC membrane.

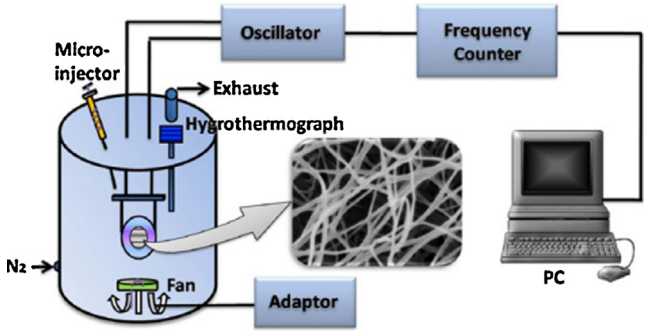

Fig. 17. Schematic of the experimental setup for humidity and gas detection (Hu, Chen, Zhou, et al., 2011).

3. Applications of BC-based functional nanomaterials

BC has been recently investigated as an attractive eco-friendly nanomaterial for the preparation of high value-added nanocomposites. The functionalization of BC with inorganic or polymeric materials opens up new pathways for the fabrication of novel multifunctional nanocomposites with promising performances. BC was used as a template for the preparation of novel functional nanocomposites that gather together excellent properties of BC with the ones displayed by typical inorganic or organic nanomaterials like antibacterial, optical, electrical and magnetic properties, as well as catalytic and biomedical activity. Several recent reviews giving a summary and discussion regarding the applications of BC-based materials as medical devices or reinforcement materials for polymer nanocomposite have been published (Eichhorn et al., 2010; Klemm et al., 2011; Petersen & Gatenholm, 2011). Here we reviewed the potential advantages and different applications of BC based functional nanomaterials, which mainly focus on the application such as sensors, photocatalytic nanomaterials, optoelectronic materials and devices, and magnetically responsive membranes.

3.1. Sensors

BC can be considered as prime material or substrate material for the construction of high-performance moisture or gas sensor due to their large specific surface areas, a large number of surface hydroxyl groups, good water absorbance and water holding capacity. With the combination of quartz crystal microbalance (QCM) system (Fig. 17), the BC nanofibrous membrane coating can be a good consideration for constructing highly sensitive humidity and gas sensors. The BC dispensed onto the surface of the QCM electrode was installed in the testing chamber. Through injecting water or gas into the chamber, the sensing properties of the sensors were examined by measuring the resonance frequency shifts of QCM due to the additional mass loading. A highly stable and sensitive humidity sensor based on BC coated QCM has been fabricated (Hu, Chen, Zhou, et al., 2011). The results showed that the sensors possessed good sensing characteristics by increasing more than two orders of magnitude with increasing relative humidity (RH) from 5 to 97%, and the Log(Δf) showed good linearity (20–97% RH). The resultant sensors exhibited a good reversible behavior and good long term stability.

By introducing other detective components to the BC substrate, the modified nanoporous BC membranes with the high specific surface area and high porosity would be an ideal candidate for further improving the sensitivity of gas sensors. A formaldehyde sensor based on nanofibrous PEI/BC membranes coated QCM has been fabricated (Hu, Chen, Liu, Ding, & Wang, 2011). PEI has been introduced as the detective material to strengthen the interaction between the sensing materials and formaldehyde molecules as shown in Fig. 18. The sensor showed high sensitivity with good linearity and exhibited a good selectivity and repeatability toward formaldehyde in the concentration range of 1–100 ppm at room temperature. It has a detection limit of 1 ppm which is enhanced compared to other nanostructured coatings because of the large specific surface area of the sensing materials. This strategy also can be applied in other system to introduce various detective materials combined with BC nanofibers to detect other gases.

BC with the ultrafine nanofibrous network, high stability, excellent biocompatibility and extensive surface area, would be a very promising support for the construction of biosensors. The gold nanoparticles–BC nanofibers (Au-BC) nanocomposite has been synthesized and used for enzyme immobilization and glucose biosensor fabrication (Wang et al., 2010, 2011; Zhang et al., 2010). The developed biosensor based on horseradish peroxidase (HRP)/Au-BC nanocomposite exhibited excellent performance in terms of a wider linear range, lower limit of detection (lower than 1 μm) and fast response toward hydrogen peroxide (Zhang et al., 2010) (Fig. 19), suggesting the Au-BC nanocomposite a suitable matrix for enzyme immobilization. The biosensor for glucose exhibits a detection limit as low as 2.3 mM with a linear range from 10 mM to 400 mM, which could be used to monitor glucose in real blood samples (Wang et al., 2010).

3.2. Photocatalytic nanomaterials

BC can be viewed as a template with the main controlling sites made up of hydroxyl and ether bonds to guide the synthesis of photocatalytic nanoparticles or nanocomposites. Well-dispersed and regular ZnO nanoparticles with a narrow size distribution of 20–50 nm and high photocatalytic activity have been successfully synthesized through decomposing BC infiltrated with zinc acetate aqueous solution at high temperature (Hu, Chen, Zhou, & Wang, 2010). In addition, the photocatalytic ZnO/BC and ZnO/Am-BC nanocomposite membranes can be synthesized through a facile polyol method using BC or Am-BC as a template (Chen et al., 2013). The resulting nanocomposites containing ZnO nanoparticles with a uniform distribution and an average diameter of 50 nm show good mechanical properties and high photocatalytic activity in the degradation of methyl orange. Compared to the ZnO/BC nanocomposite films, the ZnO/Am-BC nanocomposites with higher loading content of ZnO nanoparticles displayed a higher decolorization efficiency of 91% at 120 min, indicating an excellent candidate for photocatalyst.

The photocatalytic mesoporous TiO_2/BC hybrid nanofibers have been fabricated by surface hydrolysis with molecular precision (Sun, Yang, & Wang, 2010). The uniform and well-defined nanofibers consist of large quantities of oriented TiO_2 nanoparticle arrays implanted on the BC nanofibers with diameters in the 4.3–8.5 nm range. The TiO_2/BC nanocomposites were used as photocatalyst for methyl orange degradation under UV irradiation, and they showed higher efficiency than that of the commercial photocatalyst due to the high surface area of 208.17 m^2/g. Furthermore, the photocatalytic ability can be improved by doping with nitrogen. The BC template also can be removed by calcinations to obtain the mesoporous TiO_2 networks consisting of interconnected anatase nanowires (Zhang & Qi, 2005). The mesoporous titania networks exhibit a considerably enhanced photocatalytic activity compared with the macroporous titania networks obtained through a similar sol–gel nanocasting procedure.

The photocatalytic micrometer-long CdS/BC hybrid nanofibers have been prepared via a simple hydrothermal reaction at relatively low temperature (Yang et al., 2011). Hexagonal phase CdS nanoparticles were homogeneously deposited onto the hydrated BC nanofibers and stabilized via coordination effect. The CdS/BC

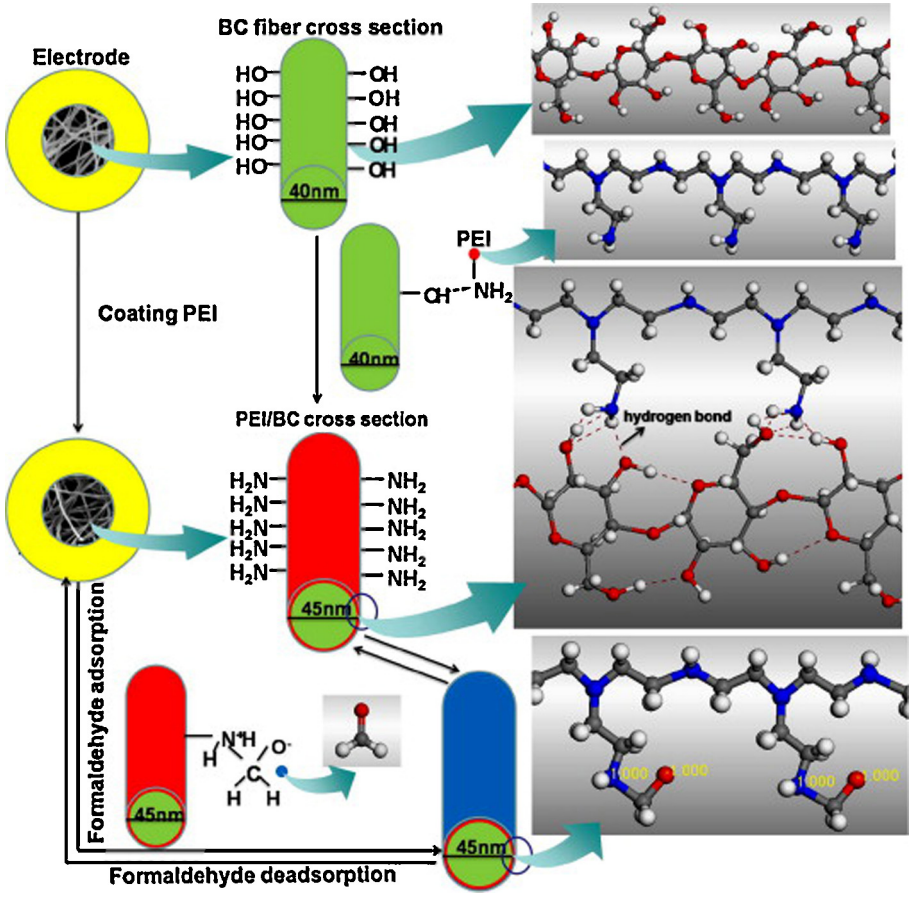

Fig. 18. Schematic diagram of the interaction of BC and PEI, and formaldehyde and PEI (Hu, Chen, Liu, et al., 2011).

hybrid nanofibers demonstrated high-efficiency photocatalysis with 82% methyl orange degradation after 90 min irradiation and good recyclability. The results indicate that the CdS/BC hybrid nanofibers are promising candidate as robust visible light responsive photocatalysts.

3.3. Optoelectronics

BC-based electro conductive composites can be prepared by combining conducting electroactive materials with hydrophilic biocompatible BC. These conductive materials including metal ions and oxides, carbon nanotubes and conducting polymers in the form of nanoparticles or nanowires can be introduced into the BC matrix by in situ synthesis, doping, blending or coating.

3.3.1. Electrically conductive films

The MWCNTs-incorporated BC was prepared by dipping a BC pellicle in an aqueous MWCNT dispersion containing a cetyl trimethyl ammonium bromide (CTAB) surfactant (Yoon, Jin, Kook, & Pyun, 2006). This composite process produced electrically conducting BC pellicles containing well-dispersed and embedded MWCNTs as shown in Fig. 20a. The electrical conductivity of the BC/MWCNT composite was found to be approximately 1.4×10^{-1} S/cm. The transparency of the MWCNTs-incorporated

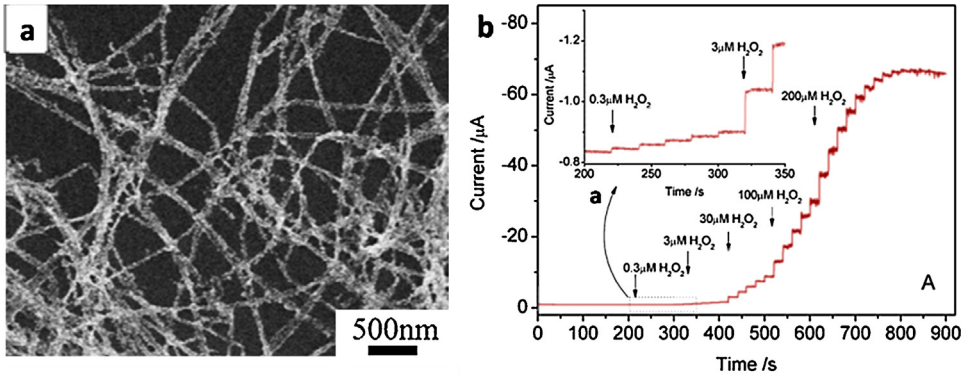

Fig. 19. (a) The SEM image of Au-BC nanocomposite. (b) Amperometric response curves of HRP/Au-BC/glassy carbon electrode for successive additions of different concentrations of H_2O_2 in stirring phosphate buffer (pH 7.4) containing 0.5 mM hydroquinone (HQ) at the applied potential of −150 mV. The inset shows the amperometric response at time range from 200 s to 350 s (Zhang et al., 2010).

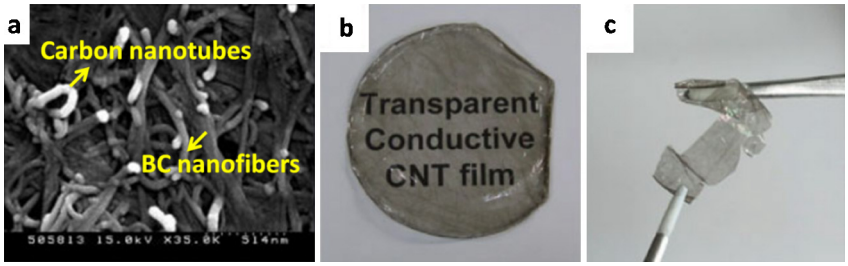

Fig. 20. (a) FESEM image of surface of the MWCNTs-incorporated BC pellicle (Yoon et al., 2006). Optical photographs of (b) electrically conductive transparent paper, and (c) flexibility of the electrically conductive transparent paper (Jung et al., 2008).

BC can also be improved by incorporating an aqueous silk fibroin solution into BC membranes to obtain an electrically conductive transparent paper (Fig. 20b) (Jung et al., 2008). Good optimal transparency and electrical properties were obtained with a transmittance of 70.3% at 550 nm and electrical conductivity of 2.1×10^{-3} S/cm. This strategy can also be applied in the preparation of single-walled carbon nanotubes (SWCNTs) adsorbed BC membranes to obtain the transparent conducting film with a transmittance of 77.1% and surface resistance of 2.8 kΩ/sq (Kim, Kim, et al., 2009). The resultant electrically conductive transparent films showed remarkable flexibility without any loss of their initial properties (Fig. 20c). Thus, the prepared electrically conductive paper can be applied as a transparent electrode in photoelectronics such as flexible displays and touch screens.

Recently, the polyaniline (PANI)/BC and polypyrrole (PPy)/BC composites have been intensively researched (Hu, Chen, Yang, Liu, & Wang, 2011; Lee, Kim, & Yang, 2012; Marins et al., 2011; Muller, Rambo, Recouvreux, Porto, & Barra, 2011; Wang, Bian, Zhou, Tang, & Tang, 2013). Our group has fabricated conductive PANI/BC nanocomposite membranes by oxidative polymerization of aniline with ammonium persulfate as an oxidant and BC as a template (Hu, Chen, Yang, et al., 2011). The schematic diagram of the formation of PANI/BC nanocomposites is shown in Fig. 21. It was found that the PANI nanoparticles deposited on the surface of BC connected to form a continuous nanosheath by taking along the BC template, and the conductivity could be enhanced when PANI is doped by protonic acids. The resulting PANI-coated BC nanofibrils exhibit excellent electrical conductivity of 5.0×10^{-2} S/cm and good mechanical properties with Young's modulus of 5.6 GPa and tensile strength of 95.7 MPa. The electrical conductivity of PANI/BC composites can be further improved to 3.8×10^{-1} S/cm by adopting the interfacial polymerization (Lee, Chung, Kwon, Kim, & Tze, 2012). Furthermore, by using $FeCl_3 \cdot 6H_2O$ as oxidant, the free-standing films of PANI/BC composites with high electrical conductivity values (0.9 S/cm) and PPy/BC with outstanding electrical conductivities as high as 77 S/cm were prepared through the in situ oxidative chemical polymerization of aniline or pyrrole on the surface of BC nanofibers (Müller et al., 2012; Wang et al., 2013). The nanocomposites synergistically combine the electronic characteristics of PANI or PPy with the outstanding mechanical characteristics of the BC matrix, which could be applied in flexible electrodes, flexible displays and other electronic devices.

3.3.2. *Optically transparent films*

BC has been applied as the flexible substrate for the fabrication of organic light emitting diodes (OLEDs) by depositing indium tin oxide (ITO) thin films onto the BC membrane at room temperature using radio frequency magnetron sputtering (Legnani et al., 2008). However, the average transmittance of BC membrane substrates at 550 nm is only 40%. Thus many researchers have made efforts to improve the clarity of BC. BC comprising weblike networks of ribbon-shaped nanofibers has high tensile strength and low coefficient of thermal expansion (CTE) of less than 0.1 pp/K in the axial direction, which is a perfect candidate to reinforce transparent plastics (Yano et al., 2005). The transparent BC/epoxy resin and BC/acrylic resin composites have been fabricated at a fiber content as high as 70%, which showed a incredibly low CTE of 3 pp/K (similar to that of silicon crystal) and a high tensile strength (325 MPa), while maintaining the flexibility and ductility of the resin plastics as shown in Fig. 22 (Yano et al., 2005). Furthermore, due to the nanofiber size effect, the high transparency was demonstrated for several different resins with a wide distribution of refractive indexes, from 1.492 to 1.636 at 20 °C (Shah & Brown, 2005). The optical transparency was also insensitive to temperature up to 80 °C. The hygroscopicity of BC nanocomposites also have been significantly reduced by using acetylated BC nanofibers to improve the dimensional stability against temperature while maintaining optical transparency and thermal stability (Ifuku et al., 2007; Nogi et al.,

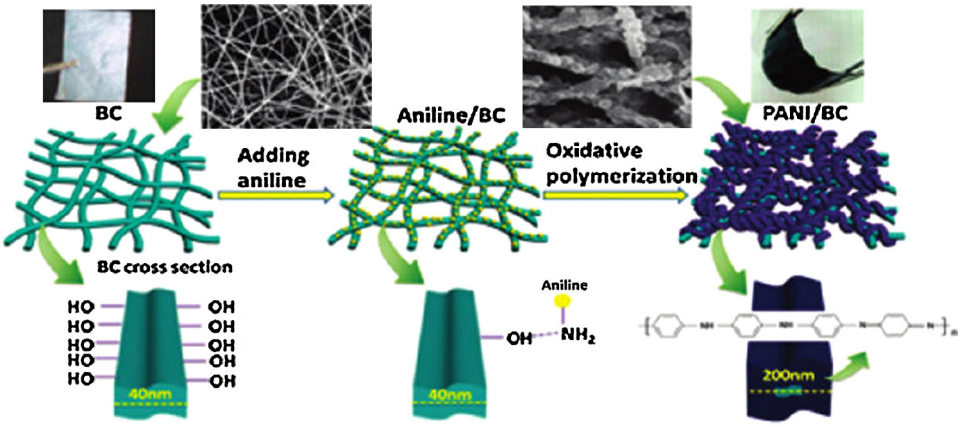

Fig. 21. Schematic diagram of the formation of PANI/BC nanocomposites (Hu, Chen, Yang, et al., 2011).

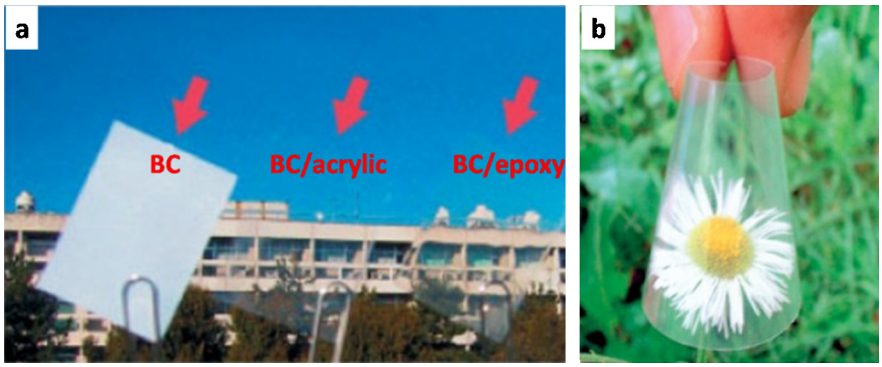

Fig. 22. (a) Appearance of 65 μm thick BC, BC/acrylic resin and BC/epoxy resin sheets. (b) Flexibility of a 65 μm thick BC/acrylic resin sheet (Yano et al., 2005).

2006). These nanofiber-network-reinforced optically transparent composites are expected to lead the way to a wider use of many different optically transparent polymers in optoelectronic devices such as substrates for flexible displays and components for precision optical devices, which demand high transparency and low thermal expansion.

3.3.3. Flexible displays

Flexible displays have been produced by using BC as the substrate or the basic optical film to improve their electronic properties. For the fabrication of OLED, the hygroscopicity and surface roughness of BC needs to be adjusted. The Si—O thin film can be deposited on BC surface via plasma enhanced chemical vapor deposition as transparent barrier against water vapor (Ummartyotin, Juntaro, Sain, & Manuspiya, 2011). The deposited Si—O layer offered uniform and exceptionally smooth surface with the surface smoothness of 15 nm. The surface roughness of BC can be further reduced to 5 nm by using the ferrofluid solution as nano-abrasion media (Ummartyotin, Juntaro, Sain, & Manuspiya, 2012b). Nanocomposite film composed of BC (10–50 wt.%) and polyurethane (PU) based resin was fabricated and utilized as a substrate for flexible OLED display (Ummartyotin, Juntaro, Sain, & Manuspiya, 2012a). The visible light transmittance of the nanocomposite film was as high as 80%. Its thermal stability was stable up to 150 °C while its dimensional stability in terms of CTE was less than 20 ppm/K. After OLED was fabricated on the substrate through thermal evaporation technique, the OLED performed highest current efficiency of 0.085 cd/A and power efficiency of 0.021 lm/W at 200 cd/m^2 while retaining its flexible feature as shown in Fig. 23, suggesting that BC nanocomposite is a promising material for the development of substrate for flexible OLED display.

3.3.4. Photoluminescent and photochromic films

For BC to be suitable for more diverse optoelectronic applications, some of its properties need to be modified such as endowing it the photoluminescent and photochromic properties. Manipulating the different methods to obtain the functional BC can be a useful approach for finetuning BC properties to satisfy appropriate applications or producing BC composites with tailored characteristics. To design and synthesize BC-based new materials is also more significant in exploring new applications for the unique natural nanofibers. Flexible luminescent CdSe/BC and CdS/BC membranes have been fabricated by the in situ synthesis of the CdSe and CdS nanoparticles on the BC nanofibers (Li et al., 2009b; Yang et al., 2012b). The formed nanoparticles with a size of 20–30 nm were homogeneously dispersed in the BC matrix. The nanocomposites exhibited good photoluminescence properties and excellent mechanical properties as shown in Fig. 24. This work provides an effective method for the construction of flexible BC membranes with photoluminescence properties, which are promising for applications in optics, electronics and biology.

The photochromic BC nanofibrous membranes containing 10,30,30-trimethyl-6-nitrospiro(2H-1-benzopyran-2,20-indoline) (NO_2SP) were successfully prepared by surface modification of BC nanofibers with spiropyran photochromes (Hu, Liu, Chen, & Wang, 2011) or in situ incorporation of sol–gel synthesized photoswitchable vanadium nanoparticles using BC as a template (Gutierrez, Fernandes, Mondragon, & Tercjak, 2012). The modified BC-NO_2SP membranes exhibited a pink color and had an absorption peak at 568 nm in the UV–visible spectrum and the color change was reversible due to the reversible isomerization of the spiropyran moieties in BC-NO_2SP as shown in Fig. 25. Alternating illumination with UV-and-visible light switches the fluorescence of the membranes on and off and makes the wetting properties

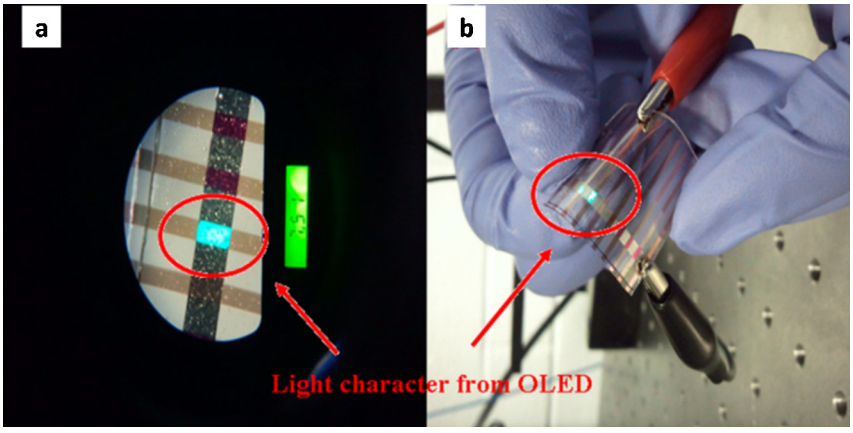

Fig. 23. OLED on BC nanocomposite (Ummartyotin et al., 2012a).

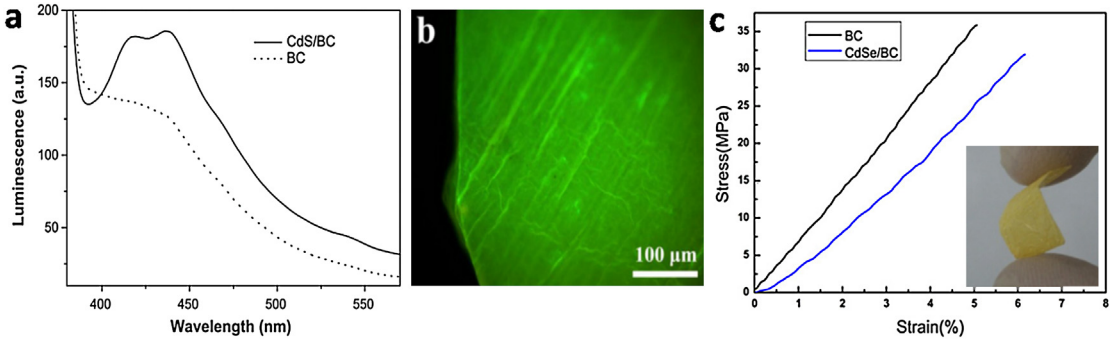

Fig. 24. (a) PL spectra of BC and CdS/BC nanocomposite with excitation wavelength at 370 nm (Li et al., 2009b). (b) Micrograph of the CdSe/BC nanocomposite membrane with excitation (Yang et al., 2012a). (c) Tensile stress–strain behaviors of pure BC and CdSe/BC nanocomposite membrane, inset is the photograph of the CdSe/BC nanocomposite membrane (Yang et al., 2012a).

of the membranes controllable, confirming that such modified BC membranes have potential application in sensitive displays and optical devices. The addition of vanadium nanoparticles led to the generation of photochromic nanopaper, which was able to reversibly switch the color from green to dark purple by irradiation under ambient conditions. Moreover, the flexible, conductive, and optically active photochromic hybrid nanopapers maintained the semiconductive properties of the well-dispersed vanadium oxide nanoparticles.

3.4. Magnetically responsive films

In recent years, the hybrid nanocomposites consisting of BC nanofibers and magnetic nanoparticles have attracted much attention due to their potential novel applications in biomedicine, security papermaking and packaging. The incorporation of the magnetic nanoparticles with controllable collective magnetic properties can endow BC with new functionalities. The magnetically responsive BC sheets containing Fe_3O_4 nanoparticles were prepared by using an ammonia gas-enhancing in situ co-precipitation method operated in a closed system without oxygen (Katepetch & Rujiravanit, 2011). The homogeneous dispersion of the magnetic nanoparticles throughout the BC matrix could enhance the percent incorporation of magnetic nanoparticles into BC samples, leading to high and uniform magnetic properties. The saturation magnetization of the magnetic nanoparticle-incorporated BC sheet ranged from 1.92 to 26.20 emu/g with very low remnant magnetization (0.15–2.67 emu/g) and coercive field (40–65 G) at the room temperature. The fluoroalkyl silane (FAS) modification on the magnetic Fe_3O_4/BC membrane can convert the surface wettability of BC membrane from amphiphilicity to amphiphobicity (Zhang et al., 2011) (Fig. 26). The fluorinated membrane with appropriate roughness showed the highest water contact angle (WCA) of 130° and oil contact angle (OCA) of 112°. Additionally, the membranes exhibited the superparamagnetic behavior and can be magnetically actuated. Magnetically responsive BC membrane with hydrophobic and lipophobic surface would have potential applications in electronic actuators, magnetographic printing, information storage, electromagnetic shielding coating and anti-counterfeit.

The BC-based magnetic nanocomposite has been constructed that enables tunability from highly porous, flexible, magnetically actuating aerogel to solid and stiff magnetic nanopaper with high particle loading as shown in Fig. 27 (Olsson et al., 2010). Magnetic ferromagnetic cobalt ferrite nanoparticles (diameter, 40–120 nm) were precipitated on a BC hydrogel, and the porosity of the resulting dried nanocomposite was controlled from 98% (upon removal of water during freeze-drying) in the aerogel to 10% (upon compaction) in the nanopaper (Fig. 27a and b). The lightweight porous magnetic aerogel can be actuated by a small household magnet as shown in Fig. 27c. Moreover, it can absorb water and release it upon compression (Fig. 27d). Owing to their flexibility, high porosity and surface area, these aerogels are expected to be useful in microfluidics devices and as electronic actuators.

In addition, the magnetically responsive BC can also been provided by precipitation of ferromagnetic Ni nanoparticles with the size of 10–60 nm by room temperature chemical reduction of Ni-chloride hexahydrate (Vitta, Drillon, & Derory, 2010). The Ni loaded BC exhibits a complex magnetic behavior with characteristics of

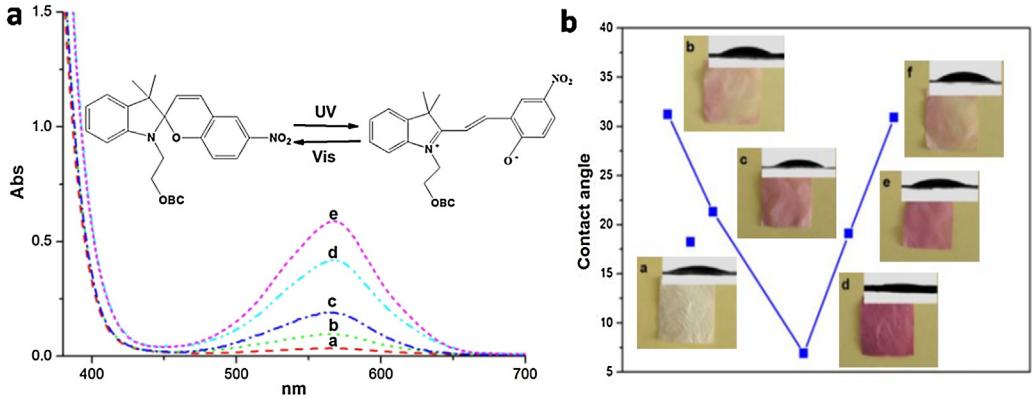

Fig. 25. (a) The UV–visible spectra of BC-NO_2SP membrane (0.06 wt.% SP) under different irradiation time at 365 nm UV light conditions: (a) before UV irradiation, (b) after UV 10 s, (c) after UV 30 s, (d) after UV 60 s, and (e) after UV 120 s. The inset shows a sketch of the immobilized spiropyran that undergoes conversions to merocyanine form and back under UV and visible irradiation, respectively. (b) BC membrane and the BC-NO_2SP membranes (0.06 wt.% SP) after being treated by UV irradiation for (b) 0 s, (c) 30 s and (d) 60 s; (e and f) were the membrane recovered in the dark for 10 and 30 min after irradiated by UV light for 60 s (Hu, Liu, et al., 2011).

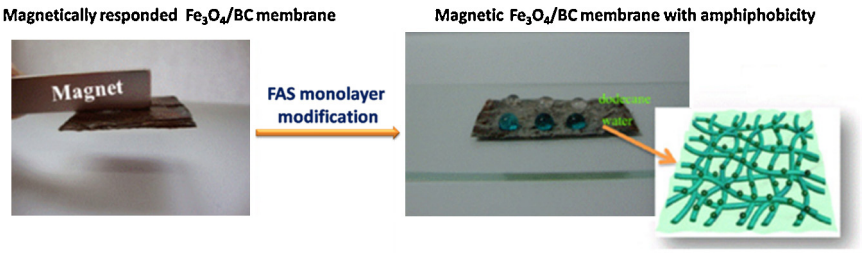

Fig. 26. The flexible magnetically responded Fe_3O_4/BC nanohybrid membrane with amphiphobic surface after FAS modification (Zhang et al., 2011).

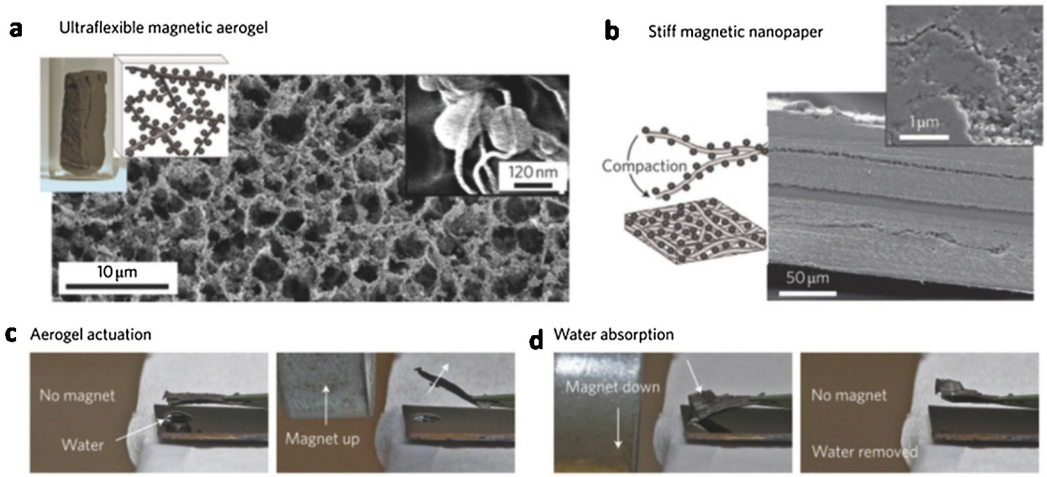

Fig. 27. (a) Representative SEM image of a 98% porous magnetic aerogel containing cobalt ferrite nanoparticles after freeze-drying. Insets: photograph and schematic of the aerogel. Right inset: nanoparticles surrounding the nanofibrils. Left insets: photograph and schematic of the aerogel. (b) SEM image of a stiff magnetic nanopaper obtained after drying and compression. Inset: higher magnification image. (c) A piece of magnetic aerogel is held using tweezers (left panel). Applying a small household magnet bends the magnetic aerogel upwards (right panel). (d) The magnetic aerogel bends downwards in response to the magnet and absorbs the water droplet below (left panel). The aerogel recovers its original shape upon removal of the magnet (right panel) (Olsson et al., 2010).

both superparamagnetism and ferromagnetism. The magnetization data shows superparamagnetism with a blocking temperature of ~20 K. The hysteresis of magnetization on the other hand, even at room temperature, clearly indicates that a ferromagnetic phase always coexists together with the superparamagnetic phase. This work clearly shows that the Ni loaded BC can be used both for nonbiological applications such as magnetic printing and biological applications such as magnetic tissue scaffolds.

4. Concluding remarks

Looking over the studies summarized in this article, the different biosynthetic or chemical modification and incorporation of various guest substrates into BC matrix bring up new opportunities for the development of novel nanostructured materials with designed functionalities. By combining the unique physicochemical properties of BC and optical, electronic and magnetic features of guest substrates, the significant synergetic effects can be observed, aiming at the advance of a great variety of advanced BC-based nanomaterials. The development and challenges of BC in functional nanomaterial application in the future include several aspects as follows.

First, it is very meaningful to conduct a systematic study of electrochemical and surface properties of BC, especially the investigation of the accurate accessible hydroxyl groups on the surface of BC nanofiber under different conditions. This is an interesting and significant topic deserving study, which can establish the reaction model system to design and simulate the in situ preparation of diversified functional nanomaterials according to the application requirements, fulfilling the controllable preparation of different nanostructures on the molecular level. It should be noted that the analysis and investigation of these inherent properties can greatly support and promote their application in the field of functional nanomaterials. Meanwhile, the more economical and environmentally friendly controllable methods should be developed to modify the surface of nanocellulose while preserving the nanostructural morphology and excellent mechanical properties. The thermal stability of BC can also be improved by choosing the appropriate modification methods, which can facilitate the processability and application of BC on a higher level and broader scope, such as high-temperature filter, catalytic carrier, and porous electrode materials.

In addition, all the applications of BC in the field of functional nanomaterials are based on their inherent physicochemical properties, such as remarkable mechanical properties, porosity, water absorbency, moldability, biodegradability, excellent biological affinity, and so on. Therefore, these unique properties should be utilized to the fullest with contributions from multidisciplinary areas like physics, chemistry, materials science and medicine to construct novel advanced functional BC-based nanomaterial system which can greatly expand the application field of BC nanomaterials. In particular, derived from the unique three-dimensional network and the interactions between formed nanoparticle and cellulosic nanofibers, BC or modified BC can be potentially useful in the application of some special nanomaterials, such as stimulus-responsive and maintenance-free self-healing materials. However, it should be pointed out that the current research on BC in the field of functional nanomaterials is still largely confined to the laboratory. Increasing attention should be devoted to produce BC in larger quantities at low cost, and to explore various construction strategies that enhance the properties of BC, making it attractive for use in a wide

range of industrial sectors. New and emerging industrial processes need to be optimized to achieve more efficient operations and this will require active research participations from the academic and industrial sectors. The next decade should witness the industrial use of a wide spectrum of products derived from this effort.

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