박테리아 셀룰로오스기반 센서 전극의 연구 동향

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1. 서론

➢박아 셀룰로오스 (bacterial cellulose; BC)기반 센서 전극[1-3]

• 박테리아 셀룰로오스 기반 기능성 고감도 센서 전극 개발에 대한 연구 개발이 최근 활발하게 진행 되고 있으며, 이에 따른 BC의 기능화 연구, 전기전도성을 갖는 BC 복합체 소재 연구가 동반되어 보고되고 있음.

•박테리아 셀룰로오스 기반 전도성 폴리머와의 복합체 재료 개발 기술은 BT/NT/ET 등이 하이브리드 된 기술로서 각 기술들의 융합에 의하여 센서 전극으로써 새로운 특성과 기술적인 면에서 시너지 효과를 기대할 수 있음.

• 박테리아 셀룰로오스 기반 기능성 고감도 센서 전극 개발에 대한 연구 결과가 아직 산업으로의 응용이 미비한 상태임.

➢응용

• 전기전자 소재로써 체내 삽입형 의료장치, 재생의학적인biology–device interface, 바이오 센서 등에 응용.

2. 박테리아 셀룰로오스기반 센서전극의 연구동향

➢Double network bacterial cellulose hydrogel to build a biology–device interface [4]

- Biology–device interface로써 double network BC–CP(conducting polymer) composite hydrogel을 만들었으며 conducting polymer로 polyaniline (PAni)과 polypyrrole (PPy)를 사용하여 BC 표면에 polymerzation 하였고 양쪽면에 SnO2:F가 코팅된 유리를 덮어 working electrode로 사용하여 cyclic voltammetry와 electrochemical impedance spectroscopy(EIS)를 측정하였음.
- BC hydrogel은 good biocompatibility, biodegradability, bioadhesion, mass transport 성질들을 가지고 있으며, CP는 electrochemical signal의 증폭, 측정하기 위한 signal 분석이 가능함.

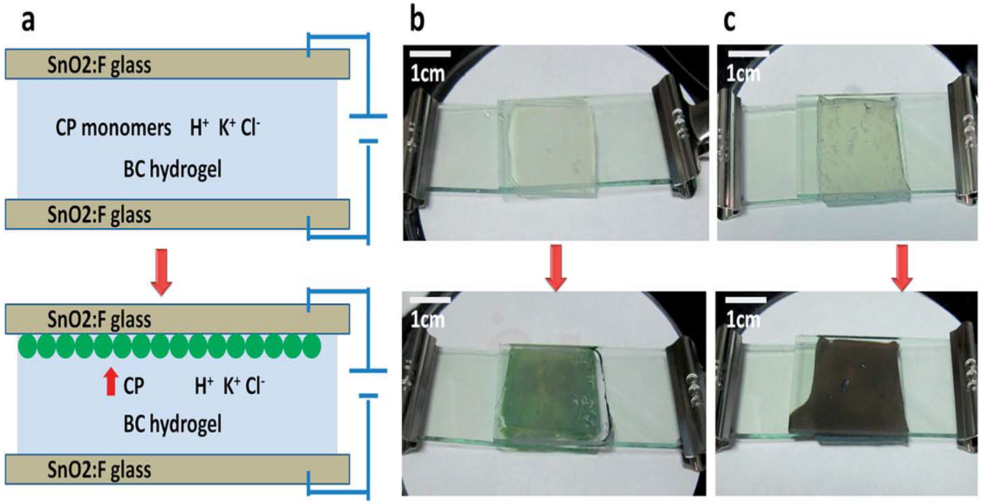

Fig. 1 (a) Schematic diagram of electropolymerization of CP on the BC hydrogel, (b) photographs showing the electropolymerization of PAni on the BC hydrogel and (c) photographs showing the electropolymerization of PPy on the BC hydrogel.

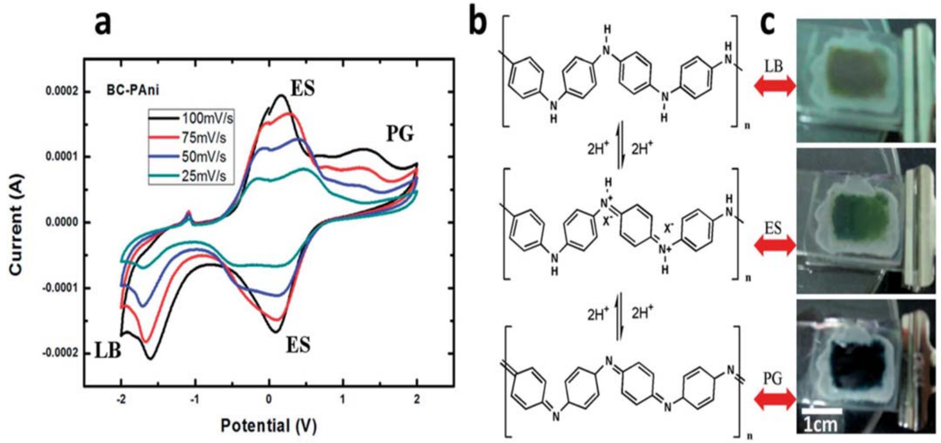

Fig. 2 (a) Cyclic voltammograms of BC–PAni with PANI films as working electrodes within 2.0 V at different scan rates of 25, 50, 75 and 100 mV s1, (b) schematic diagram showing the chemical structure of three forms of polyaniline and (c) the colour changes of BC–PAni.

• Double network BC–CP hydrogels은 생체적합적 특성과 electroactivity가 직접화된 biphasic Janus hydrogels의 장점을 가진 체내 삽입형 의료장치 및 재생의학적인biology–device interface임을 입증함.

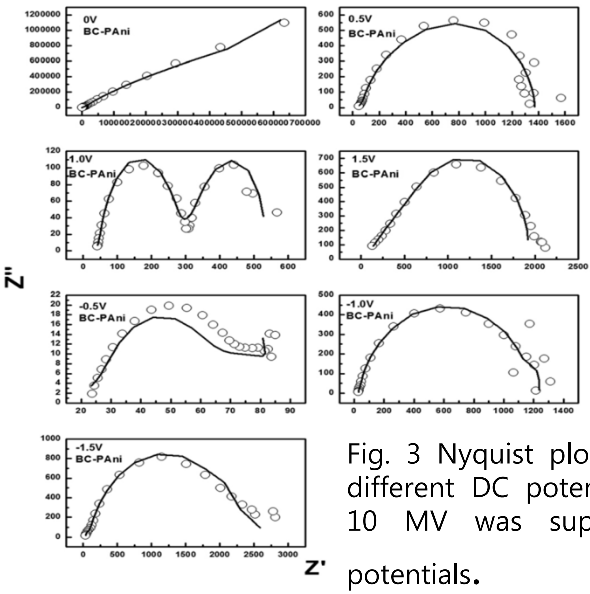

Fig. 3 Nyquist plots of BC–PAni recorded at different DC potentials; an AC amplitude of 10 MV was superimposed over the DC potentials.

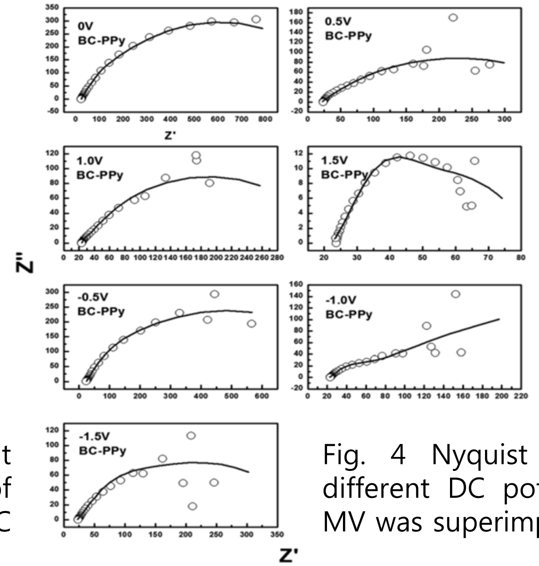

Fig. 4 Nyquist plots of BC–PPy recorded at different DC potentials; an AC amplitude of 10 MV was superimposed over the DC potentials.

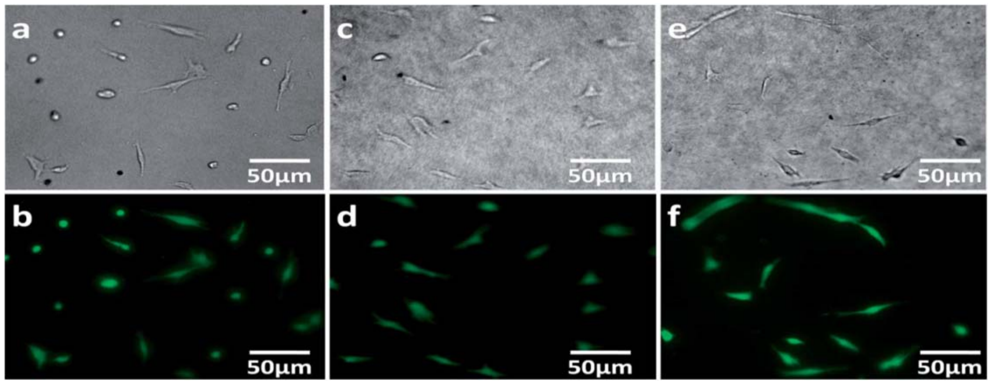

Fig. 5 Light microscopy images of fibroblast cells incubated on the surface of (a) BC hydrogels, (c) BC layer of BC–PAni, and (e) BC layer of BC–PPy. Calcein AM/PI dual-fluorescence stain of fibroblast cells incubated on the surface of (b) BC hydrogels, (d) BC layer of BC–PAni, and (f) BC layer of BC–PPy.

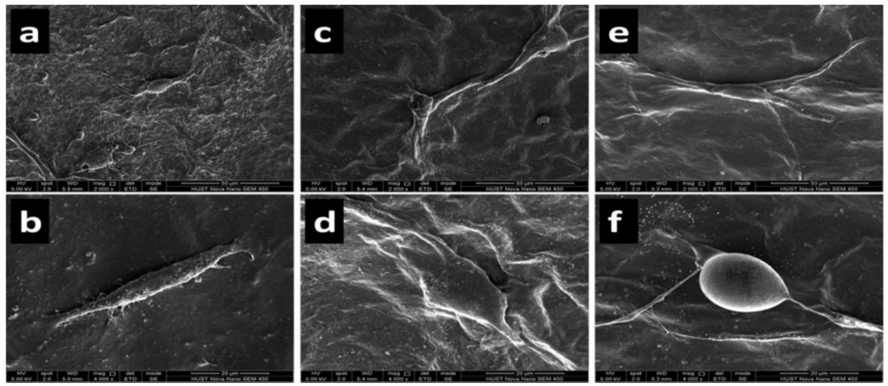

Fig. 6 SEM images of fibroblast cells incubated on the surface of (a and b) BC hydrogels, (c and d) BC layer of BC–PAni, and (e and f) BC layer of BC–PPy.

➢ Highly conductive and stretchable conductors fabricated from bacterial cellulose[5]

- Flexible electronics 로 응용하기 위한 신소재로 BC 기반 열분해 BC(p-BC)/polydimethylsiloxane(PDMS) 복합체를 준비하였고 이 소재는 높은 전도도 (0.20–0.41 Scm^{-1}), 전기와 기계적으로 안정성과 함께 높은 신축성을 가지고 있음.
- 이와 같은 소재 개발은 large-scale flexible, stretchable, foldable electronics등의 장점을 가지고 있어 저 비용으로 산업적으로 응용하기에 적합함.

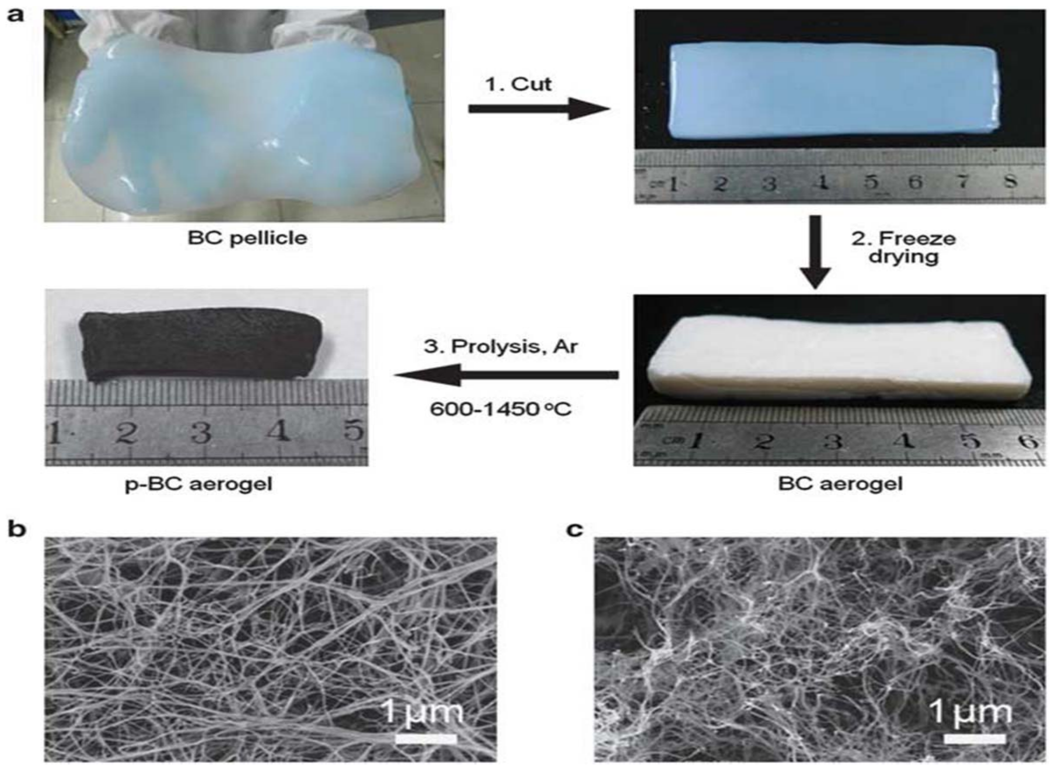

Figure 1. (a) The fabrication process of BC-based materials. (1) A large-sized BC pellicle (2002303mm3) was cut into the desired shape with a sharp blade. (2) After freeze-drying of the wet BC pellicles, the ultralight BC aerogel was obtained. (3) Further pyrolysis treatment of the BC aerogel under flowing argon produced the black p-BC aerogel. (b, c) Scanning electron microscopy images of the BC and p-BC aerogels, respectively.

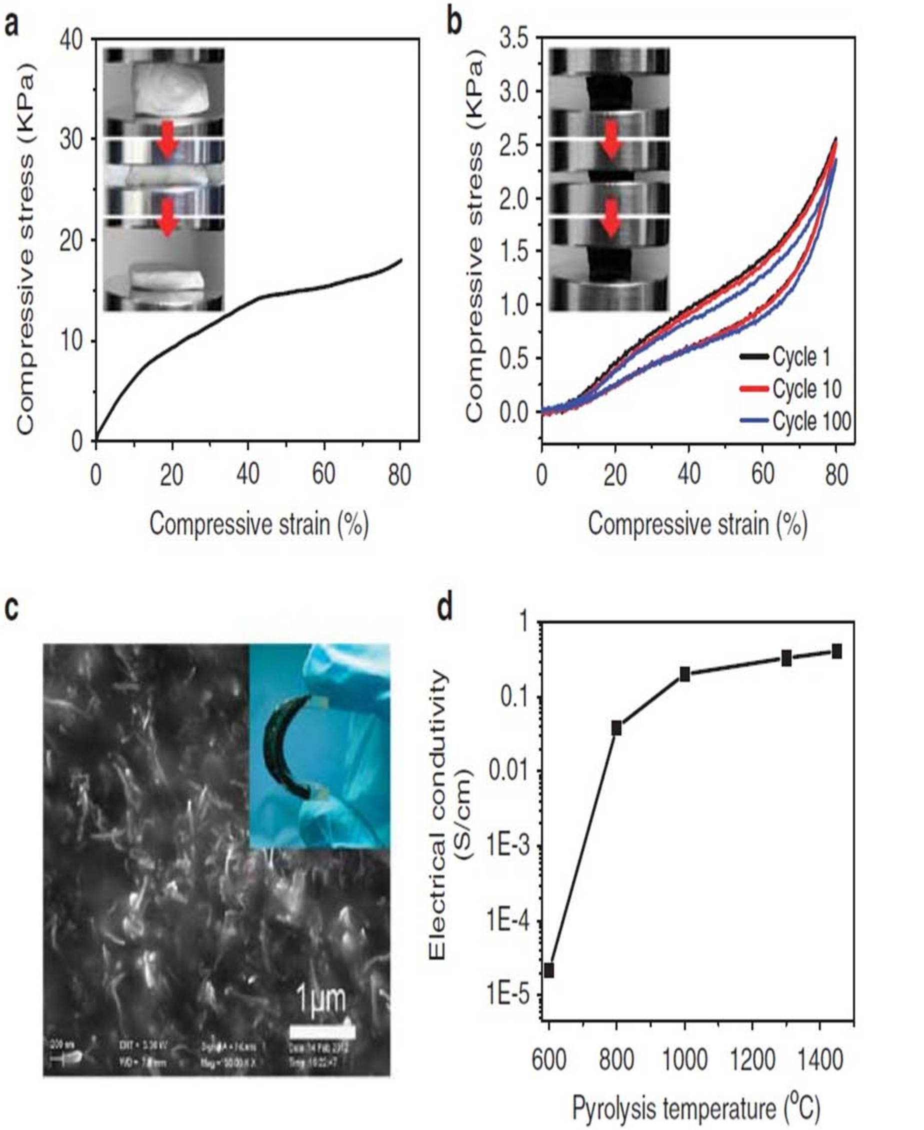

Figure 2. (a) Compressive stress–strain curve of the BC aerogel at a set strain of 80%. (b) Cyclic stress–strain curves of the p-BC aerogel at a maximum strain of 80%, showing a very small permanent deformation after 100 compression cycles. The insets in (a) and (b) show the sequential photographs of the BC and p-BC aerogels during the compression process, illustrating their different mechanical properties. (c) Scanning electron microscopy image of the fracture surface of the typical p-BC/PDMS composite.

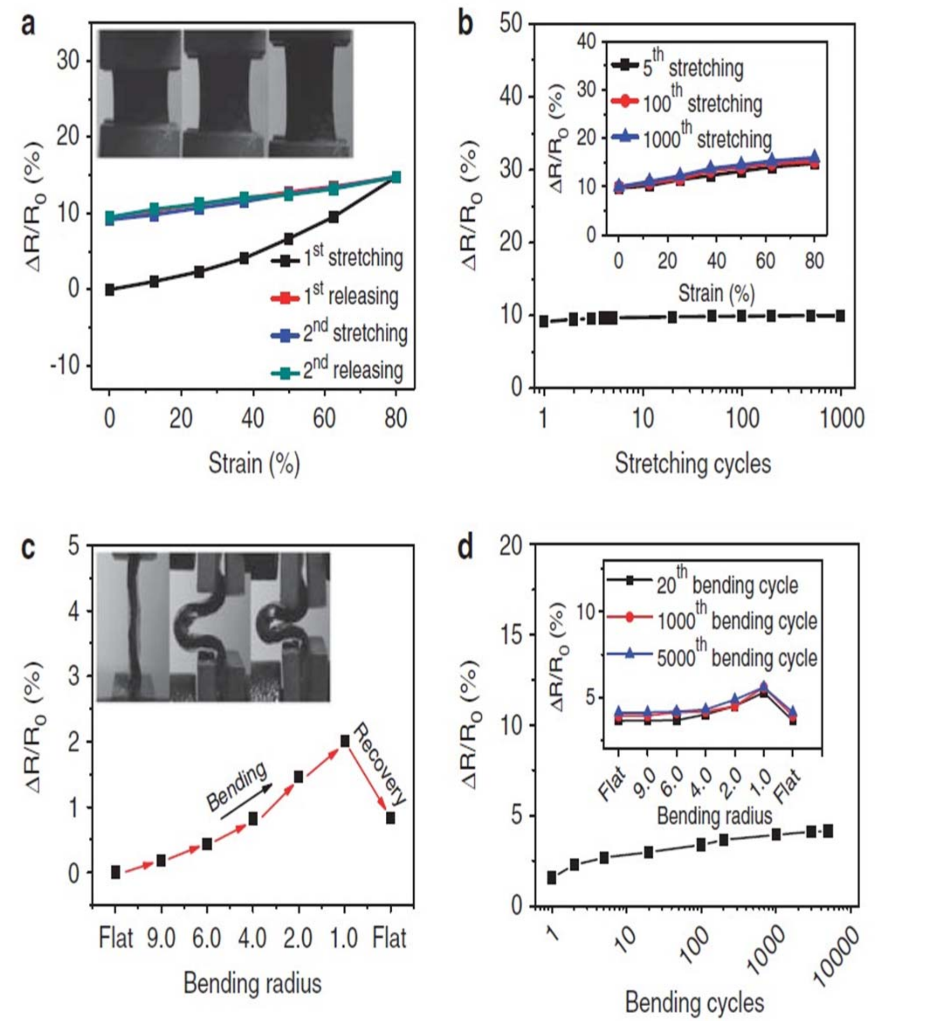

Figure 3 Resistance change of the p-BC/PDMS composite under mechanical deformations. (a) Variation of the normalized resistance (DR/R0) of the composite as a function of tensile strain up to 80% in the first two stretch-release cycles. The inset shows the stretching process. (b) DR/R0 as a function of stretching cycles at a strain up to 80%. The inset shows the fifth, hundredth, thousandth stretching cycles. (c) DR/R0 of the composite at a bend radius of up to 1.0 mm in the first bending cycle. The inset shows the bending process. (d) DR/R0 as a function of the bend cycles at a maximum bend radius of 1.0mm. The inset shows the twentieth, thousandth, fivethousandth bending cycles.

➢ Flexible Electrically Conductive Nanocomposite Membrane Based on Bacterial Cellulose and Polyaniline[6]

• Conductive polyaniline/bacterial cellulose (PANI/BC) nanocomposite membranes은 PANI 나노입자가 산처리된 BC 파이버위에 나노크기로 균일하게 연속적으로 감싸고 있어 코팅이 전체적으로 uniform하고 flecxible membrane을 형성함.

• PANI/BC nanocomposite membranes은 뛰어난 전기전도도, 훌륭한 mechanical properties, thermal stability를 가지고 있어 sensors, flexible electrodes, flexible displays로의 응용이 가능함.

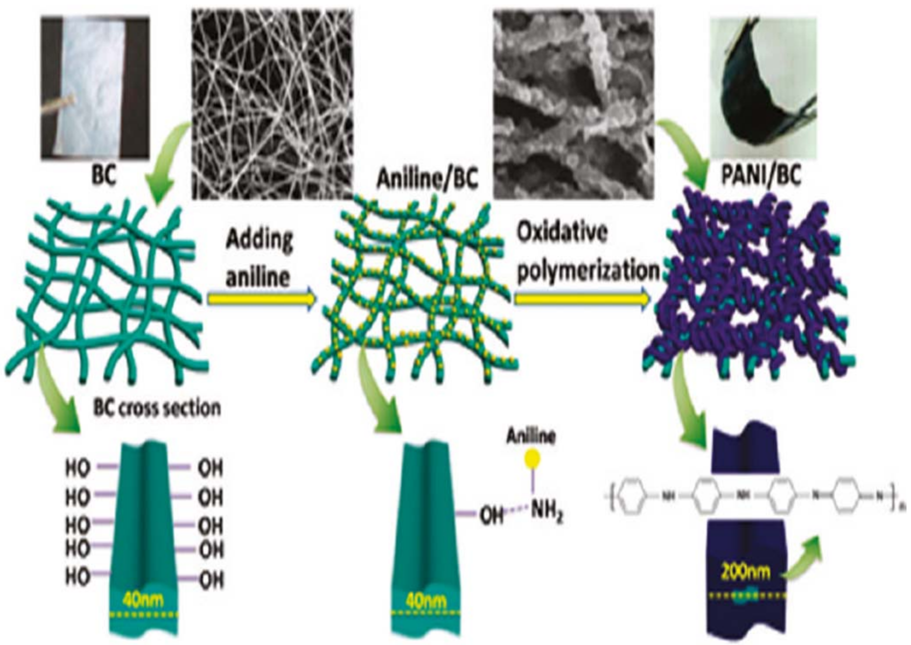

Figure 1. Schematic diagramof the formation of PANI/BCnanocomposites.

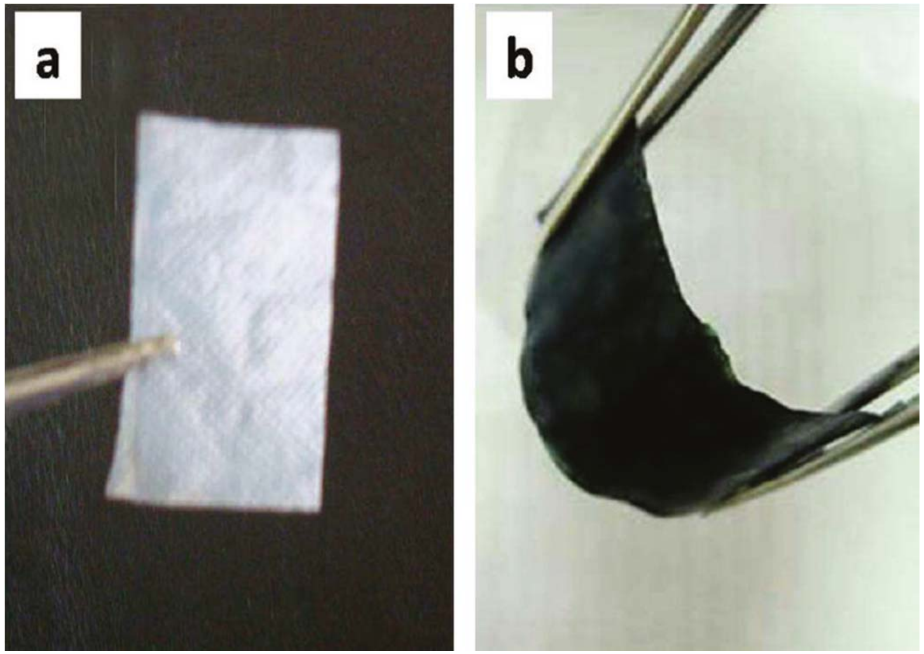

Figure 2. Optical images of the (a) pure BCmembrane and (b) PANI/BC composite membrane (10.7 wt % PANI).

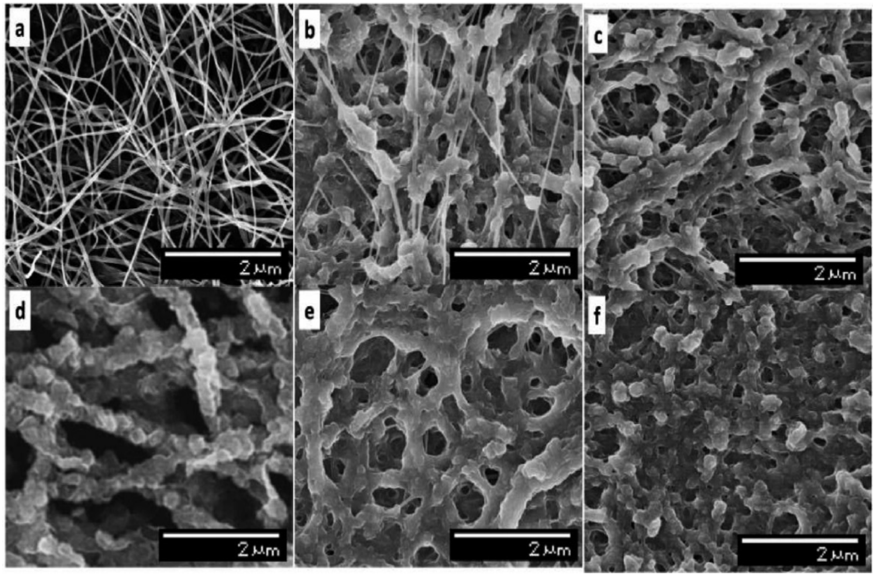

Figure 3. FE-SEM images of (a) pure BC and the PANI/BC composites formed with the reaction time of (b) 30 min, (c) 60 min, (d) 90 min, (e) 120 min, and (f) 180 min, respectively.

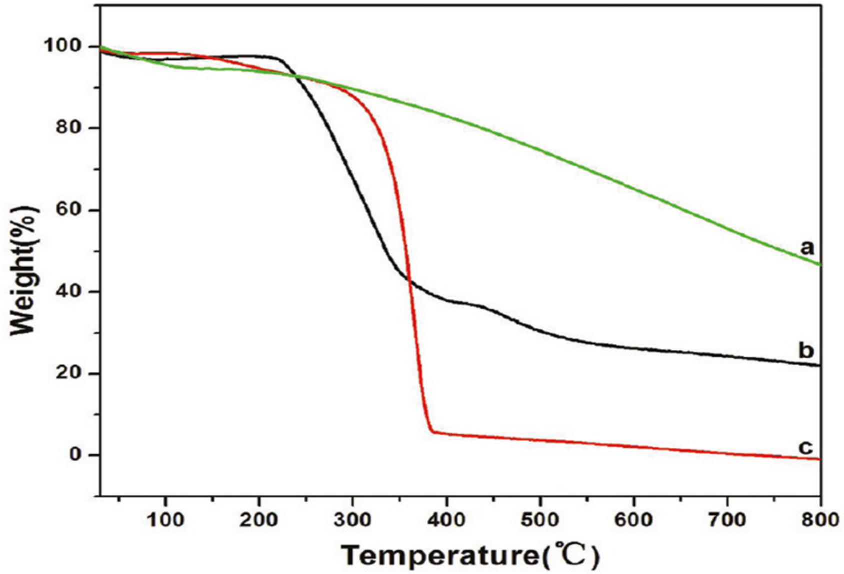

Figure 4. TG curves of (a) PANI (doped by HCl), (b) the PANI/BC composite with 10.7 wt % PANI (doped by HCl), and (c) pure BC.

Table 1. Effects of Reaction Time on the Content of PANI and the Electrical Conductivity of PANI/BC Composites

reaction time (min)	content of PANI (wt %)	electrical conductivity (S/cm)
30	5.8	2.0×10^{-4}
60	9.1	4.7×10^{-3}
90	10.7	5.0×10^{-2}
120	13.1	2.3×10^{-3}
180	15.3	9.5×10^{-3}

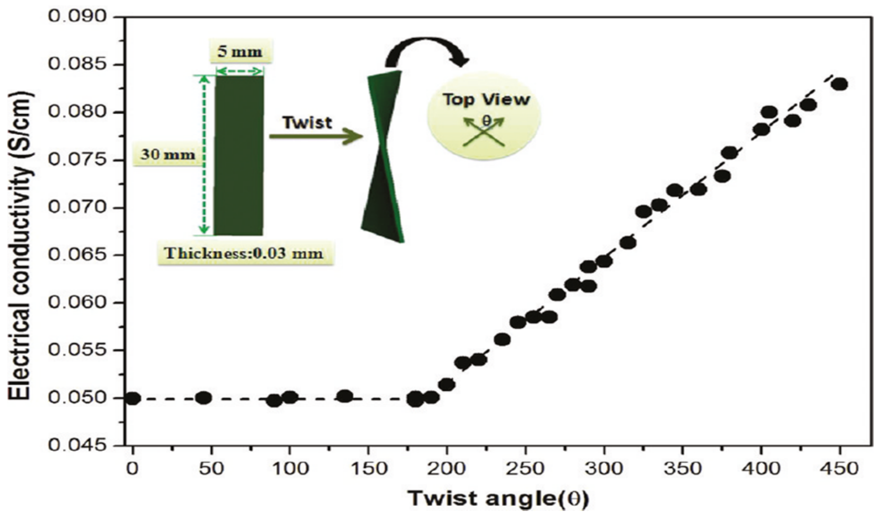

Figure 5. Conductivity of PANI/BC composite membranes with 10.7 wt % PANI as a function of twist angle (θ). The inset shows the sample size and twist of the composite membrane.

➤ Formaldehyde sensors based on nanofibrous polyethyleneimine/bacterial cellulose membranes coated quartz crystal microbalance[7]

• Formaldehyde sensor 는 nanofibrous polyethyleneimine (PEI)/bacterial cellulose (BC) membranes을 quartz crystal microbalance (QCM)에 코팅하여 제작함. Nanoporous three-dimensional PEI/BC membranes은 직경이 30–60 nm 인 나노파이버를 이용하여 센서전극을 제작하였음.

• Formaldehyde sensor는 훌륭한 sensitivity, selectivity, reversibility, 1–100 ppm의 농도 영역에서 repeatability와 같은 특징을 가지며 제조 방법이 간단하고 저가로 제작공정으로 산업적 응용이 기대됨.

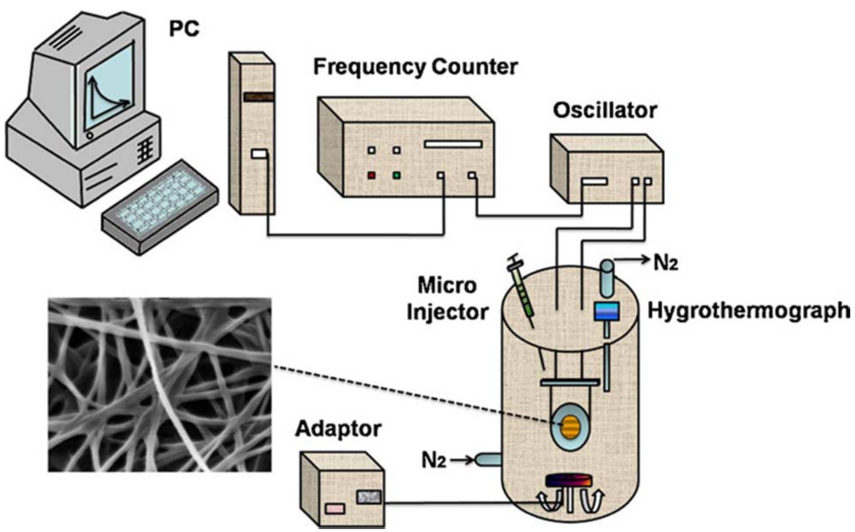

Fig. 1. Schematic of the experimental setup for formaldehyde detection.

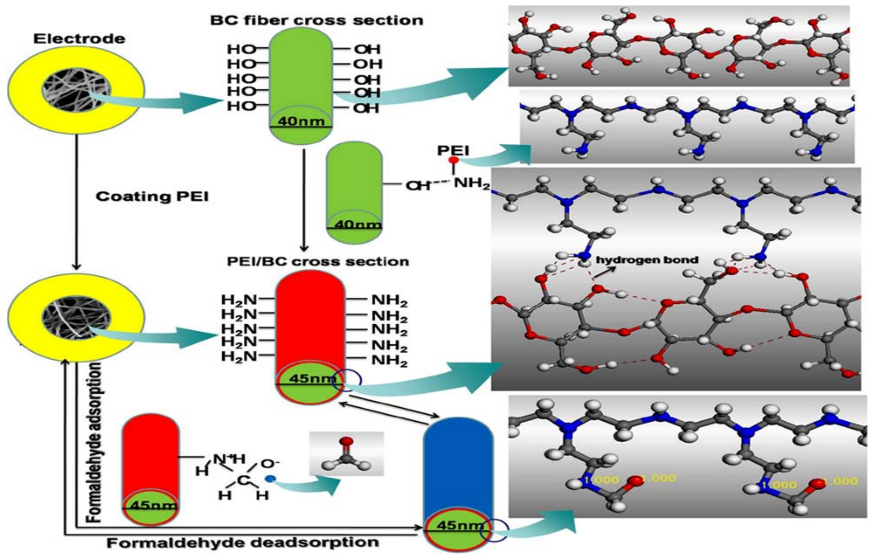

Fig. 2. Schematic diagram of the interaction of BC and PEI, and formaldehyde and PEI.

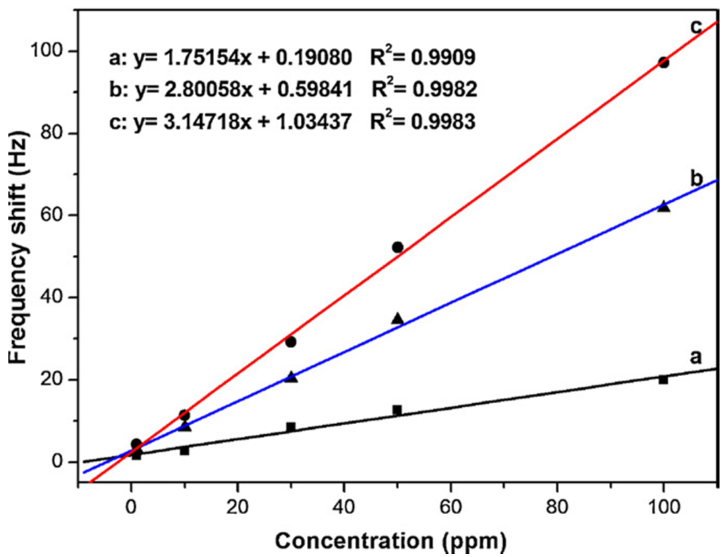

Fig. 3. Dependence of the frequency shift of sensors coated with (a) PEI membrane, (b) PEI/BC membranes with a weight ratio of 0.67/1 and (c) PEI/BC membranes with a weight ratio of 1.34/1 on formaldehyde concentration

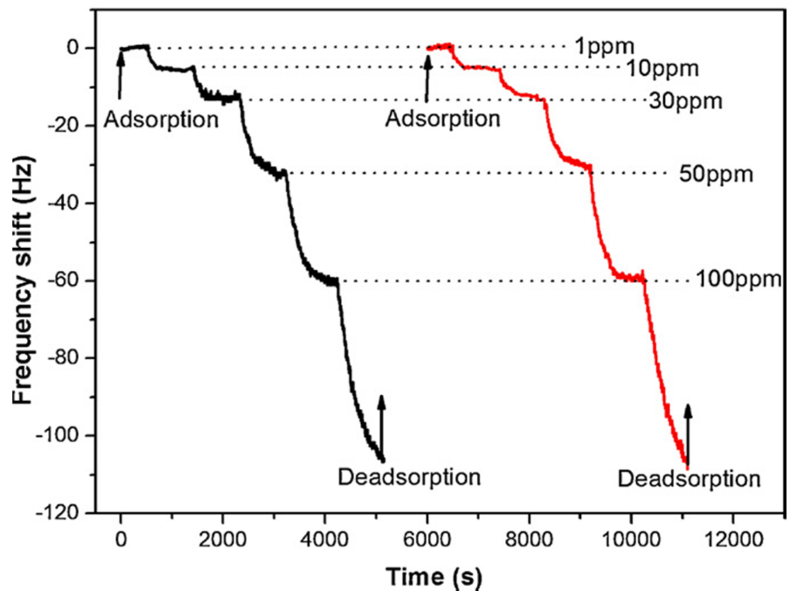

Fig. 4. Reproducibility test for frequency shifts of the PEI/BC nanofibrous membranes with a weight ratio of 1.34/1 coated QCM sensors exposed to formaldehyde at the relative humidity of 60%.

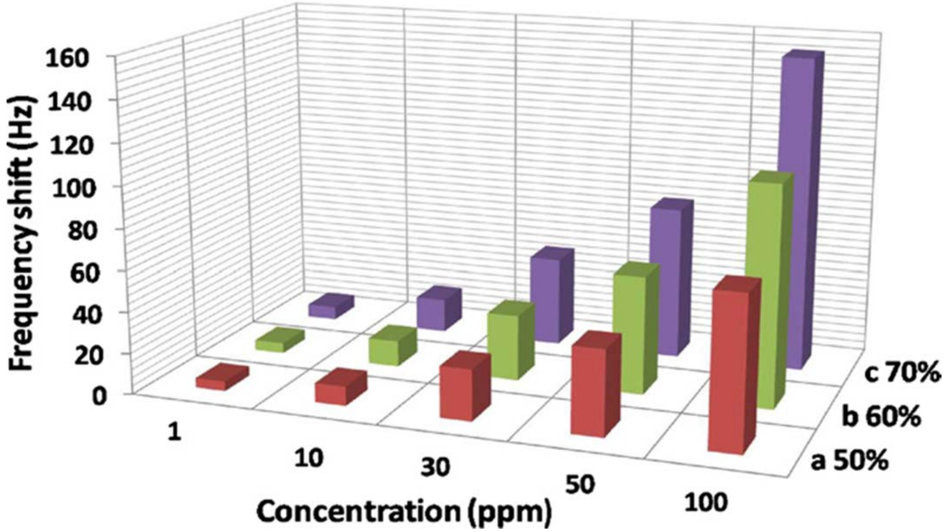

Fig. 5. Response of the PEI/BC nanofibrous membrane coated QCM sensor with a weight ratio of 1.34/1 when exposed to 1, 10, 30, 50, and 100 ppm of formaldehyde at various relative humidity of (a) 50%, (b) 60%, and (c) 70%, respectively.

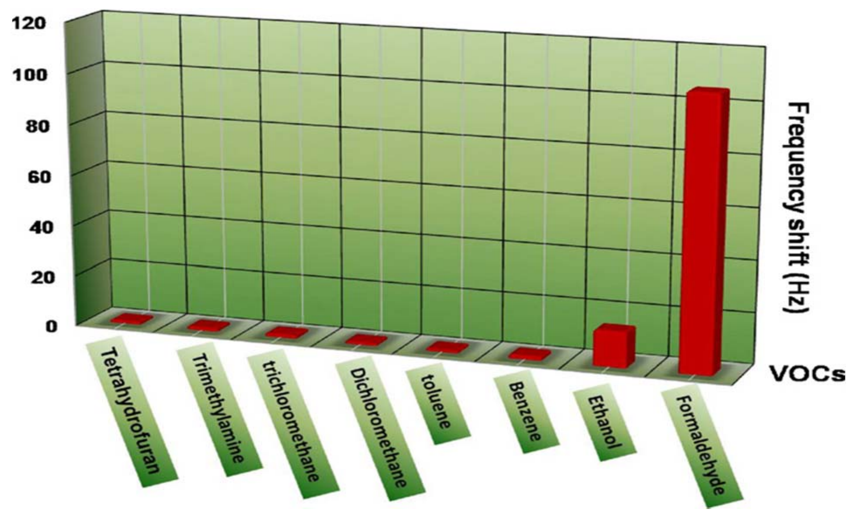

Fig. 6. Response of the nanofibrous membrane coated QCM sensor with a PEI/BC weight ratio of 1.34/1 exposed to various volatile organic compounds at the relative humidity of 60%.

3. 결론

- BC 기반 전도성 폴리머 복합 hydrogels은 생체적합적 특성과 electroactivity가 직접화된 biphasic Janus hydrogels의 장점을 가진 double network로 체내 삽입형 의료장치, 재생의학적인 biology–device interface로의 응용 가능성을 입증함.[4]

- Flexible electronics로 응용하기 위한 신소재로, BC 기반 열분해 BC(p-BC) 기반 폴리머 복합체 개발은 높은 전도도, 전기와 기계적으로 안정하면서 높은 신축성을 가지고 있어 large-scale flexible, stretchable, foldable electronics등의 산업적 응용분야에 적합함을 보고하고 있음.[5]

- 이와 같은 소재 개발연구는 고기능성, 경량화, 생체적합성 및 친화성, 친환경적인 특성을 가지는 첨단 소재로 다양한 분야에 응용되고 있는 센서 전극소재로써의 중요성이 부각되고 있음.

4. 참고 문헌

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