

Fabrication and evaluation of bacterial cellulose-polyaniline composites by interfacial polymerization

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Abstract The fabrication and evaluation of nanocomposites based on microbial cellulose and polyaniline (PANi) are described. Microbial cellulose, so called, bacterial cellulose (BC) was introduced to interfacial polymerization of aniline. Two different phases based on water and chloroform made it easy for nanosized PANi particles to be synthesized on BC. Without any help of a surfactant or templates, BC played a critical role of supporting the growth of PANi. As a function of aniline concentration, the corresponding PANi content and volume resistivity were checked. From morphological images observed by FE-SEM, PANi nanoparticles were densely arrayed along every fiber of BC. The conjugated backbone of PANi was thought to contribute to the improvements of thermal stability of PANi/BC composites. The

stiffness and brittleness of PANi were compensated by more ductile BC, suggesting BC can be a promising substrate for it. By the simple and facile interfacial polymerization, the electrical conductivity of PANi/BC composites reached up to 3.8×10^{-1} S/cm when 0.32 M of aniline was used. This PANi/BC nanocomposite can be useful in applications requiring biocompatibility and electrical conductivity such as biological and chemical sensors.

Keywords Interfacial polymerization · Polyaniline (PANi) · Bacterial cellulose (BC) · Nanocomposite

Introduction

Cellulose is an old material that is familiar to mankind, as the word *cellulose* is derived from a Greek word meaning *material* (Siro and Plackett 2010). Unlike cellulose achieved from lignocellulosic biomass, another kind of cellulose produced by genus *Acetobacter*, bacterial cellulose (BC), has been getting more attention than ever (Chen et al. 2010; Nakayama et al. 2004). This material can be categorized into nanocellulose based on its three dimensional and nanostructured network inside the pellicles and the use of BC as a promising substrate and membrane were reported (Gardner et al. 2008; Shah and Malcolm Brown 2005). There is no need to get rid of biogenic compounds such as lignin and hemicellulose. For these reasons, there has been increasing momentum recently in the

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application of BC into science and technology to substitute materials derived from fossil fuels. Specifically, in polymer science, there have been different methods and modifications of BC, for example, treatment of culture medium (Yoon et al. 2006), dispersion or impregnation in polymer matrix (Yano et al. 2005), introduction of inorganic material (Yano et al. 2008) and so on. Moreover, its highly hydrophilic property has been opening possible applications to biomedical uses (Czaja et al. 2007; Maneerung et al. 2008). From all these efforts, BC has been also adopted to process the composites with electrically conductive polymer such as polyaniline (PANi) and polypyrrole (Lee et al. 2012; Marins et al. 2011; Muller et al. 2011).

Polyaniline is one of important and popular conductive polymers and its pH sensitivity and easiness of synthesis make it fascinating. This has been opening the door to chemical sensor (Huang et al. 2003), antistatic coatings (Maziarz et al. 2000) and lithium secondary battery (Ryu et al. 2007). However, one of the major disadvantages of PANi is its poor processability due to the rigid-rod macromolecular chains (Samuelson et al. 1998). This limits the practical applications and therefore, the fabrications of composites with cellulosic materials to compensate this weakness have been reported so far (Huang et al. 2005; Pron et al. 1997). A simple PANi membrane based on monomer and oxidant separated by semipermeable cellulose membrane was reported (Blinova et al. 2007).

Interfacial polymerization has been suggested as a facile way to synthesize nanofibers of PANi. In an immiscible two-phase system, the polymerization of aniline at the interface is observed in few min. Compared with PANi synthesized by conventional oxidative polymerization, mostly containing aggregated particles, interfacial polymerization allows the distribution between PANi particles to be controlled uniformly (Huang et al. 2003). By interfacial polymerization, PANi/PAAm (Polyacrylamide) composites were achieved and its electrical conductivity reached 10^{-2} S/cm (Dai et al. 2010). This kind of method is economical because it enables the organic solvent to be reused after distillation or purification.

In this study, the polymerization of aniline was commenced on never-dried BC. The purpose is to fully make use of the affinity and adsorption of BC to monomer or water. In that sense, the measurement of tensile strength, for example, was investigated on wet

BC. This is based on the potentials of BC to biomedical uses requiring highly absorbable and mechanically stable properties, at the same time (Czaja et al. 2007).

Polyaniline/BC composites were fabricated by interfacial polymerization in the aim of representing a promising candidate for substrate of conductive polymer, taking advantage of the size effect of nanostructured BC and electrical conductivity of PANi. This combination can lead to a functional material platform for a host of various applications such as biomedical sciences and low-capacity battery.

Experimental

Materials

Monomer aniline and ammonium persulfate (APS) as initiator were purchased from Duksan pure chemical Co. Korea. Hydrochloric acid (HCl) for a doping agent as well as solvent and chloroform as an organic solvent were supplied from Samchun chemical Co. Korea. All starting materials were reagent grade and used as purchased. The strain of *Gluconacetobacter xylinus* (ATCC 10,245) was purchased from Korean culture center of microorganisms (KCCM).

Cultivation of bacterial cellulose (BC)

Gluconacetobacter xylinus was statically cultured in HS (Hestrin and Schramm) medium. The composition of medium is mentioned elsewhere (Reese et al. 1950). After sterilized at 121 °C for 1.5 h, the medium containing cell colony was kept for 10 days at 30 °C. A 10-day old BC pellicle on the surface of medium was washed thoroughly with de-ionized water, thereafter with 1 M sodium hydroxide solution. After removing cells left on the cellulose, it was kept in 20 % ethanol solution below 15 °C. For a preparation of polymerization, BC pellicles were cut by 2 cm × 2 cm and the variation in weight after vacuum drying at 60 °C was 0.03 ± 0.001 g. The specifications of this pure BC in detail were mentioned in Table 1.

Polyaniline (PANi) synthesis by interfacial polymerization

Polyaniline was synthesized by interfacial polymerization mentioned somewhere else in detail (Huang and

Table 1 Specifications of raw bacterial cellulose (BC) samples sized 2 cm × 2 cm

Specifications	
Thickness (mm)	5.90 ± 0.02 ^a 0.20 ± 0.01 ^b
Maximum diameter of fibers (nm)	50 ^c
Weight (g)	4.26 ± 0.55 ^d 0.03 ± 0.001 ^e

^{a,d} Never-dried BC^{b,e} Vacuum dried at 60 °C for 24 h under pressure of –60 cmHg^c Observed by FE-SEM

Kaner 2004a, b, c). Different concentrations of aniline were dissolved in 10 mL of chloroform. The solution was placed on a 50 mL vial and 10 mL of 1 M HCl solution containing ammonium persulfate (APS) was poured over it. The molar ratio of oxidant to aniline was fixed to 1.25:1 to achieve better yield of PANi on BC (Stejskal and Gilbert 2002). The never-dried BC samples were placed above the organic phase carefully. The reaction was performed at ambient temperature for 24 h. The PANi/BC composites colored dark blue after polymerization was thoroughly washed by DI water, methanol and HCl repetitively in order to remove impurities, followed by being dried in a vacuum oven at 60 °C for another day.

Physico-chemical and electrical characterization

PANi/BC composites were investigated by Fourier transform infrared (FTIR) analysis. The IR spectra were recorded using FTIR-6100 (JASCO) equipped with a miracle accessory, an attenuated total reflectance (ATR). The specimens were analyzed over the range from 4,000 to 600 cm⁻¹ with a spectrum resolution of 4 cm⁻¹. All spectra were averaged over 30 scans.

The PANi content on BC was calculated by the following equation (Dai et al. 2010).

PANi content (%)

$$= \frac{\text{Weight of dried PANi/BC} - \text{Weight of dried BC}}{\text{Weight of dried PANi/BC}}$$

All data were averaged over five different samples. The samples of BC and PANi/BC for this measurement were vacuum-dried for 24 h at 60 °C under pressure of –60 cmHg.

A thermogravimetric analyzer, TGA Q5000 IR (TA instruments) was used for measurements on the 10 mg of the composites over a temperature ranging from 25 to 800 °C at a heating rate of 10 °C/min under a nitrogen flow of 40 mL/min.

Tensile measurement was carried out by UTM (Universal Testing Machine, Zwick) at 23 ± 2 °C and 65 % of relative humidity. Never dried BC samples were cut into rectangular strips 40 mm long and 5 mm wide. The cross head speed of 1 mm/min over a span of 25 mm was applied.

The morphology was observed by field emission scanning electron microscopy, JSM 7600F (JEOL) at an accelerating voltage of 5 kV. All the samples were pre-coated with a homogeneous platinum (purity 99.99 %) layer by ion sputtering to eliminate electron charging.

A 4-probe conductivity equipment (Changmin tech) was used for the conductivity tests. The conductivity was calculated according to the following equation:

$$\sigma = \frac{1}{(R \times d)}$$

where σ , R, and d mean conductivity (S/cm) (volume resistivity (Ω cm), and thickness of the sample (cm), respectively.

Results and discussion

Figure 1 shows that the diffusion and polymerization starting from the boundary between organic and aqueous phase could be observed in a few min. Because interfacial polymerization is diffusion-controlled reaction, overnight was enough to complete the reaction. This similar phenomenon was also observed in the case of interfacial polymerization of PANi nanofibers without any substrate or template (Huang and Kaner 2004a, b, c). The exclusive dispersion of PANi into the aqueous phase can be explained as follows. Anilinium hydrochloride monomer at the interface acts like a surfactant having a polar hydrophilic part and an organic hydrophobic part. The generated radical when this monomer meets APS in aqueous phase initiates polymerization and the growing hydrophilic PANi chains act as interfacial stabilizers. This separation leads to suppress unwanted side reactions resulting in, such as ortho-coupling reactions

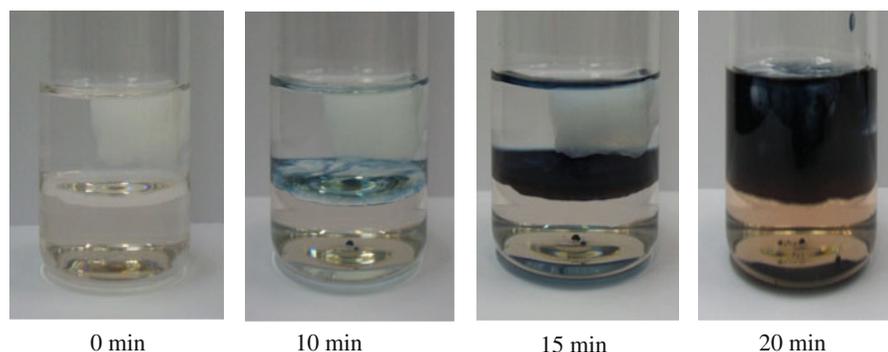


Fig. 1 Snapshots taken in first 20 min after interfacial polymerization of sample 1 commenced. 0.08 M of aniline was used for preparation of sample 1

between reactive chain ends (Lee et al. 2006). Huang and Kaner suggested that interfacial polymerization can be the effective method to suppress secondary growth of PANi by carrying the polymerized species from the reactive interface to diffusion into aqueous phase (Huang and Kaner 2004a, b, c).

IR spectra of vacuum-dried samples of pure BC, PANi powder and PANi/BC are displayed in Fig. 2. For pure BC, peaks observed at $3,344\text{ cm}^{-1}$ are derived from hydroxyl groups on cellulose and water. Absorption bands at $2,895\text{ cm}^{-1}$ (C–H stretching of CH_2), $1,427\text{ cm}^{-1}$ (CH_2 symmetric bending), and $1,360\text{ cm}^{-1}$ (C–H bending) can be assigned to stretching and bending modes of hydrocarbons in cellulose backbone.

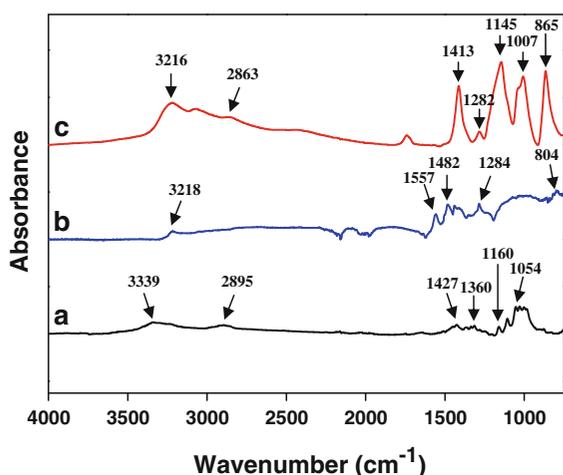


Fig. 2 FTIR spectra of samples of **a** pure BC **b** PANi powder and **c** PANi/BC (Sample 4, 84.42 wt% of PANi was contained in the dried sample). All samples were vacuum-dried at $60\text{ }^\circ\text{C}$ for 24 h. Sample **b** and **c** were prepared by interfacial polymerization

Some characteristic peaks of cellulosic material also appeared at $1,160\text{ cm}^{-1}$ (asymmetric bridge C–O stretching), $1,106$ and $1,054\text{ cm}^{-1}$ (skeletal vibrations involving C–O stretching) (Barud et al. 2008).

For PANi powder synthesized by interfacial polymerization, two characteristic peaks at $1,557$ and $1,482\text{ cm}^{-1}$ correspond to frequencies of aromatic ring in the PANi, which are stretching of quinone ring and benzene rings, respectively (Kapil et al. 2010). The peak at $3,218\text{ cm}^{-1}$ indicates N–H stretching which also can be found in PANi/BC composites by interfacial polymerization. Peaks attributed to out-of-plane bending vibration of C–H band of para-substituted benzene ring were observed near 800 cm^{-1} in both PANi powder and PANi/BC composites. The stretching of C–N band of benzene ring was confirmed by the peak at $1,284\text{ cm}^{-1}$ (Gok et al. 2004). Hydroxyl groups at $3,339\text{ cm}^{-1}$ were hardly seen in PANi/BC composites due to the breakage of intermolecular hydrogen bond of BC. This result matched the case in which PANi was synthesized by in situ oxidative polymerization on dried BC samples (Hu et al. 2011). From this result, it can be assumed that most hydroxyl groups on BC contributed the uniform distribution of PANi, interacting with aniline monomer and furthermore providing a substrate for PANi synthesis. Based on FTIR analysis, PANi was successfully deposited on BC. Therefore, the nanosized and nanostructured fibers of BC facilitated the diffusion and adsorption of aniline monomers onto the cellulose substrate. It is also plausible that hydrogen bonding between the hydroxyl of BC and amine of aniline contributed to the polymerization of aniline (Hu et al. 2011).

In Fig. 3, the increase in PANi content was observed as a function of aniline monomer

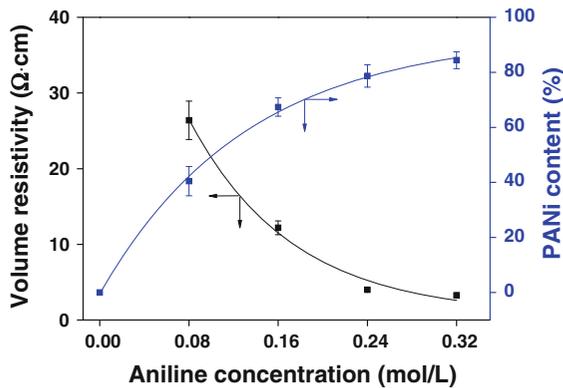


Fig. 3 Dependence of PANi content and volume resistivity of PANi/BC composites on the aniline concentration

concentration. These values exceed the reported PANi content only reaching to 27.8 wt% which was achieved by incorporation of PANi on PAAm (Polyacrylamide) hydrogel (Dai et al. 2010). The better achievements in PANi content are mainly due to the increased ability of BC to absorb water and more possibility to form hydrogen bond with amines of aniline. This also can be explained by the better adsorption of never-dried BC which can contain more reagents such as aniline, contributing to the improvements in electrical conductivity as well. Once nano and micropores of BC were collapsed, this effect has disappeared and the ability of absorbing reagents and water drops drastically. However, PANi content did not increase linearly as a function of aniline concentration. In this case, the dependence of PANi content on aniline concentration seems to fit for the exponential distributions which yielded a coefficient of correlation of 0.997. By the way, the distribution of volume resistivity corresponding to concentration of monomer follows exponential distribution with a coefficient of correlation of 0.980. The effect of monomer

concentration on these two properties is not significant above the point at which 0.32 M of aniline was used. The volume resistivity of PANi/BC composites was converted to electrical conductivity (σ , S/cm) and mentioned in Table 2.

To investigate the effect of PANi on thermal degradation of PANi/BC composites, thermogravimetric analysis was performed for pure BC, PANi powder and sample 4. Pure BC experienced mass losses in two steps, as shown in Fig. 4. Two significant losses were observed from room temperature to 200 °C and from 200 to 400 °C (Barud et al. 2007). At the first step, 4 wt% of moisture contained in BC sample and some volatile matters were eliminated below 100 °C. This is mainly due to the hydration of water absorbed physically or bound by hydrogen bond on BC. The second mass loss was seen at approximately 336 °C where the thermal degradation of BC took place drastically. For PANi/BC composites, its thermal degradation proceeded from 133 °C in contrast with the behavior of BC which showed the thermally stable property below 176 °C. This can be explained that the adoption of PANi to BC may weaken inter or intramolecular hydrogen bonding in BC (Al-Ahmed et al. 2004). However, a thermal instability of pure BC above 330 °C was compensated by impregnation of PANi in it. At 400 °C, for example, only 36 % of BC remained while 47.16 % of PANi/BC was still there. The rigid π -conjugated backbone molecular structure of PANi delayed the sharp decomposition of PANi/BC composites above 330 °C. The further decomposition of PANi above this point is mainly due to chemical oxidative degradation of PANi. In summary, PANi played a critical role of bringing thermal stability to PANi/BC composites, which is consistent with the thermal behaviour of composites composed of PANi and corn straw powder (Mo et al. 2009).

Table 2 Composition of pure BC and PANi/BC composites

Sample	M (mol/L)		PANi content (%)	Maximum tensile stress (MPa)	Electrical conductivity (S/cm)
	Oxidant	Monomer			
Pure BC	–	–	–	2.08×10^{-1}	–
1	0.1	0.08	40.46	5.07×10^{-1}	3.81×10^{-2}
2	0.2	0.16	67.40	4.81×10^{-1}	1.03×10^{-1}
3	0.3	0.24	78.69	3.75×10^{-1}	3.12×10^{-1}
4	0.4	0.32	84.42	2.73×10^{-1}	3.82×10^{-1}

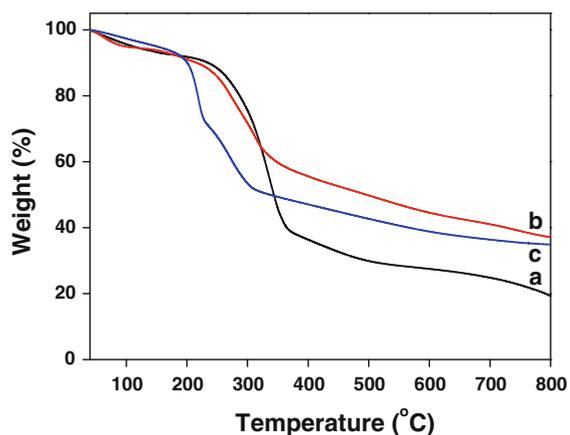


Fig. 4 TGA curves of **a** pure BC, **b** PANi powder, and **c** PANi/BC (Sample 4 containing 84.42 wt% of PANi). **b** and **c** were achieved by interfacial polymerization

The mechanical property of BC and PANi/BC composites which were never-dried was shown in Fig. 5. The maximum tensile stress at failure is higher than the one of pure BC due to the reduced porosity resulted from incorporation of PANi into BC. The fact that PANi filled in nanopores of BC brought the increase in maximum tensile stress of PANi/BC seems to conflict with the innate brittleness and stiffness of PANi, as more PANi was loaded on PANi/BC composites (Liau et al. 2006). The tensile behavior of PANi/BC composites behaved closer to pure BC as more PANi was loaded. A proper amount of PANi deposited on BC helped to achieve the improved maximum tensile stress and this supplemented the

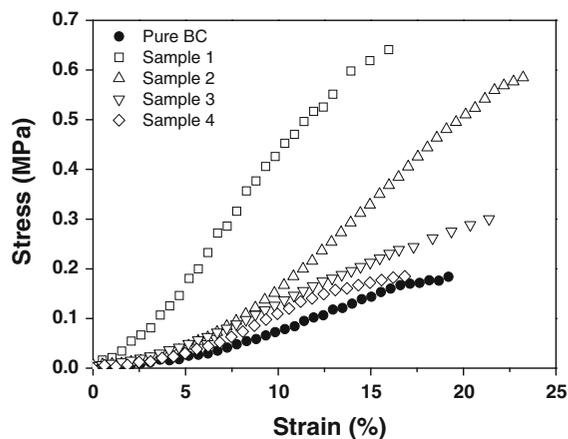


Fig. 5 Tensile stress–strain behaviors of never-dried BC and PANi/BC composites prepared with different concentration of aniline

flexibility of BC which showed the maximum tensile stress of 2.08×10^{-1} MPa.

Bacterial cellulose acted as the nanostructured substrate during the interfacial polymerization of aniline resulting from increased surface porosity, leading the better adsorption of reagents. This assumption matches to the results observed by optical microscopy shown in Fig. 6. In the FE-SEM image of vacuum dried BC, the nanosized fibers were stuck together after vacuum drying and nanopores between them were hardly observed. This is because size effect disappeared and BC could not play a critical role of nanosized and nanostructured substrate for electrical conductive polymer. When polymerization of aniline started from never-dried BC, it can fully take advantage of three dimensional nanostructured network of BC and its absorbency. This brings the increase in PANi content and electrical conductivity, accordingly.

As shown in Fig. 6, the vacuum dried BC fibers sized less than 50 nm collapsed together. Even though it was freeze-dried the pores remained more than vacuum dried one, the fibers were merged together because of the breakage of hydrogen bond. But for BC with PANi synthesized on it, each fiber seems to be preserved as it was. Until 0.16 M of aniline was used, the nanopores and space between fibers were still observed. PANi was grown along the BC nanofibers and it became thicker and denser as the amount of aniline increased. This is assumed that once PANi particles were polymerized on never dried BC, nanopores may collapse less because PANi interrupted the hydrogen bond and collapse occurring between each fiber of BC when dried. Hindering inter or intra molecular hydrogen bond of BC, the formation of PANi contributed to the conserve nanofibers of BC and took advantage of size effect. However, when the amount of aniline exceeds to 0.24 M and the PANi content reached to approximately 80 wt% of composites, no individual fibers were observed as shown in Fig. 6.

Conclusions

By interfacial polymerization, PANi/BC composites were fabricated successfully. Without the help of template or surfactants, the nanosized PANi onto BC was readily synthesized. The nanostructured BC provided a good substrate environment which expanded its surface area and absorbency. As a function of

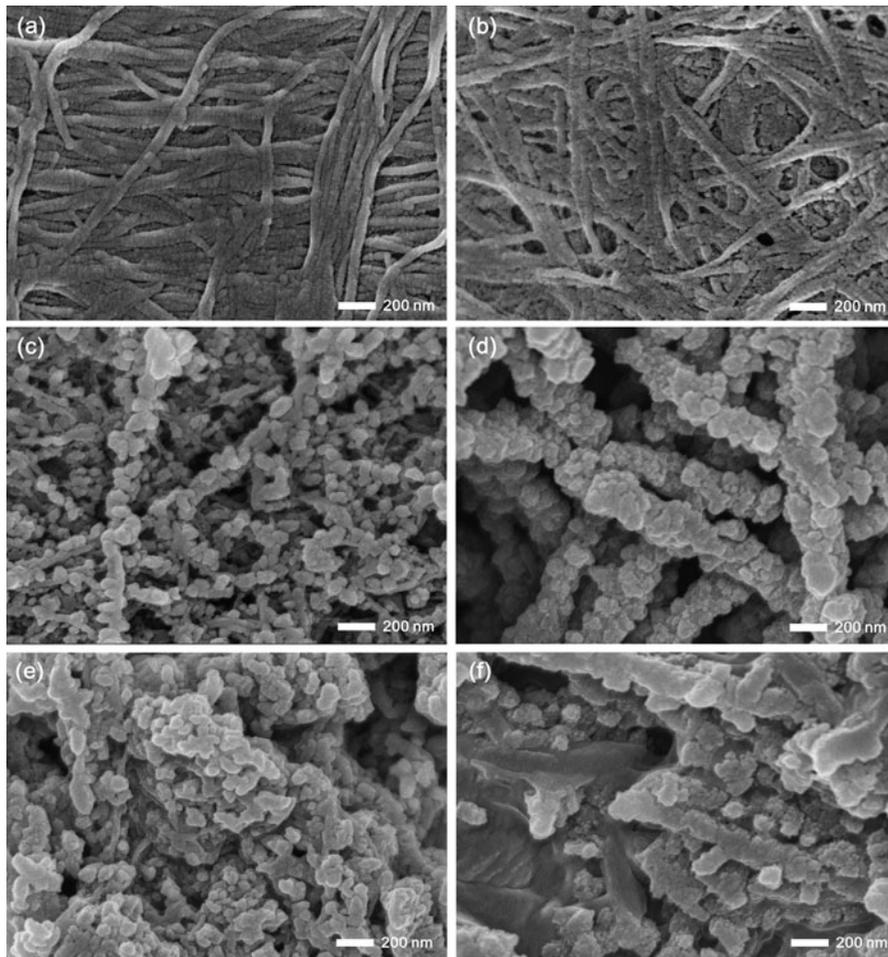


Fig. 6 FE-SEM images of **a** pure BC, **b** pure BC after freeze drying, **c** sample 1, **d** sample 2, **e** sample 3 and **f** sample 4 (all samples were magnified 50,000 times real sized). Samples except freeze-dried BC were prepared after vacuum drying at 60 °C for 24 h

aniline concentration, the PANi content and electrical conductivity of PANi/BC composites were traced. There was a limit point at which those two properties do not increase significantly any more when 0.3 M of aniline was used. The brittleness of PANi seemed to be adjusted by its fabrication on BC substrate, which was demonstrated by tensile stress–strain curves. The thermal instability of BC above 330 °C was supplemented by incorporation of PANi on it based on the rigid backbone of PANi. The electrical conductivity reached up to 3.8×10^{-1} S/cm which are relatively higher than the conductivity reported before, resulting from the better affinity to reagents and absorbency of wet BC. This conductive nanocomposite can be applied to biocompatible composite actuators, clothing sensor and so on.

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References

- Al-Ahmed A, Mohammad F, Zaki Ab Rahman M (2004) Composites of polyaniline and cellulose acetate: preparation, characterization, thermo-oxidative degradation and stability in terms of DC electrical conductivity retention. *Synth Met* 144:29–49
- Barud HS, Ribeiro CA, Crespi MS, Martines MAU, Dexpert-Ghys J, Marques RFC, Messaddeq Y, Ribeiro SJL (2007) Thermal characterization of bacterial cellulose-phosphate composite membranes. *J Therm Anal Calorim* 87:815–818
- Barud HS, Assuncao RMN, Martines MAU, Dexpert-Ghys J, Marques RFC, Messaddeq Y, Ribeiro SJL (2008) Bacterial

- cellulose-silica organic-inorganic hybrids. *J Sol-Gel Sci Technol* 46:363–367
- Blinova NV, Stejskal J, Trchova M, Ciric-Marjanovic G, Sapurina I (2007) Polymerization of aniline on polyaniline membranes. *J Phys Chem B* 111:2440–2448
- Chen P, Cho SY, Jin HJ (2010) Modification and applications of bacterial celluloses in polymer science. *Macromol Res* 18:309–320
- Czaja WK, Young DJ, Kawecki M, Brown RM (2007) The future prospects of microbial cellulose in biomedical applications. *Biomacromolecules* 8:1–12
- Dai TY, Qing XT, Wang J, Shen C, Lu Y (2010) Interfacial polymerization to high-quality polyacrylamide/polyaniline composite hydrogels. *Compos Sci Technol* 70:498–503
- Gardner DJ, Oporto GS, Mills R, Samir M (2008) Adhesion and surface issues in cellulose and nanocellulose. *J Adhes Sci Technol* 22:545–567
- Gok A, Sari B, Talu M (2004) Synthesis and characterization of conducting substituted polyanilines. *Synth Met* 142:41–48
- Hu WL, Chen SY, Yang ZH, Liu LT, Wang HP (2011) Flexible electrically conductive nanocomposite membrane based on bacterial cellulose and polyaniline. *J Phys Chem B* 115:8453–8457
- Huang J, Kaner R (2004a) A general chemical route to polyaniline nanofibers. *J Am Chem Soc* 126:851–855
- Huang J, Kaner RB (2004b) Nanofiber formation in the chemical polymerization of aniline: a mechanistic study. *Angew Chem* 116:5941–5945
- Huang JX, Kaner RB (2004c) A general chemical route to polyaniline nanofibers. *J Am Chem Soc* 126:851–855
- Huang JX, Virji S, Weiller BH, Kaner RB (2003) Polyaniline nanofibers: facile synthesis and chemical sensors. *J Am Chem Soc* 125:314–315
- Huang JG, Ichinose I, Kunitake T (2005) Nanocoating of natural cellulose fibers with conjugated polymer: hierarchical polypyrrole composite materials. *Chem Commun* 13:1717–1719
- Kapil A, Taunk M, Chand S (2010) Preparation and charge transport studies of chemically synthesized polyaniline. *J Mater Sci-Mater Electron* 21:399–404
- Lee K, Cho S, Park SH, Heeger AJ, Lee CW, Lee SH (2006) Metallic transport in polyaniline. *Nature* 441:65–68
- Lee BH, Kim HJ, Yang HS (2012) Polymerization of aniline on bacterial cellulose and characterization of bacterial cellulose/polyaniline nanocomposite films. *Curr Appl Phys* 12:75–80
- Liau WB, Sun YT, Yang LY, Wang LY, Chiu WY, Hsieh KH, Tseng SM (2006) Morphology and characterization of conductive films based on polyaniline-coated polystyrene latexes. *J Appl Polym Sci* 102:5406–5413
- Maneerung T, Tokura S, Rujiravanit R (2008) Impregnation of silver nanoparticles into bacterial cellulose for antimicrobial wound dressing. *Carbohydr Polym* 72:43–51
- Marins JA, Soares BG, Dahmouche K, Ribeiro SJL, Barud H, Bonemer D (2011) Structure and properties of conducting bacterial cellulose-polyaniline nanocomposites. *Cellulose* 18:1285–1294
- Maziarz EP, Lorenz SA, White TP, Wood TD (2000) Polyaniline: a conductive polymer coating for durable nanospray emitters. *J Am Soc Mass Spectrom* 11:659–663
- Mo Z-l, Zhao Z-l, Chen H, Niu G-p, Shi H-f (2009) Heterogeneous preparation of cellulose-polyaniline conductive composites with cellulose activated by acids and its electrical properties. *Carbohydr Polym* 75:660–664
- Muller D, Rambo CR, Recouvreux DOS, Porto LM, Barra GMO (2011) Chemical in situ polymerization of polypyrrole on bacterial cellulose nanofibers. *Synth Met* 161:106–111
- Nakayama A, Kakugo A, Gong JP, Osada Y, Takai M, Erata T, Kawano S (2004) High mechanical strength double-network hydrogel with bacterial cellulose. *Adv Funct Mater* 14:1124–1128
- Pron A, Nicolau Y, Genoud F, Nechtschein M (1997) Flexible, highly transparent, and conductive polyaniline-cellulose acetate composite films. *J Appl Polym Sci* 63:971–977
- Reese ET, Siu RGH, Levinson HS (1950) The biological degradation of soluble cellulose derivatives and its relationship to the mechanism of cellulose hydrolysis. *J Bacteriol* 59:485
- Ryu KS, Jeong SK, Joo J, Kim KM (2007) Polyaniline doped with dimethyl sulfate as a nucleophilic dopant and its electrochemical properties as an electrode in a lithium secondary battery and a redox supercapacitor. *J Phys Chem B* 111:731–739
- Samuelson LA, Anagnostopoulos A, Alva KS, Kumar J, Tripathy SK (1998) Biologically derived conducting and water soluble polyaniline. *Macromolecules* 31:4376–4378
- Shah J, Malcolm Brown R (2005) Towards electronic paper displays made from microbial cellulose. *Appl Microbiol Biotechnol* 66:352–355
- Siro I, Plackett D (2010) Microfibrillated cellulose and new nanocomposite materials: a review. *Cellulose* 17:459–494
- Stejskal J, Gilbert RG (2002) Polyaniline preparation of a conducting polymer (IUPAC technical report). *Pure Appl Chem* 74:857–867
- Yano H, Sugiyama J, Nakagaito AN, Nogi M, Matsuura T, Hikita M, Handa K (2005) Optically transparent composites reinforced with networks of bacterial nanofibers. *Adv Mater* 17:153–155
- Yano S, Maeda H, Nakajima M, Hagiwara T, Sawaguchi T (2008) Preparation and mechanical properties of bacterial cellulose nanocomposites loaded with silica nanoparticles. *Cellulose* 15:111–120
- Yoon SH, Jin HJ, Kook MC, Pyun YR (2006) Electrically conductive bacterial cellulose by incorporation of carbon nanotubes. *Biomacromolecules* 7:1280–1284