



# Flexible conductive nanocellulose combined with silicon nanoparticles and polyaniline



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## ABSTRACT

Here we describe a unique conductive bacterial cellulose (BC) composite with silicon nanoparticles (SiNPs) and polyaniline. BC was used as a template for binding SiNPs resulting in a very promising anode material for Li-ion rechargeable batteries that showed a high specific capacity. The surfaces of the SiNPs were modified with phytic acid to enhance the binding of aniline monomer to the surface. A conformal coating of polyaniline (PANI) was formed on the modified SiNPs by *in situ* polymerization of aniline monomers. We also found that the phytic acid on the SiNPs was critical to ensure encapsulation of SiNPs with PANI. In addition, the phosphoric acid-tagged surface of the SiNPs enhanced the adhesion of SiNPs to the BC fibers. The resulting three dimensional network of BC was flexible and provided stress dissipation in the conductive BC composites. Flexural testing of conductive BC composites showed stable electrical conductivity even after repetitive bending over 100 times.

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## 1. Introduction

The purpose of the investigation is the introduction of silicon nanoparticles (SiNPs) to bacterial cellulose (BC) having a unique three-dimensional networked structure and the conformal coating of polyaniline (PANI) to the SiNPs-bound BC composites. Since it is hard to polymerize aniline monomers at the surface of SiNPs, the surface of the SiNPs needs to be modified to enhance the binding of aniline monomers to the surface.

Rechargeable lithium ion batteries (LIBs) are one of the most promising systems for energy storage (Armand & Tarascon, 2008; Winter, Besenhard, Spahr, & Novak, 1998). Due to increasing demand for LIBs with low cost, high energy density and long cycle life, the development of new materials with high performance is required (Whittingham, 2004; Wu et al., 2012). The energy density of LIBs is able to be improved by replacing the graphitic carbonaceous anode with advanced anode materials which yield much higher capacities.

Silicon is a very promising anode material for Li-ion rechargeable batteries because its specific capacity is higher than that of graphite (Chiang, 2010; Wu & Cui, 2012; Zhang, 2011). However, silicon has poor conductivity and exhibits significant volume expansion upon Li-ion insertion, and these properties have restricted its application in anode materials (Ge, Rong, Fang, & Zhou, 2012; Kasavajjula, Wang, & Appleby, 2007). Recently, major efforts have been undertaken to address the conductivity problems of SiNPs using conducting polymers (Cui, Yang, Hsu, & Cui, 2009; Liu, Soares, Checkles, Zhao, & Yu, 2013; Liu et al., 2012). PANI is a popular option for increasing the conductivity of anode materials because it is chemically stable, lightweight and easy to synthesize. However, PANI is brittle and therefore cannot be used in applications like flexible batteries (Bhadra, Khastgir, Singha, & Lee, 2009; Genies, Boyle, Lapkowski, & Tsintavis, 1990). The fracture of electrodes can be prevented by introducing a flexible supporting matrix, which can dissipate stresses around the structure. A three-dimensionally networked fibrous structure can provide both flexibility and stress dissipation. BC biosynthesized by *Gluconacetobacter xylinus* can be a good supporting matrix for flexible conductive composites because of its unique 3D-networked structure and high mechanical and flexible properties (Chen, Huang, Liang, Guan, & Yu, 2013; Chen, Huang, Liang, Yao, et al., 2013; Siro & Plackett, 2010).

Several methods for the preparation of conductive cellulose have been reported. Carbonization of BC increased the

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conductivity significantly, but it could not maintain the mechanical property of cellulose due to the severe chain cleavage and loss of hydrogen bonding between the chains (Chen, Huang, Liang, Guan, et al., 2013; Wang et al., 2013). As a result, it was too brittle to handle and the application for the flexible devices could be restricted without incorporating with flexible elastomeric materials (Liang et al., 2012). The introduction of carbon nanotubes (CNTs) to BC was simple and effective for the increase of conductivity of cellulose (Choi, Park, Cheng, Park, & Hyun, 2012; Yoon, Jin, Kook, & Pyun, 2006). However, it was difficult to obtain the uniform conductivity due to the rapid aggregation and the localization of entangled CNTs.

The conformal coating of cellulose nanofibers with PANi is an important issue in conductive BC nanocomposites. Coating non-conductive cellulose fibers with PANi minimizes the loss of the conductivity compared with the simple incorporation of conductive nanoparticles such as CNTs. In spite of the effective coating on the cellulose nanofibers, the adsorption of aniline monomers is critical for the conformal coating of PANi at the surface of SiNPs. In this paper, phytic acid, which has six phosphoric acid groups, is introduced to the SiNPs to enhance the reaction with aniline monomers. The electrical stability of the conductive BC embedded with SiNPs when subjected to bending stress.

## 2. Experimental

### 2.1. Biosynthesis and purification of BC

*G. xylinus* (KCCM 40216) was obtained from the Korean Culture Center of Microorganisms. The bacterium was cultured on a mannitol medium composed of 2.5% (w/w) mannitol, 0.5% (w/w) yeast extract, and 0.3% (w/w) bacto-peptone. Bacteria were introduced into petri dishes containing culture medium at 28 °C for 5 days. After incubation, the BC membrane, which was biosynthesized on the surface of the liquid culture medium, was harvested and purified with 1 wt% NaOH (SAMCHUN Chemical, Korea) followed by washing with distilled water. The membrane was stored in distilled water prior to use.

### 2.2. Preparation of the silicon nanoparticle-embedded BC (Si-BC) composite

Forty milligrams of SiNPs (APS ≈ 100 nm, Alfa Aesar, USA) were dispersed in 100 mL deionized water by ultrasonication for 3 min. Subsequently, 200 μL phytic acid (Sigma–Aldrich, USA) was added and the mixture was vigorously agitated using a magnetic stirrer for 1 h at room temperature. Then, SiNPs modified with phytic acid were collected by centrifugation at 1000 rpm and re-dispersed in 100 mL of deionized water. BC pellicles were cut into 4 cm × 4 cm square pieces, which were then immersed in the SiNPs dispersion solution for 1 day with stirring. The Si-BC composite was washed with deionized water and stored in water for further experiments. The immersion time of BC pellicles in the SiNPs dispersion solution was optimized by comparing the weight increase of Si-BC as shown in Supplementary Information (Fig. S1). The amount of SiNPs bound to the BC pellicles was calculated by the difference of weight between the BC and Si-BC dried at 60 °C for 1 day.

### 2.3. PANi polymerization with BC (PANi-BC) and Si-BC composite (PANi-Si-BC)

Aniline (0.91 mL, Sigma–Aldrich, USA) was added to 50 mL of a 0.5 N HCl solution containing BC and Si-BC composites. Then, the solution was stirred for 1 h to disperse the aniline monomers in the BC membranes. Subsequently, 2.28 g of ammonium persulfate (Duksan pure chemical, APS, Korea), was added to the solution as an oxidant to initiate the polymerization. The polymerization of

aniline was carried out at 20 °C for 1 h. After polymerization, the composites were purified using methanol, distilled water and a 0.1 N HCl solution. The optimal conditions of polymerization were obtained by varying the molar ratio of APS to aniline monomer, the reaction temperature and the reaction time at the constant HCl concentration (Figs. S2–S4). The amount of PANi polymerized with Si-BC was calculated by the difference of weight between the Si-BC and PANi-Si-BC dried at 60 °C for 1 day. The samples were dried in a vacuum oven or in a freeze dryer prior to characterization of the composites.

### 2.4. Characterizations

The morphologies of the samples were observed using field emission scanning electron microscopy (FE-SEM, SUPRA 55VP, Carl Zeiss, Germany). The freeze-dried samples were cut into 1 cm × 1 cm sized pieces and were placed on conductive adhesive tape on aluminum stubs. To obtain the cross-sectional images of a BC hydrogel and SiNPs bound BCs, the samples were broken immediately after dipping in liquid nitrogen. The sample surfaces were coated with platinum using a sputter coater (SCD 005, BAL-TEC GmbH, Germany) before imaging. The imaging was performed in the “Inlens mode” at an acceleration voltage of 2 kV.

Electron transmission images of samples were captured by energy-filtering transmission electron microscopy (EF-TEM, LIBRA 120, Carl Zeiss, Germany). The Si-BC, PANi-BC, and PANi-Si-BC samples were immersed in separate vials with DI water and were ultrasonicated (VCX130, Sonic & Materials, USA) for 3 min at 40 W. Then, the solution with dispersed particles was dropped onto copper grids. The images were obtained at an acceleration voltage of 200 kV.

The crystal structure of the BC, phytic acid treated BC, Si-BC and PANi-Si-BC was determined using a high-resolution x-ray diffractometer (XRD, D8 DISCOVER, Bruker, Germany). For XRD experiments, 1 cm × 1 cm samples were cut from vacuum dried specimens. X-ray diffractometry (XRD) was performed using Cu Kα radiation.

Thermal degradation stability was measured by thermogravimetric analysis (TGA, TGA Q5000, TA Instruments, USA). About 10 mg of a vacuum dried sample was placed in an alumina crucible and was heated from room temperature to 600 °C at a heating rate of 10 °C min<sup>-1</sup> under flowing nitrogen.

The electrical conductivity of the composites after exposure to flexural stress was measured by bending the samples using a universal testing machine (UTM, GB/LRX Plus, Lloyd, UK). To perform this test, 4 cm × 1 cm vacuum dried specimens were loaded into the machine and were bent at a constant speed of 50 mm min<sup>-1</sup> at room temperature and 20% relative humidity. A 3 cm × 1 cm piece of aluminum foil was bonded to each end of the sample using silver paste (ELCOAT P-100, CANS, Korea) to allow connection of a digital multimeter (Chekman, Tae Kwang Electronics, Korea) for measuring the electrical conductivity. The bending radius of the samples was calculated as suggested in the literature (Wu et al., 2014). Specifically, the radius of the curvature (bending radius) was calculated as follows:

$$R = (d^2 + 4h^2)/8h$$

Here,  $d$  and  $h$  are the diameter and height of a dome, respectively. The change in electrical conductivity of the composites was measured after 100 repetitive bending cycles.

The percentage change in resistance was calculated as follows:

$$\Delta R(\%) = \{(R_0 - R_n)/R_n\} \times 100$$

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