Preparation od conductive nanofilms using bacterial cellulose and double walled carbon nanotube (DWCNT).

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Introduction - Due to the increased use of portable electronic devices, there has been an increasing demand for renewable energy storage devices to improve of batteries, fuel cells and capacitors. Recently, electrochemical capacitors, also called supercapacitors, are being studied owing to higher density than conventional energy storage devices, such as batteries and fuel cells, and longer cycle life. With the increased demand for flexible device, besides display, energy storage device requires the flexibility. Bacteria-celluloses have an excellent mechanical property, too. Compared to the cellulose from wood, bacteria cellulose (BC) has a lot of hydrogen bonds, long length of molecular chain and large aspect ratio and high crystallinity. Tensile strength of bacteria-cellulose was higher than the nanocellulose. In this work, we demonstrate that high performance flexible supercapacitors can be fabricated using carbon nanotube (CNT) and series of cellulose papers. conductive films with BC and double wall carbon nanotube (DWNT) were fabricated by mixing method and filtering method, respectively. Also we were able to produce flexible and all-solid-state supercapacitors with DWNT/bacteria-cellulose and ionic-liquid-based gel electrolytes.

Materials and methods - DWNT ink was fabricated by adding 2 mg of DWNTs grown by the water-assisted CVD and 10 mg of sodium dodecylbenzenesulfonate (SDBS) surfactant in 20 mL of DI water. The DWNT solution was bath-sonicated for 5 min and then bar-sonicated for 20 min. Bacteria cellulose paper was fabricated by pressing lump of bacteria. The DWNTs were placed on a less dry condition of bacteria cellulose paper and filtered by vacuum filtering. The DWNTs/bacteria cellulose dried at 80 in an oven for 24h. An [EMIM][NTf2]–silica electrolyte was coated on each DWNT/bacteria-cellulose using Meyer rods and dried at room temperature under vacuum for ~36h. Once a thin layer of solid electrolyte was formed on each paper, another electrolyte layer was applied to one of DWNT/bacteria-cellulose to attach two of them together. The stacked DWNT/bacteria-cellulose papers dried under the same condition. Supercapacitor properties were measured using a two electrode system. Cyclic voltammetry (CV) and galvanostatic charge/discharge measurement were carried out in the voltage range of 0 to 3.0 V in [EMIM][NTf2]–silica gel electrolyte. Electrochemical impedance spectroscopy (EIS) was performed to measure equivalent series resistance (ESR). Focus ion beam (FIB, FEI company, Quanta 200 3D) was performed for observation of cross section. The morphology and structure of the DWNT on bacteria-cellulose papers were characterized by SEM (Carl zeiss, AURIGA). Tensile strength and modulus were measured by ASTM D882 method at the tensile rate of 10 mm/min with a sample size of 10 mm × 100 mm (Universal Testing Machine, UTM, Zwick testing machine Ltd., UK).

Results and discussion - The tensile strength of bacteria cellulose was 196 MPa, indicating an excellent mechanical property. The three characteristic peaks at 14.5, 16.9 and 22.8° in XRD analysis were observed from the XRD pattern, indicating that the strong and sharp signals suggest that BC has high crystallinity. Diameter of the BC was about 20 to 50 nm. The conductive DWNT/BC papers had a low sheet resistance of ~6 Ω/sq with a mass loading of 0.40 mg/cm2. Diameter of the DWNTs was 6.5 ± 1.5 nm. FIB was performed for observation of stacking structure between DWNT and bacteria-cellulose. A thin layer of DWNTs covered the bacteria-cellulose and the layer was about 6 μm thickness. The layer of DWNT has a very compact structure and the layer of bacteria-cellulose has a little more pore structure. The supercapacitors showed excellent electrochemical properties. The CV curve had almost rectangular shape at the scan rate of 100 mV/s. Electrochemical performance was maintained at a faster scan rate of 500 mV/s. ESR was ~33 Ω and the supercapacitor was performed...
excellent cyclability. During 3000 charge-discharge cycles, the $C_{sp}$ varied only 4%. The supercapacitors could be repeatedly bent without significant variations in electrochemical properties as specific capacitance and energy density (<7%). Power density did not change after bending test. The DWNT/bacteria-cellulose papers were prepared by filtering method. Specific capacitance, energy and maximum power density were 65.2 F/g, 19.7 Wh/kg, 85.2 kW/kg, respectively. The supercapacitors were performed good cyclability, and the variation of $C_{sp}$ was less than 4% during 3000 charge/discharge cycles. Also the supercapacitors had good flexibility, and electrochemical properties changed by less than 7% over 100 bending cycles with radius of 4.5 mm. Flexible and all-solid-state supercapacitors may have great potential for high-mechanical, low-density and high-performance flexible electronic applications.

Fig. 1. BC culture and conductive film fabrication.

Fig. 2. SEM morphology of BC and CNT

Fig. 3. FIB photograph of conductive film

Fig. 4. Cyclic voltametry of supercapacitor BC/DWCNT

Fig. 5. Galvanostatic charge/discharge curve

Fig. 6. Nyquist plot of the supercapacitor