

All-Solid-State Flexible Supercapacitors Fabricated with Bacterial Nanocellulose Papers, Carbon Nanotubes, and Triblock-Copolymer Ion Gels

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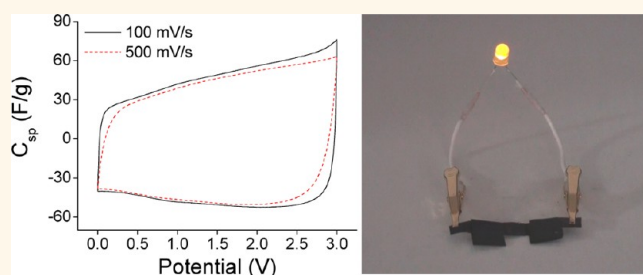
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Supercapacitors are attractive energy-storage devices for flexible and wearable applications^{1,2} because they have high power characteristics compatible with wireless communications and long cycle-lifetime, requiring no maintenance or replacement.^{3–6} Moreover, supercapacitors are safer and have lower environmental impact than batteries. To successfully realize high-performance flexible supercapacitors, various aspects of materials should be considered such as physical flexibility, electrochemical properties, and mechanical integrity between different materials.^{7–9}

Papers are good candidates for substrates of flexible energy-storage applications, since they not only are flexible but also can be readily integrated with conductive materials such as carbon nanotubes.¹⁰ While papers are mostly made of celluloses derived from plants, it is possible to make papers with superior material properties using bacterial nanocellulose (BNC).¹¹ The BNC has high purity and high crystallinity, and hence BNC-based papers have higher mechanical strength and better chemical stability than regular papers.^{11,12} Excellent mechanical properties of BNC papers also arise from the enlarged interfacial area between the BNC fibers in the papers due to the nanometer size of the BNC fibers. In general, BNC fibers (20–100 nm) are smaller by approximately 2 orders of magnitude than conventional cellulose fibers (~10 μm).¹² Owing to the reduced size of the BNC fibers, BNC papers can be made thinner, yet their mechanical strength can be higher than that of regular office papers. The superior chemical stability and mechanical strength of BNC

ABSTRACT



We demonstrate all-solid-state flexible supercapacitors with high physical flexibility, desirable electrochemical properties, and excellent mechanical integrity, which were realized by rationally exploiting unique properties of bacterial nanocellulose, carbon nanotubes, and ionic liquid based polymer gel electrolytes. This deliberate choice and design of main components led to excellent supercapacitor performance such as high tolerance against bending cycles and high capacitance retention over charge/discharge cycles. More specifically, the performance of our supercapacitors was highly retained through 200 bending cycles to a radius of 3 mm. In addition, the supercapacitors showed excellent cyclability with C_{sp} (~20 mF/cm²) reduction of only <0.5% over 5000 charge/discharge cycles at the current density of 10 A/g. Our demonstration could be an important basis for material design and development of flexible supercapacitors.

KEYWORDS: bacterial nanocellulose · carbon nanotube · ion gel · triblock copolymer · supercapacitor

papers would make them more compatible with various electrochemical conditions under which supercapacitors operate. However, the use of BNC in flexible supercapacitors has not been explored so far.

On the other hand, carbon nanotubes (CNTs) are excellent electrode materials, which may outperform conventional activated carbon, especially for flexible electrochemical capacitor applications.¹³ CNTs

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have a high aspect ratio with a nanometer-scale diameter as opposed to activated carbons, which have a micrometer-scale particulate form. The one-dimensional structure of CNTs not only ensures high flexibility of the CNT layer formed on substrates but also provides long continuous conductive paths along the lengths of the CNTs.⁷ Moreover, their geometry facilitates conformal coatings of the CNTs on a rough surface such as papers, ensuring high integrity.^{10,14} In addition, the CNTs have a high specific surface area, high electrical conductivity, excellent electrochemical properties, and controllable regular pore structure, which are highly desirable for supercapacitor applications.^{15,16}

Finally, ionic liquid based polymer gels, or ion gels, may be promising solid-state electrolytes for applications in flexible supercapacitors.¹⁷ First, ionic liquids have desirable properties as electrolytes, such as excellent electrochemical and thermal stability, high ionic conductivity, and negligible vapor pressure.¹⁸ Furthermore, a combination of polymers with ionic liquids provides mechanical integrity and persistent structure of the supercapacitors, which can overcome intrinsic leakage problems of liquid electrolytes that limit flexible operations.¹⁹ Especially, block copolymers that have different constituent units may dramatically increase flexibility in designing ion gels.^{20,21} However, introduction of ion gels with deliberately designed block copolymers to the flexible supercapacitors has not been demonstrated so far.

In this work, we demonstrate the fabrication of all-solid-state flexible supercapacitors that may have great potential for applications in flexible and wearable electronics by exploiting unique properties of BNC, CNTs, and ionic liquid based triblock-copolymer gel electrolytes. The resulting flexible supercapacitors showed specific capacitance (C_{sp}), specific energy (E_{cell}), and specific power (P_{cell}) of 50.5 F/g, 15.5 mWh/g, and 1.5 W/g (measured at 1 A/g), respectively. Moreover, these properties were generally retained through 200 bending cycles to a radius of 3 mm. In addition, the supercapacitors showed excellent cyclability with a C_{sp} reduction of only <0.5% over 5000 charge/discharge cycles at a current density of 10 A/g. The demonstrated flexible supercapacitors achieved by rational design of each component may enlighten the way toward fabricating high-performance, flexible energy-storage devices.

RESULTS AND DISCUSSION

Fabrication process of BNC papers and the subsequent CNT coating process are described in Figure 1. First, BNC pellicles were produced by culturing *Gluconacetobacter xylinus*, which is the most efficient BNC producer among various microorganisms including *Acetobacter*, *Pseudomonas*, *Rhizobium*, *Sarcina*, and *Azotobacter*.²² During the culture, nanocellulose is extracellularly secreted by the bacteria. The BNC

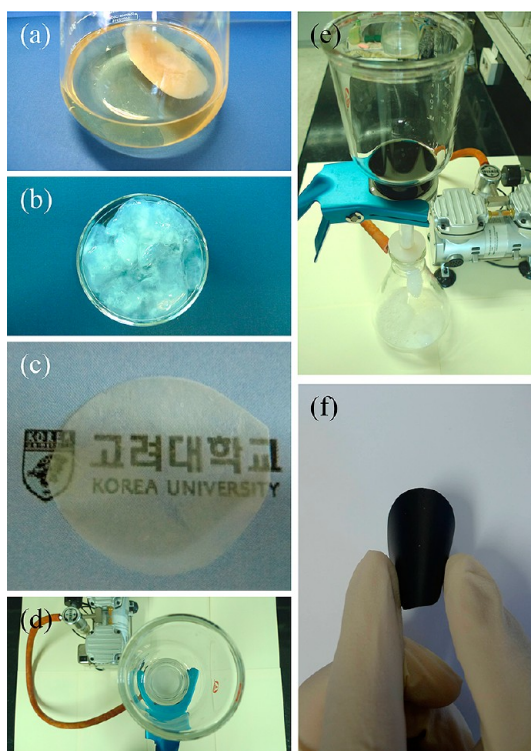


Figure 1. Fabrication process of bacterial nanocellulose (BNC) papers coated with carbon nanotubes (CNTs). (a) BNC pellicle produced by culturing *Gluconacetobacter xylinus*. (b) Bleached pellicles. (c) Semitransparent BNC paper. (d) Vacuum filtering apparatus loaded with a BNC paper. (e) Deposition of a CNT layer by the filtering process. (f) Flexible CNT-coated BNC paper.

pellicles start to form at the surface of the culture medium and grow downward over ~2 weeks. A BNC pellicle in the culture medium is shown in Figure 1a. Subsequently, pellicles can be bleached by removing bacteria and residues from the culture medium *via* heat treatment in aqueous sodium hydroxide solution, as shown in Figure 1b. Finally, thin papers were produced by pressing the pellicles under 10 MPa. Since pellicles contain a large amount of water (>90%),¹² simple pressing and drying of a pellicle leads to a BNC paper with a thickness of less than ~10 μm . The paper is semitransparent, as shown in Figure 1c.

A CNT layer was deposited onto the BNC paper *via* a vacuum filtering process as follows (Figure 1d, e). This step was carried out before the BNC paper was completely dried. First, the CNT ink was prepared by simply dispersing CNTs using sodium dodecylbenzenesulfonate surfactants in deionized water *via* a sonication process.^{7,14} Subsequently, the CNT solution was poured onto the BNC paper placed on a vacuum filter apparatus. Upon filtration and evaporation of the solvent, CNTs were conformally coated on and integrated with the BNC paper *via* hydrogen bonding and van der Waals interaction. Owing to the excellent interfacial properties, the CNT-coated BNC papers showed high mechanical stability over hundreds of

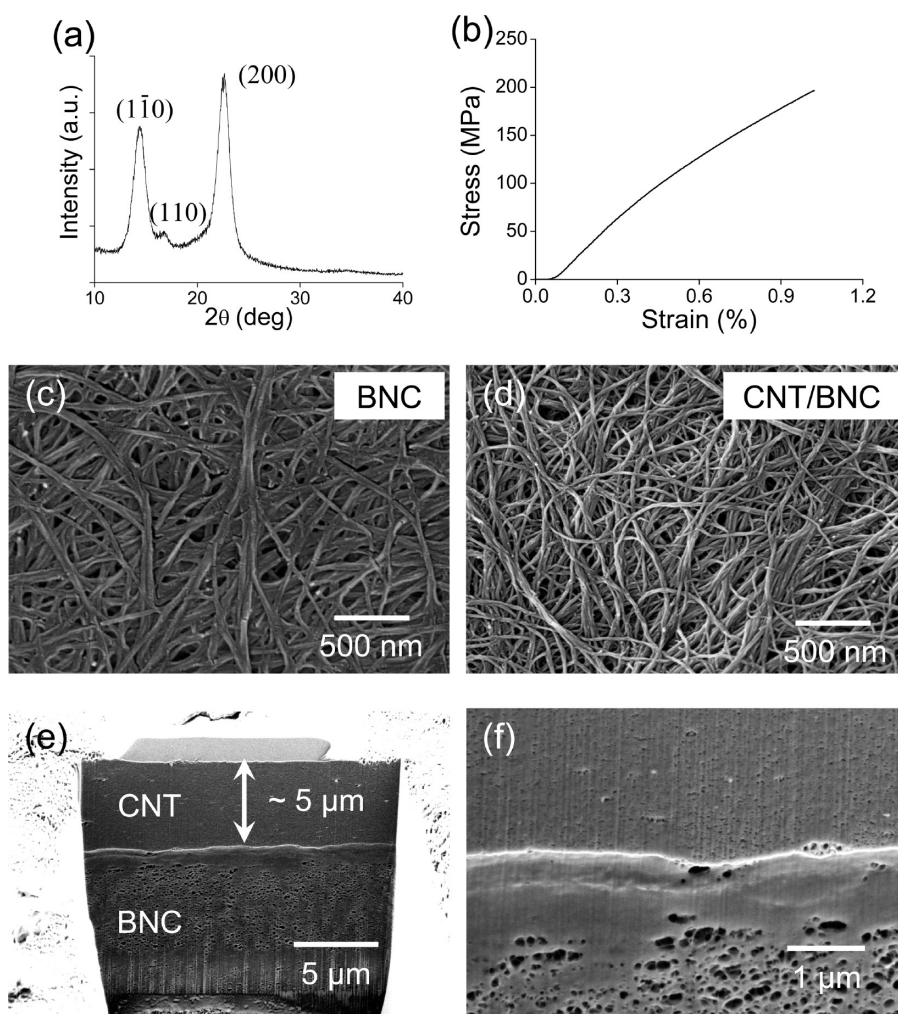


Figure 2. Characteristics of bacterial nanocellulose (BNC) papers and carbon nanotube (CNT)-coated BNC papers: (a) X-ray diffraction pattern and (b) stress–strain characteristics of a BNC paper. Scanning electron microscopy (SEM) images of (c) a BNC paper and (d) CNTs coated on a BNC paper. (e) Cross-sectional view of a CNT/BNC paper and (f) magnified SEM image of the interface between the CNT and the BNC layer.

bending cycles without being separated into individual layers (Figure 1f). The sheet resistance of CNT/BNC papers was typically $\sim 7 \Omega/\text{sq}$.

The BNC papers have excellent mechanical and chemical properties arising from the high purity, crystallinity, and degree of polymerization (DP) of individual BNC (Figure 2 and Table 1). BNC is generally purer than plant cellulose because it is free of hemicelluloses, lignin, and other extractives.²² The high crystallinity of BNC papers was confirmed by X-ray diffraction (XRD). The XRD peaks corresponding to (1–10), (110), and (200) planes were clearly observed (Figure 2a). The crystallinity index (I_c) was estimated to be $\sim 82\%$ based on the intensity of the (200) peak and the baseline intensity of amorphous material at $2\theta = 18^\circ$ using the equation $I_c = (I_{200} - I_{\text{am}})/I_{200}$.²³ DP and molecular weight were estimated to be 2843 and $\sim 460\,981$ g/mol, respectively (Table 1).²⁴ Together with the high crystallinity of BNC, the entangled network structure of BNC fibers in papers led to high tensile strength.²⁵ More specifically, Young's modulus and tensile strength

TABLE 1. Properties of Bacterial Nanocellulose and BNC-Based Papers

bacteria	DP ^a	M_w ^b [g/mol]	I_c ^c [%]	tensile strength	tensile modulus
				[MPa]	[GPa]
KCCM 41431	2843	460 981	82.3	196.6	21.0

^aDP: degree of polymerization. ^b M_w : molecular weight. ^c I_c : crystallinity index.

of the BNC paper were 21.0 GPa and 196.6 MPa, respectively (Figure 2b and Table 1), and these values are consistent with those previously reported by other researchers.¹¹ BNC papers also showed much higher chemical resistance than regular office papers. For example, the CNT/BNC papers retained their flexibility, while the CNT/regular papers became very brittle after being soaked in 1 M H_2SO_4 aqueous electrolyte for 24 h (Supporting Information, Figure S1).

The interface between the BNC and the CNT layer was apparently seamless, as revealed by scanning electron microscopy (SEM) combined with focused

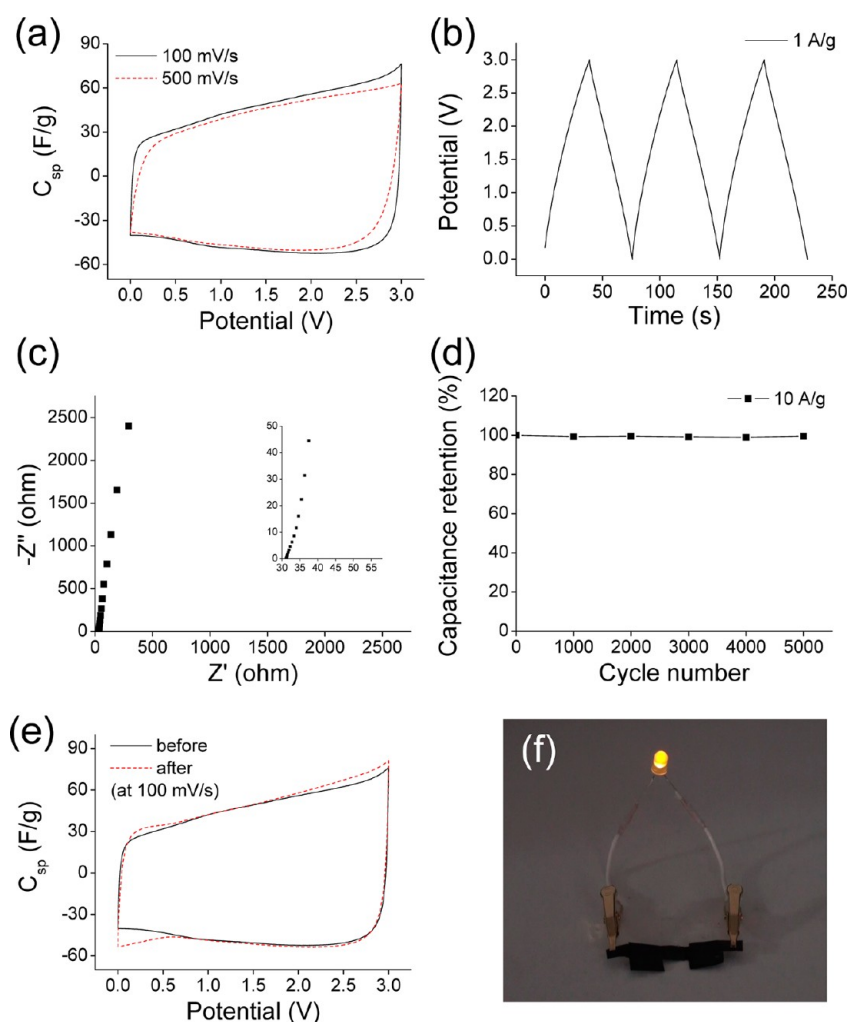


Figure 3. Characteristics of the CNT/BNC/ion gel-based all-solid-state flexible supercapacitors. (a) Cyclic voltammetry (CV) curves measured at scan rates of 100 and 500 mV/s. (b) Galvanostatic charge/discharge curve measured at a current density of 1 A/g. (c) Nyquist plot and equivalent series resistance (inset). (d) Capacitance retention over 5000 cycles of charge/discharge at a current density of 10 A/g. (e) CV curves measured before and after 200 bending cycles. (f) Photograph of a light-emitting diode (LED) turned on by the flexible supercapacitors.

ion beam (FIB) technique. The BNC fibers and CNTs have similar one-dimensional structures that are intertwined into two-dimensional sheets. The width of BNC fibers estimated from the SEM images was 38.0 ± 11.7 nm (average \pm one standard deviation, number of samples = 150) (Figure 2c), and the diameter of the CNTs estimated from transmission electron microscopy (TEM) images was 6.5 ± 1.5 nm (Figure 2d). A cross-sectional view of a CNT-coated BNC paper is shown in Figure 2e. Thicknesses of the CNT and BNC layer were around 5.0 and 8.5 μm , respectively. Different sizes and shapes of CNTs and BNC fibers presumably led to different pore sizes of each layer (Figure 2e, f and Supporting Information, Figure S2). It is likely that the seamless interface of the CNT and the BNC layer ensures good mechanical integration between the two different materials (Figure 2f). The high-quality interface might be due to the similar one-dimensional geometry of CNTs and BNC fibers that can be easily integrated and also due to strong forces between the

two layers such as van der Waals interaction and hydrogen bonding.^{7,10} Finally, fabrication of supercapacitors was completed by incorporating ionic liquid based polymer gels between two BNC papers coated with CNTs.

The supercapacitors based on BNC/CNT/ion gel showed superb device characteristics for flexible energy-storage applications. The rectangular shapes of the cyclic voltammograms (CVs) indicate excellent capacitive behaviors (Figure 3a).²⁶ The shape was generally retained even when the scan rate was increased to 500 mV/s. Specific electrode capacitances (C_{sp}) estimated from CV curves were 46.9 F/g (=18.8 mF/cm²) and 42.0 F/g (=16.8 mF/cm²) at scan rates of 100 and 500 mV/s, respectively. Consistently, the symmetric triangular forms of galvanostatic charge/discharge curves indicate nearly ideal capacitive behaviors with high Coulombic efficiency, $\eta = 97\%$ (Figure 3b). The capacitance estimated from the charge/discharge curve ($C_{sp} = 50.5$ F/g) was similar to

the value obtained from the CV curves. Current density used for the charge/discharge is defined as an applied current divided by the CNT mass of two electrodes ($=I/2m$). The capacitance was estimated using the equation $C_{sp} = (2I \times \Delta t)/(m \times \Delta V)$, where I , m , and $\Delta V/\Delta t$ are applied current, CNT mass of an electrode, and slope of the discharge curve after IR drop, respectively. Nyquist plots consistently show excellent capacitive behavior, as indicated by the near vertical line over the low-frequency ranges (Figure 3c). Equivalent series resistance (ESR) estimated from the intercept of the curve on the x -axis was about 31.3Ω . Encouragingly, the supercapacitor showed excellent capacitance retention over charge/discharge cycles. Figure 3d shows that the change in capacitance is less than 0.5%, *i.e.*, from 46.3 to 46.1 F/g, over 5000 cycles of charge/discharge at a high current density of 10 A/g.

Furthermore, the supercapacitors with the ion gel showed excellent mechanical integrity without any sign of delamination under various mechanical stress applied during handling and intentional bending. This superb mechanical integrity of our supercapacitors can be attributed to the polystyrene (PS) unit of the triblock copolymer composed of two different constituent units, PS and poly(ethylene oxide) (PEO). The hydrophobic PS block ensures good adhesion to the hydrophobic CNT electrode material *via* van der Waals interaction. On the other hand, the PEO block can effectively retain a hydrophilic ionic liquid in the polymer matrix as discussed in the following paragraphs. Owing to the adhesive chemical properties of ion gels, the supercapacitor performance was generally maintained over 200 bending cycles to a radius of 3 mm (Figure 3e and Supporting Information, Figure S3). We note that the mechanical integrity of the supercapacitors with the triblock-copolymer-based ion-gel electrolyte is superior to that of supercapacitors with a silica-based ionic liquid gel that was developed previously by our group.⁷ The supercapacitor with the triblock-copolymer ion-gel electrolyte tolerates a higher number of bending cycles to a sharper bending curvature without significant degradation of performance and also shows much stronger adhesion to CNT/BNC electrodes. Additionally, it was demonstrated that a yellow light-emitting diode (LED) can be lit by the all-solid-state flexible supercapacitors (Figure 3f).

The supercapacitors with ion gels showed comparable power performance to the supercapacitors with liquid electrolytes. For direct comparison, the same kind of ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][NTf₂]), was used for both supercapacitors. The power is highly dependent on how fast ions move toward and away from the surface of the electrode materials.^{15,27} Nyquist plots show that data points obtained from two different supercapacitors generally overlap with each other (Figure 4a). ESRs of both types of supercapacitors

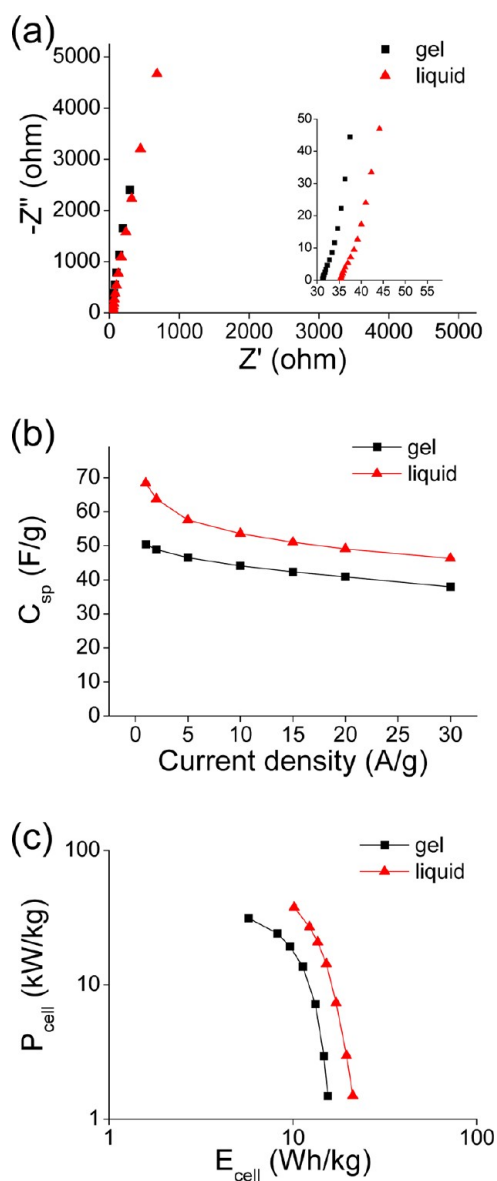


Figure 4. Performance comparison of supercapacitors made of ion-gel electrolytes vs neat ionic liquid electrolytes.

also fall in the same range of $30\text{--}35 \Omega$, as shown in the inset of Figure 4a. This implies that ion mobility of the gel electrolyte is comparable to that of the neat liquid electrolyte.²⁸ The conductivity and viscosity of the [EMIM][NTf₂] ionic liquid are $5\text{--}10 \text{ mS/cm}$ and 28 cP , respectively.^{19,21} The ion gel shows similar conductivity ($\sim 8 \text{ mS/cm}$ at 7 wt % of polymer) to that of a neat ionic liquid.²⁹ Furthermore, the specific capacitance of both supercapacitors decreases in a similar fashion as the current density increases from 1 to 30 A/g (*i.e.*, from 0.8 to 24 mA/cm^2) (Figure 4b). Although the C_{sp} of flexible supercapacitors was lower than that of liquid electrolyte based supercapacitors, a similar degree of C_{sp} reduction observed over a wide range of current density suggests that the ion mobility in both electrolytes is comparable. We suspect that the ion-gel-based supercapacitors have lower C_{sp} because

the surface of the CNTs may be partially coated with block copolymers, which reduces the CNT surface area accessible to the ions.⁷ The comparable power characteristics can also be seen in a Ragone plot (Figure 4c). Curves from both the ion gel and liquid electrolytes showed a similar trend except that the gel-based supercapacitors showed a lower specific energy due to the reduced C_{sp} . The specific energy and power were calculated using $E_{cell} = (1/2)C_{cell} \times V^2$ and $P_{cell} = E_{cell}/\Delta t$. The specific capacitance of a cell, C_{cell} , is 1/4 of the specific capacitance of an electrode, C_{sp} , in a two-electrode configuration.¹⁵ The V is voltage after IR drop and Δt is discharge time in the galvanostatic charge/discharge curves.

The comparable ion mobility of two types of electrolytes can be explained as follows. Owing to the immiscibility of different repeating units of the block copolymer, *i.e.*, PS and PEO, segregated nanostructures can be formed *via* a self-assembly process.²⁸ The ionic liquids can be held in the nanoscale space surrounded by PEO blocks, which are miscible with ionic liquids, whereas PS blocks are not. Since the space filled with an ionic liquid in the polymer matrix is greater than the

ions, the ion mobility in the gels can be comparable to that in the neat ionic liquid.²⁸ There are a large number of possible combinations of ionic liquids and block copolymers, and thus the properties of ion gels can be further improved by finding an optimal combination for application in supercapacitors.

CONCLUSION

In summary, we have demonstrated all-solid-state flexible supercapacitors fabricated with BNC, CNTs, and ion gels. The supercapacitors showed a specific capacitance, energy, and power of 50.5 F/g (~ 20.2 mF/cm²), 15.5 mWh/g, and 1.5 W/g, respectively. Moreover, they showed excellent cyclic stability with less than 0.5% change in C_{sp} over 5000 charge/discharge cycles. Owing to the excellent interfacial quality between the three different layers, the performance of the supercapacitors was well-retained over the bending cycles. Our first demonstration of a BNC/CNT/ion gel for flexible supercapacitors may greatly contribute to the advance of fundamental research and development technologies of flexible energy-storage devices.

METHODS

Culturing *Gluconacetobacter xylinum*. *G. xylinum* purchased from Korean Culture Center of Microorganisms (KCCM 41431, Seoul, Korea) was cultured for 48 h in a test tube containing Hestrin and Schramm (HS) medium. The medium was composed of 2% (w/v) glucose, 0.5% (w/v) yeast extract, 0.3% (w/v) bacto-peptone, 0.27% (w/v) disodium phosphate, and 0.115% (w/v) citric acid. The precultured cells were inoculated into 100 mL of the HS medium (pH ~ 6) in a 500 mL Erlenmeyer flask and incubated at 30 °C for ~ 14 days, which led to the formation of pellicles of BNC at the air/medium. The pellicles were purified by washing them with water, subsequently treating them with 2% (w/v) sodium hydroxide (NaOH) solution for 24 h at 60 °C, and finally rinsing them again with water. The purified BNC pellicles were stored in distilled water at 4 °C to prevent them from drying.

Preparation and Characterization of Carbon Nanotube/Bacterial Nanocellulose (CNT/BNC) Papers. A BNC pellicle was sliced into two pieces. Each piece was formed into a paper by pressing them under 10 MPa using a press (Carver, 2731) for 5 min. The BNC paper, which was still wet, was placed on a vacuum filter. Subsequently, a CNT ink solution (~ 40 mL) was poured onto the BNC paper. The CNT-coated BNC films were placed between filter papers that were sandwiched between two stainless plates (160 mm in diameter and 2 mm in thickness). The assembly was placed under a 10 kg steel and dried in an oven at 80 °C for 24 h. The areal density of the CNT on the BNC papers was ~ 0.4 mg/cm². The CNT ink was prepared by dispersing 2 mg of double-walled CNTs with 10 mg of sodium dodecylbenzenesulfonate surfactant in 20 mL of deionized water. The solution was bath-sonicated for 5 min and then bar-sonicated (Sonics & Materials, VC 750) for 20 min. The CNTs were grown by water-assisted chemical vapor deposition, as described elsewhere.^{7,30}

Morphologies of BNC films and CNT-coated BNC films were observed using field-emission scanning electron microscope (SUPRA 55VP or AURIGA, Carl Zeiss, Germany). Cross sections of the films were investigated using focused ion beam (FEI Company, Quanta 200 3D). Degree of polymerization of the BNC fibers was measured using a viscometer as reported in the

literature. Molecular weight of the BNC was obtained by the multiplication of the DP and the M_w (162.146 g/mol) of the cellulose unit. Mechanical properties of the BNC films were measured with a Universal Testing Machine (Zwick Testing Machine Ltd., United Kingdom) according to ASTM D882. Tensile properties were measured at a test speed of 10 mm/min and at the distance between grips of 25 mm. The mean value from 10 different specimens was reported. An X-ray diffractometer (Rigaku, Japan) was used. Cu K α radiation was used ($\lambda = 1.54$ Å), and the angle 2θ was scanned between 10° and 40°. The crystallinity index was calculated as $I_c = (I_{200} - I_{am})/I_{200}$, where I_{200} is the intensity of the peak at 2θ about 22.7° and I_{am} is the intensity of the baseline at $2\theta = 18^\circ$.

Fabrication and Characterization of All-Solid-State Flexible Supercapacitors. A poly(styrene-block-ethylene oxide-block-styrene) (PS-PEO-PS) triblock copolymer was purchased from Polymer Source, Inc. The number average molecular weight and polydispersity index of the copolymer was 83 kg/mol ($M_n(\text{PS}) = 12$ kg/mol and $M_n(\text{PEO}) = 59$ kg/mol) and 1.18, respectively. An ionic-liquid-based polymer electrolyte was fabricated by adding 192 mg of the copolymer (4 wt %) in 3 mL of [EMIM][NTf₂] (C-TRI).²⁹ The mixture was dissolved in 20 mL of acetonitrile and magnetically stirred for 12 h in a nitrogen atmosphere using a Schlenk line. The acetonitrile was removed at 130 °C for 24 h using a vacuum line. The solid electrolyte was placed between CNT/BNC papers and gently spread over the entire area of the papers. The total thickness of the assembly was approximately 340 μm . The size of the electrodes was 1 cm by 1 cm. The Brunauer–Emmett–Teller surface area of the CNT was ~ 460 m²/g. Electrochemical properties were investigated in a two-electrode configuration using an electrochemical analyzer (Ivium Technologies, CompactStat). A supercapacitor cell with liquid electrolyte was fabricated by dipping two BNC/CNT electrodes separated by poly(tetrafluoroethylene) film (Millipore, thickness ~ 65 μm and pore size ~ 0.2 μm) in neat [EMIM][NTf₂] ionic liquid under nitrogen or a vacuum environment as described elsewhere.¹⁵

Conflict of Interest: The authors declare no competing financial interest.

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Supporting Information Available: This material is available free of charge via the Internet at <http://pubs.acs.org>.

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