

# Core-sheath Structured Bacterial Cellulose/Polypyrrole Nanocomposites with Excellent Conductivity as Supercapacitors

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## Supplementary Information

**Preparation of BC/PPy conductive nanocomposites.** The BC/PPy conducting nanocomposites were prepared via in-situ oxidative polymerization of Py self-assembled onto BC nanofibers. By fine-tuning the reaction parameters including the feeding mass ratio of Py/BC (1:1 to 1/20), molar ratio of oxidizer  $\text{FeCl}_3/\text{Py}$  (0.25:1 to 1.25:1), molar ratio of dopant  $\text{HCl}/\text{Py}$  (0:1 to 1.4:1), composition of mixture solvent of  $\text{DMF}/\text{H}_2\text{O}$  (0:1 to 1.5:1), reaction temperature ( $0^\circ\text{C}$  to  $25^\circ\text{C}$ ), and reaction time (1 min to 24 h) in sequence, a large spectrum of BC/PPy nanocomposites were prepared. With the as-prepared nanocomposites at hand, the electrical conductivity was measured with a conventional four-point probe technique and morphology was observed via field-emission gun scanning electron microscopy (FESEM).

**Characterization.** FT-IR spectra were obtained using a Bomen MB154S Fourier transform infrared (FTIR) spectroscopy. The sample was cut into very little particles and characterized by a Fourier transform infrared spectrometer for the evaluation of chemical structures in the range of  $4000$  to  $500\text{ cm}^{-1}$  by accumulating 64 scans at a resolution of  $2\text{ cm}^{-1}$ .

Polymer surface composition was determined using X-ray photoelectron spectroscopy (XPS) (PHI-5300, Perkin Elmer) with a  $\text{Mg-K}\alpha$  excitation source ( $1253.6\text{ eV}$ ) at high- resolutions wide scans ( $71.55\text{ eV}$  analyzer pass energy). The

core-level signals were obtained at a photoelectron take off-angle ( $\alpha$ ) of  $45^\circ$  with respect to the samples surface. After linear background subtraction, N1s and O1s spectra were fitted with Gaussian component peaks allowing slight variations in the full-width at half maximum (fwhm) to reflect their chemical-state dependence.<sup>1</sup> Binding energies (BE) were referenced to the maxima in the smoothed C1s envelopes, defined at 285.0 eV,<sup>2</sup> to compensate for surface-charging. Surface atomic stoichiometries were obtained from peak areas corrected with experimental sensitivity factors and are expected to have a  $\pm 10\%$  error.

X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (D8 Advance, Bruker, Germany) by using Cu K $\alpha$  radiation at 40kV and 30mA. The diffraction angle was ranged from 10 to  $45^\circ$ . The crystallinity index was calculated as the ratio of the area of the resolved crystalline peaks to the total area of a diffraction profile for 10 to  $45^\circ$ . The crystallite size was estimated from the integrated width of the resolved crystalline peak by using Scherrer's equation.

The thermal stability of BC and BC/PPy nanocomposites was carried out with a Mettler Toledo SDTA815<sup>o</sup> thermogravimetric analyser. All analyses were performed with 1.9 mg samples in aluminum pans and were heated from 50 and 800 $^\circ$ C at a scanning rate of 20 K/min in the presence of a 30 ml/min nitrogen flow.

For field-emission gun scanning electron microscopy (FESEM) observations, samples of BC and PPy/BC nanocomposites were sputtered with gold. The morphology of BC and PPy/BC nanocomposites was observed with a Hitachi S4800 FESEM at an accelerating voltage of 15 kV. For fracture surface observations the composites were immersed in liquid nitrogen and subsequently fractured.

**XPS spectra analysis.** The binding energy (BE) for Curve-resolved C1s and O1s core levels of BC and C1s, O1s, N1s and Cl2p core levels of pristine PPy and BC/PPy composites were summarized in Table S1.

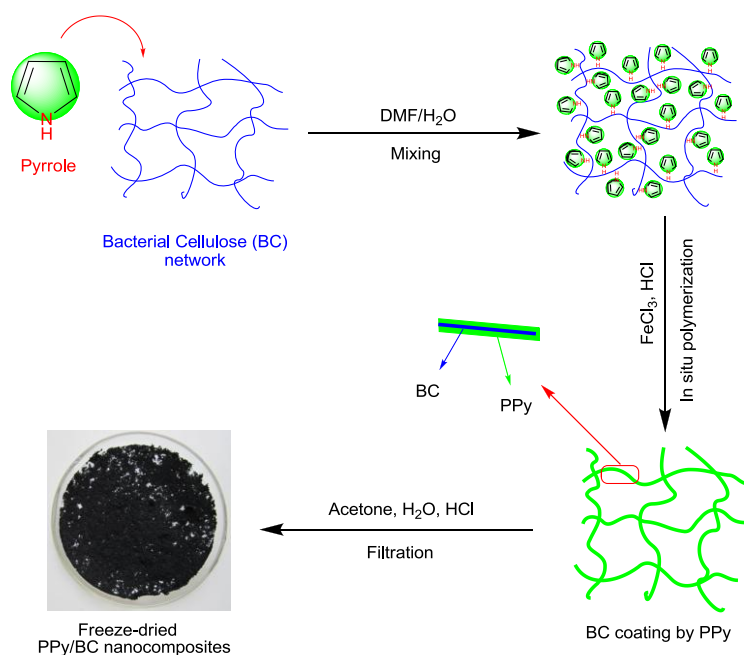
**Table S1.** Curve-resolved C1s and O1s core levels of BC and C1s, O1s, N1s and Cl2p core levels of BC/PPy composites<sup>2-4</sup>

BE(eV)	C1s				O1s		N1s			Cl2p		
Samples	C-H	C-OH	C=O, C-N	O-C-O	C-OH	C-OC	-N=	-NH-	-N <sup>+</sup> -	Cl <sup>-</sup>	Cl <sup>+</sup> *	-Cl

BC	281.0	283.2	285.0	286.2	528.6	531.3						
PPy							397.8	399.3	401.1			
*BC/PPy	284.1	285.4	287.0	288.4	531.4	533.5	398.7	399.9	401.2	197.1	198.5	199.8

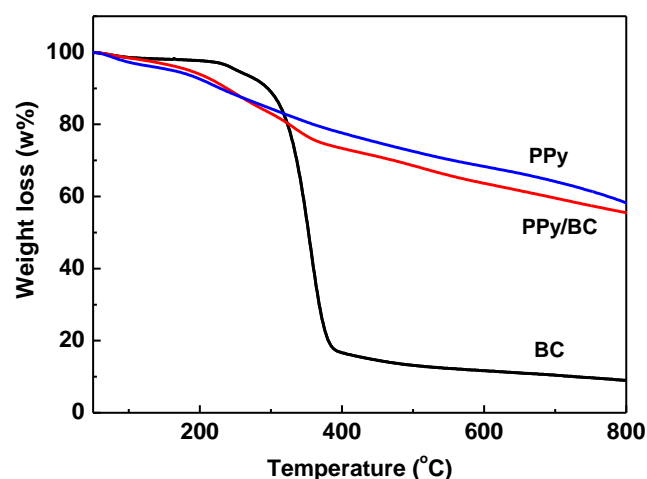
\*BC/PPy refers to the BC/PPy composites prepared under the optimized reaction conditions.

**Proposed mechanism for PPy coating onto BC nanofibers.** According to the morphology evolution during fine-tuning reaction parameters for PPy coating, the synthesis mechanism of BC/PPy nanocomposites was speculated and shown in Figure S1. It can be clearly seen that three processes were: (a) pyrrole monomer be dispersed into the 3D-network of BC nanofibers in the medium of DMF/H<sub>2</sub>O (DMF played an important role in dispersing process, which could be proven by the surface area and FESEM images of materials); (b) the polymerization coincided with the doping process by oxidant of FeCl<sub>3</sub> and dopant of HCl; (c) PPy/BC nanocomposites were formed after filtration and lyophilization.



**Figure S1.** Schematic illustration of the process of preparation of PPy/BC in DMF/H<sub>2</sub>O solvent.

**TGA analysis:** The thermal stability of as-prepared BC/PPy nanocomposite was studied by thermal gravimetric analysis (TGA).



**Figure S1.** TG curves of pure BC, pure PPy and PPy/BC nanocomposites.

## References

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