

박테리아 셀룰로오스기반 supercapacitor의 연구 동향

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1. 서론

▶ 박테리아 셀룰로오스 (bacterial cellulose; BC) 기반 supercapacitor 특징¹⁻⁴

- AOAS 2014 를 개최한 대한민국은 미세조류 기반 차세대 바이오매스사업을 통하여 바이오연료 및 바이오소재 생산을 위한 기초연구를 진행 중에 있으며, BC 기반 차세대 바이오 매스산업이 유망하다고 판단됨.
- BC 기반 재료 개발 기술은 BT/NT/ET 등이 하이브리드 된 기술로서 각 기술들의 융합에 의하여 새로운 특성과 기술적인 면에서 시너지 효과를 기대할 수 있음
- 바이오 매스로부터 얻을 수 있는 BC paper는 우수한 기계적 강도와 화학적 안정성을 가지고 있어 CNT와 같은 전도성 물질과 친화적이며서 유연성이 있는 에너지 저장 소자의 지지체로서 유용하여 슈퍼캐패시터에 응용이 용이함.
- 박테리아 셀룰로오스를 이용한 플렉서블슈퍼 커패시터는 기계적 강도, 화학적 안정성, 굽힘에 대한 저항성 및 내구성에서 매우 우수한 특성을 가지며 신소재 공학적 지식이 미래의 플렉서블슈퍼 커패시터 개발에 근본적인 토대가 될 수 있음이 보고되고 있음.

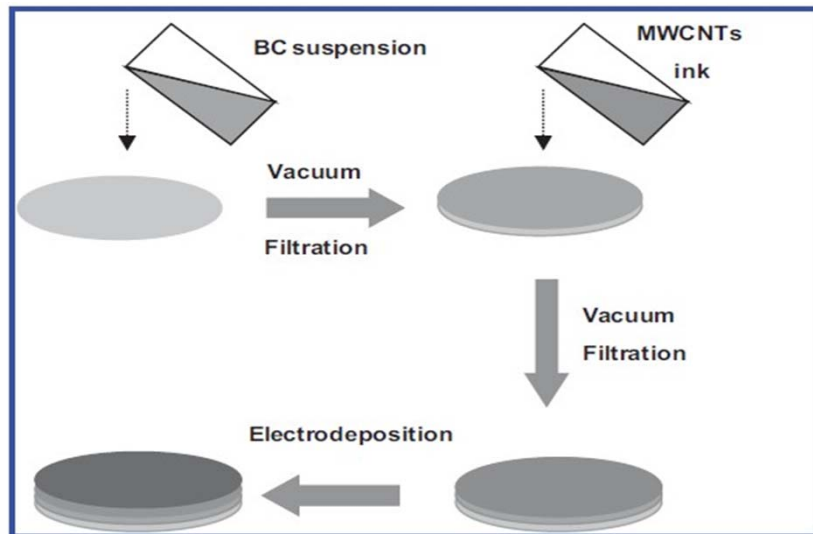
▶ 응용

- 전기전자 소재로서 supercapacitor, 리튬이온전지용 분리막, 디스플레이, 태양전지, 전자종이, 센서

2. 박테리아 셀룰로오스 기반 supercapacitor 연구동향

➤ Flexible Supercapacitors Based on Bacterial Cellulose Paper Electrodes⁵

- BC 기반 multiwalled carbon nanotubes(MWCNTs)와 polyaniline(PANI)의 하이브리드로 Supercapacitors를 만들었으며 간단한 제조 방법, 낮은 비용으로 flexible energy-storage devices로서의 개발하기 위한 새로운 전극재료로서 응용이 기대됨.
- Specific capacitance(656 F g^{-1} at a discharge current density of 1 A g^{-1})와 뛰어난 cycling stability를 보고함.



Scheme 1. Schematic of the fabrication process of BC-MWCNTs-PANI x freestanding paper electrodes.

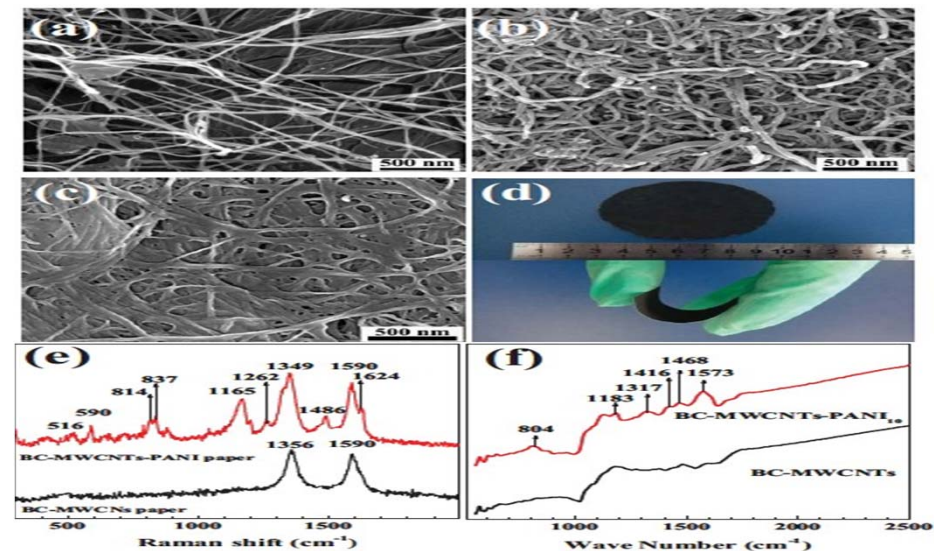


Figure 1. SEM images of a) BC paper, b) BC-MWCNTs paper, c) BCMWCNTs-PANI₁₀ paper electrode, and d) digital image of BC-MWCNTs paper and BC-MWCNTs-PANI₁₀ paper electrode. e) Raman spectra and f) FTIR spectra of BC-MWCNTs paper and BC-MWCNTs-PANI₁₀ paper.

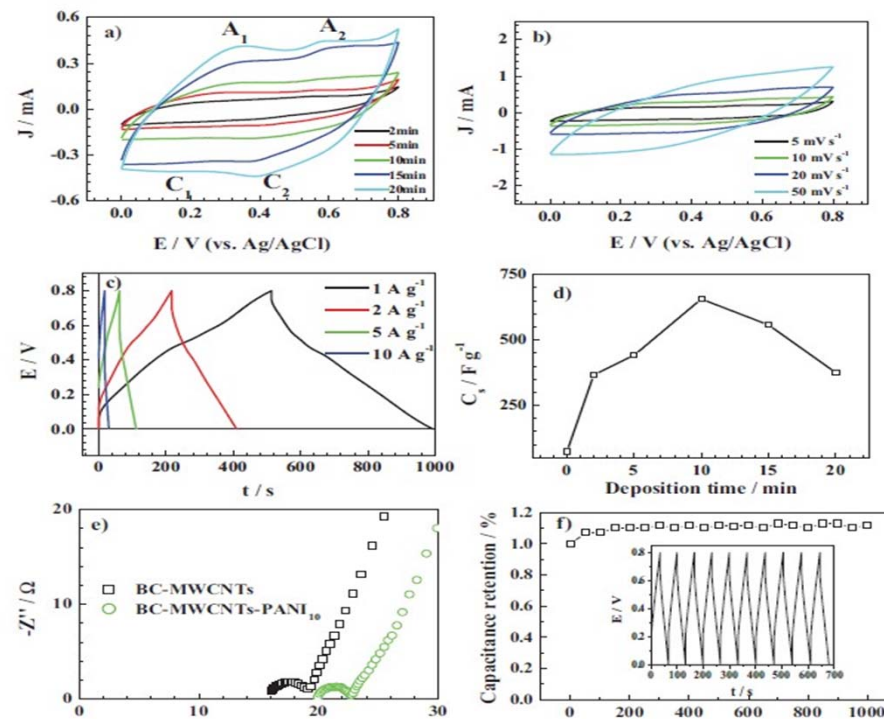


Figure 2. a) CV curves of BC-MWCNTs-PANI x electrodes measured at scan rate of 10 mV s^{-1} with x at different PANI electrochemical deposition time. b) CV scans of BC-MWCNTs-PANI $_{10}$ electrode. c) Galvanostatic charging/discharging curves of BC-MWCNTs-PANI $_{10}$ electrode. d) Specific capacitance of electrodes under different PANI deposition time at a discharge current density of 1 A g^{-1} . e) Nyquist electrochemical impedance of BC-MWCNTs and BC-MWCNTs-PANI $_{10}$ electrodes. f) Cycling stability of a BC-MWCNTs-PANI $_{10}$ electrode in $1 \text{ M H}_2\text{SO}_4$ electrolyte at a discharge current density of 10 A g^{-1} at room temperature. The inset shows the first 10 cycles of galvanostatic charging/discharging curves.

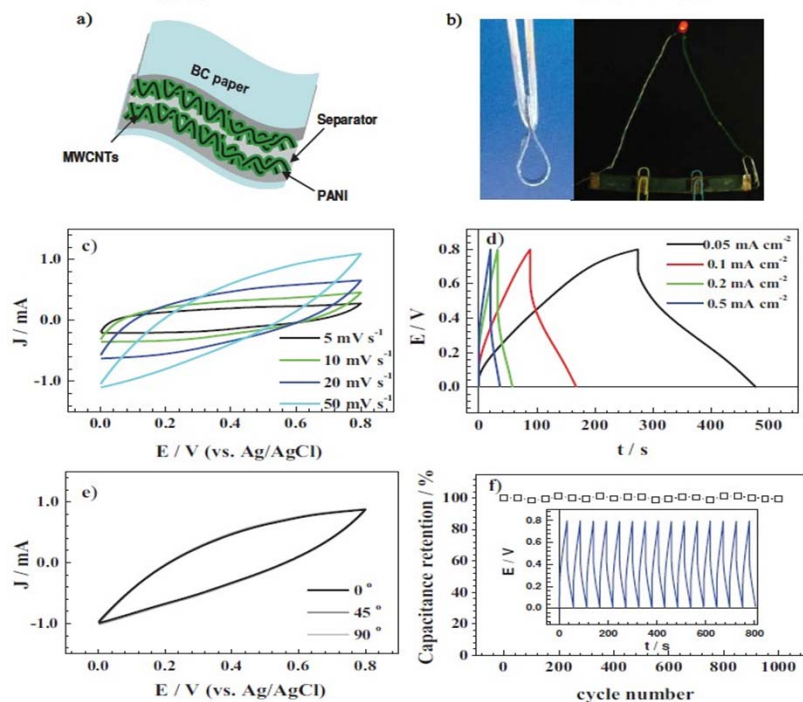


Figure 3. a) A schematic structure of solid-state supercapacitor device. b) The optical images of flexible supercapacitor device based on BC-MWCNTs-PANI $_{10}$ (left) and a red LED lighted by such devices (right). c) CV curves at different scan rate, d) galvanostatic charging/discharging curves at different discharge rates, and e) CV scans at different curvature for solid-state devices based on BC-MWCNTs-PANI $_{10}$ electrode. f) Cycling stability of solid-state device over 1000 cycles. The inset shows the galvanostatic charge/discharge curves.

➤ Flexible all-solid-state high-power supercapacitor fabricated with nitrogen-doped carbon nanofiber electrode material derived from bacterial cellulose⁶

- 전극 소재로 Bacterial cellulose (BC) nanofiber-supported polyaniline (PANI) nanocomposites을 개발하여
- 390.53kW kg⁻¹의 최대 power density, ~95.9%의 specific capacitance 와 뛰어난 cycling durability를 보고함.

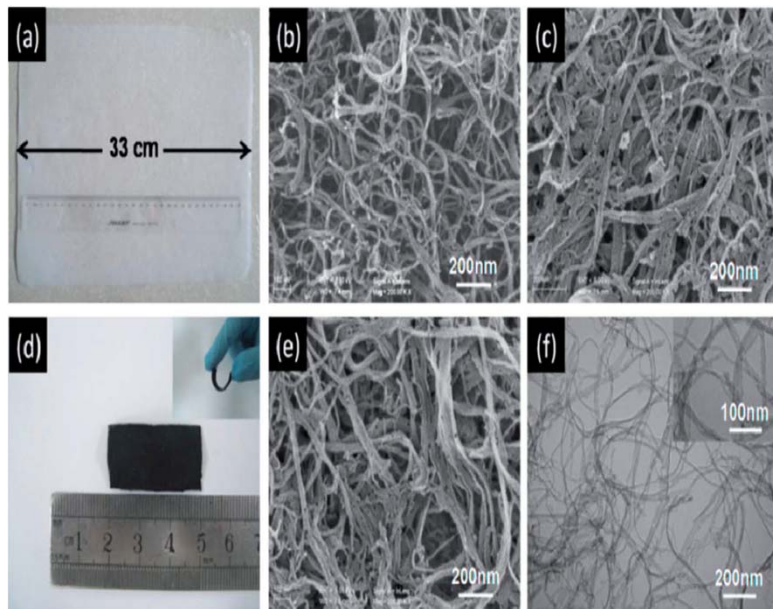


Fig. 1 (a) Photograph of the bacterial cellulose (BC) pellicle. (b) SEM image of the pyrolyzed BC (p-BC). (c) SEM image of activated p-BC (A-p-BC). (d) Photograph of the typical free-standing flexible nitrogen-doped A-p-BC (A-p-BC-N-25) being bent (3 cm 1.3 cm). (e) SEM image of the A-p-BC-N-25. (f) TEM image of the A-p-BC-N-25 (inset: magnified image).

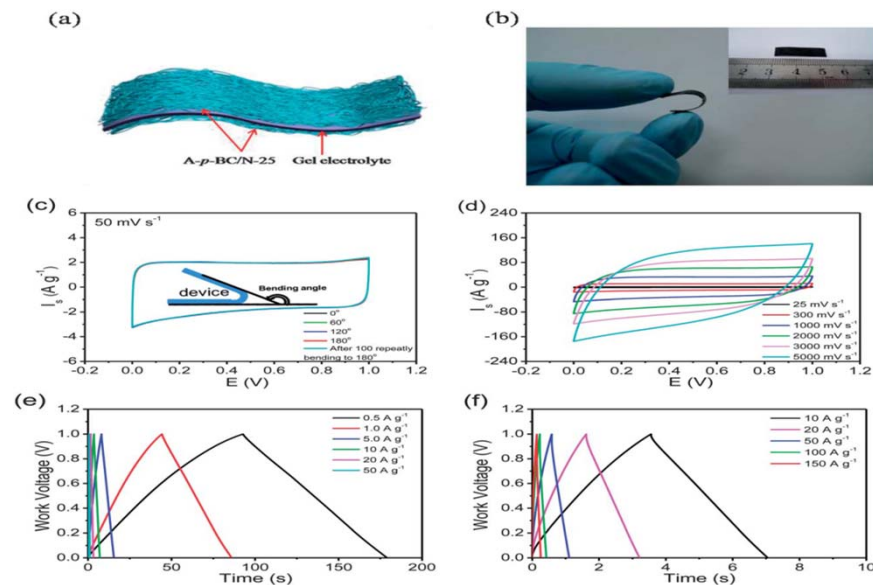


Fig. 4 (a) A schematic diagram of the all-solid-state supercapacitor illustrating that the gelled electrolyte can serve as both the electrolyte and separator. (b) A digital photograph of a bent A-p-BC-N-25 flexible supercapacitor device (2.4 cm 1.0 cm), showing its good flexibility. (c) CV curves collected at a scan rate of 50 mV s⁻¹ for the A-p-BC-N-25 flexible supercapacitor device under different bending angles. Inset is the schematic showing the device under stress and defining the bending angle. (d) Cyclic voltammetry (CV) curves of the A-p-BC-N-25 flexible supercapacitor at different scan rates. (e and f) Galvanostatic charge-discharge curves of the A-p-BC-N-25 flexible supercapacitor at different current densities.

➤ Bacterial Cellulose Nanofiber-Supported Polyaniline Nanocomposites with Flake-Shaped Morphology as Supercapacitor⁷

- 높은 전도도, thermal stability, well-controlled microstructure의 특징을 가지는 BC/PANI (polyaniline) composites를 전극소재로 사용한 Supercapacitor로 개발하였고 향후 다양한 energy-storage devices로의 응용이 기대됨.
- BC/PANI (polyaniline) composites은 높은 electrical conductivity (ca. 5.1 S/cm), 높은 표면적 (~33.969 m²/g), specific capacitance (273 F/g at 0.2 A·g⁻¹ current density)와 뛰어난 cycling stability를 보고함.

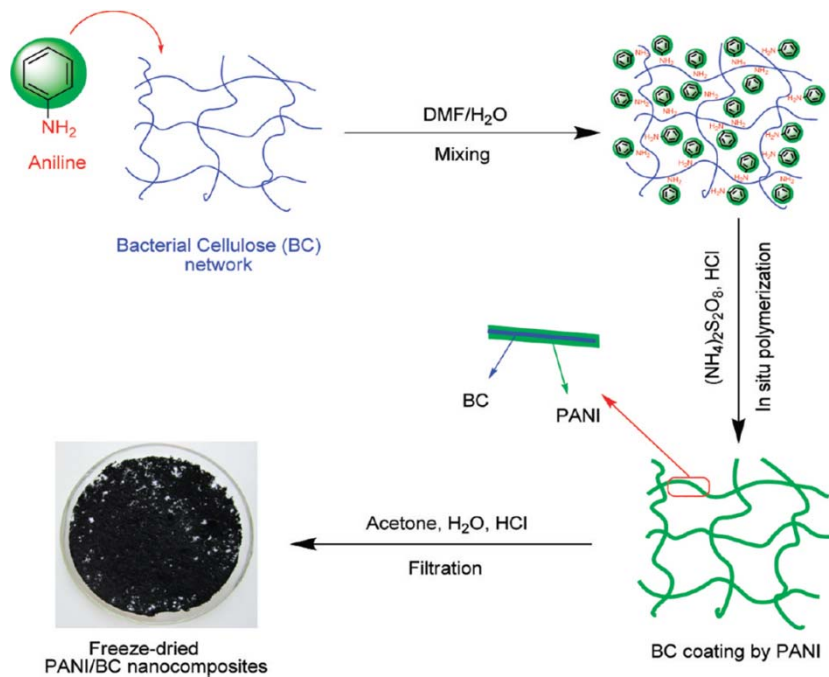


Figure 8. Schematic illustration of the process of preparation of BC/PANI in DMF/H₂O mixed solution.

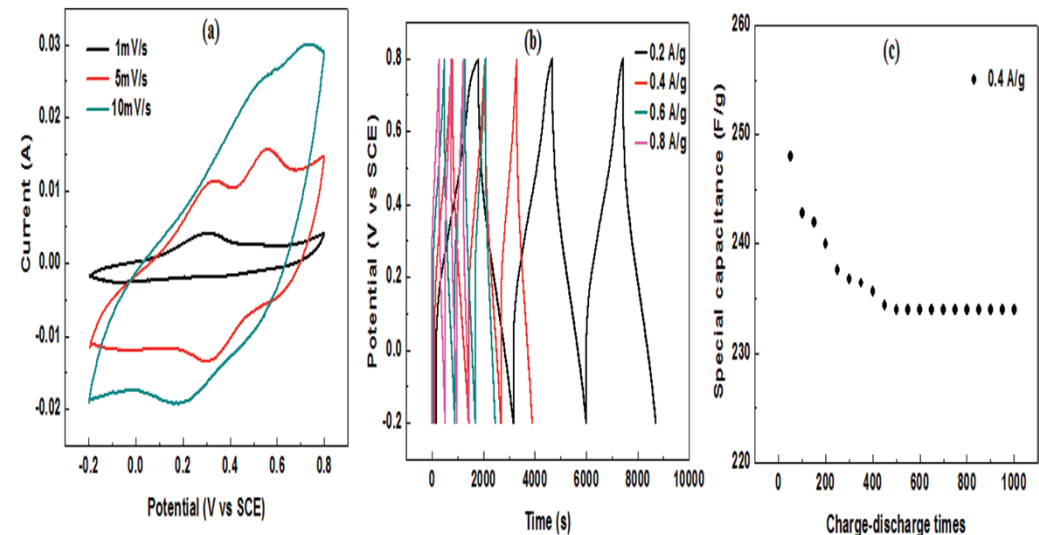


Figure 9. Cyclic voltammogram and galvanostatic charge/discharge for the electrochemical character of BC/PANI nanocomposites with potential (vs SCE) from -0.2 to 0.8 V: (a) 1, 5, and 10 mV/s; (b) specific capacitance at different current density, and (c) cycle life of BC/PANI at 0.4 A/g in 1 M H₂SO₄ solution.

➤ Dyeing bacterial cellulose pellicles for energetic heteroatom doped carbon nanofiber aerogels⁸

- Supercapacitor의 electrode materials로써 다양한 heteroatom (N, B, S and P) doped carbon (HDC) nanomaterials을 toxic organic dyes를 가지고 BC에 염색하여 열분해에 의하여 제조하였고 toxic dye를 제거 한 후 precursors로써 염색된 BC 박막에서 carbon nanofiber(CNF) aerogels를 합성함. 이러한 방법은 기존의 HDC방법으로 제조된 재료들에 비교하여 간단하면서 낮은 비용, 친 환경적인 장점들을 가지고 있음.
- HDC nanomaterials는 large electrochemical capacitance, good retention capability, high power density와 long-term cycling stability를 가지고 있어 supercapacitor electrode materials로 사용함.

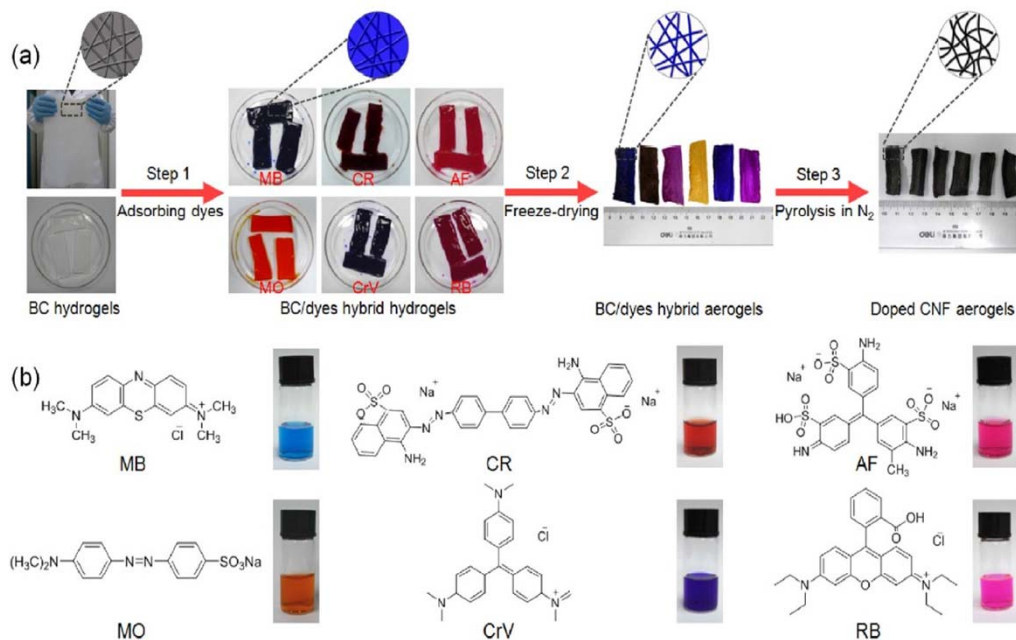


Figure 1 The fabrication process of doped CNF aerogels. (a) (1) BC hydrogels were soaked in various organic dye solutions (imitating waste-water) until saturation sorption; (2) after freeze-drying of the as-obtained BC/dye hybrid hydrogels, various BC/dye hybrid aerogels were obtained; (3) further pyrolysis of BC/dye hybrid aerogels under flowing N₂ produced doped CNF aerogels. (b) Molecular formulae of organic dyes (methylene blue, Congo red, acid fuchsin, methyl orange, crystal violet, and Rhodamine B) used in the fabrication process and corresponding digital images of their solutions. The high heteroatom contents in organic dyes make them be excellent precursors for preparing doped CNF aerogels.

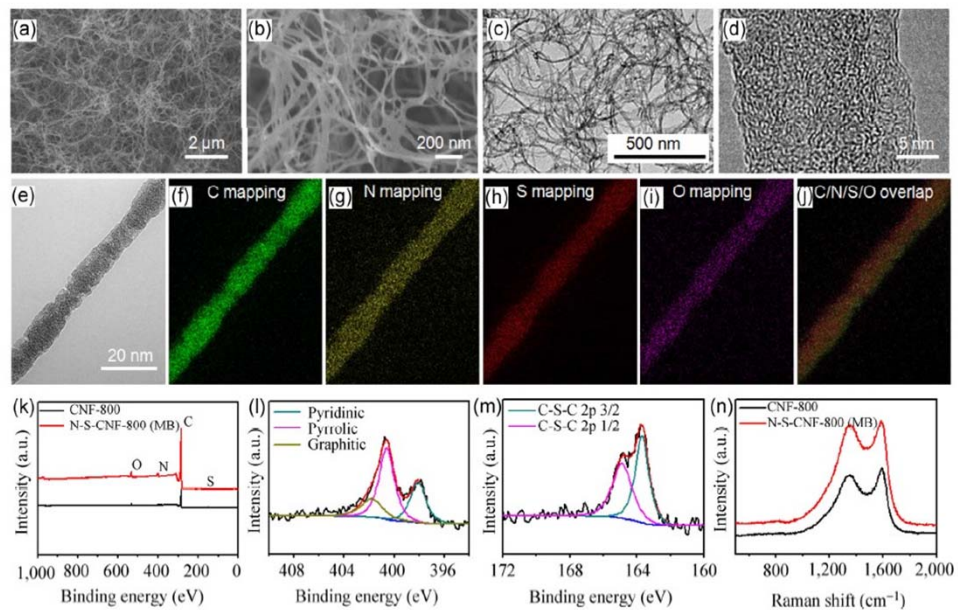


Figure 2 The morphologies and chemical compositions of N-S-CNF-800 (MB). (a) and (b) SEM images and (c) TEM image of N-S-CNF-800 (MB) aerogel revealing its 3D network nanostructure with 10–20 nm nanofibers. (d) HRTEM image of an individual N-S-CNF-800 (MB). (e)–(j) Energy filter TEM (EFTEM) image and elemental mapping of an individual N-S-CNF-800 (MB). (k) XPS survey spectra of N-S-CNF-800 (MB) and CNF-800. High-resolution XPS spectra of the deconvoluted (l) N 1s peak and (m) S 2p peak of N-S-CNF-800 (MB). (n) Raman spectra of N-S-CNF-800 (MB) and CNF-800.

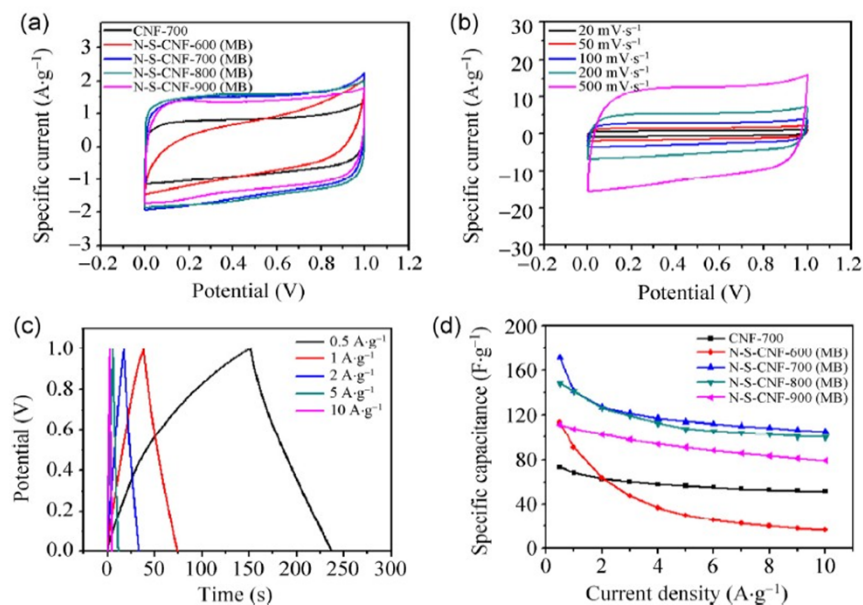


Figure 4 Electrochemical capacitive behaviors of N-S-CNF-y (MB) aerogels and CNF-700 aerogel. (a) CV curves of CNF-700, N-S-CNF-600, 700, 800, 900 (MB) in 1 M aqueous H₂SO₄ electrolyte at a scan of 50 mV·s⁻¹. (b) CV curves of N-S-CNF-700 (MB) at different scan rates. (c) Galvanostatic charge/discharge curves of N-S-CNF-700 (MB) with different current densities. (d) The variation of specific capacitances of the above samples as a function of current density.

3. 결론

- Supercapacitor는 높은 출력 밀도와 긴 수명을 가지고 있어 휴대용 전자장치, 백업전원, 다양한 마이크로장치에 적용가능성이 크며, 급속 충/방전 특성 및 고출력이 요구되는 분야에서 차세대 에너지 저장 장치로 그 가능성이 커 다양한 연구 및 개발을 하고 있음.⁸
- 최근 휴대용 개인 전자 장치가 각광을 받아 소형화, 장비 두께의 슬림화, 경량화, flexible electronic device화 하는 연구 및 제품 개발이 추진되고 있으며, 이러한 결과로 high power capability, good operational safety, long cycling life와 같은 특징을 가지는 supercapacitor가 주목받고 있음.⁵
- Low-cost, next-generation inexpensive, flexible, lightweight한 energy storage device를 만들기 위한 하이브리드 복합 소재 개발이 절실히 필요하여, 이와 같은 소재개발로 BC 기반 carbon material이 보고되고 있으며, large power densities, long cycle life, good operational safety를 가지는 지속적인 systems 연구가 꾸준히 보고되고 있음.⁴



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