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 FeCl₃/Py (0.25:1 to 1.25:1), molar ratio of dopant HCl/Py (0:1 to 1.4:1), composition of mixture solvent of DMF/H₂O (0:1 to 1.5:1), reaction temperature (0°C to 25°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 cm⁻¹ by accumulating 64 scans at a resolution of 2 cm⁻¹.

Polymer surface composition was determined using X-ray photoelectron spectroscopy (XPS) (PHI-5300, Perkin Elmer) with a Mg-Kα excitation source (1253.6 eV) at high- resolutions wide scans (71.55eV analyzer pass energy). The
core-level signals were obtained at a photoelectron take off-angle ($\alpha$) of 45° with respect to the samples surface. After linear background subtraction, Nls 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.\(^1\)

Binding energies (BE) were referenced to the maxima in the smoothed Cls envelopes, defined at 285.0 eV,\(^2\) to compensate for surface-charging, Surface atomic stoichiometries were obtained from peak areas corrected with experimental sensitivity factors and are expected to have a ±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°. 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°. 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° thermogravimetric analyser. All analyses were performed with 1.9 mg samples in aluminum pans and were heated from 50 and 800°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\(^2\)\(^-\)\(^4\)

<table>
<thead>
<tr>
<th>BE(eV)</th>
<th>Samples</th>
<th>C-H</th>
<th>C-OH</th>
<th>C=O, C-N</th>
<th>O-C-O</th>
<th>C-OH</th>
<th>C-OC</th>
<th>-N=</th>
<th>-NH-</th>
<th>-N(^+)-</th>
<th>Cl</th>
<th>Cl(^+)</th>
<th>-Cl</th>
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<tr>
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<td>C1s</td>
<td>O1s</td>
<td>N1s</td>
<td>Cl2p</td>
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<td>285.0</td>
<td>286.2</td>
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<td>285.4</td>
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<td>*BC/PPy</td>
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*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/H₂O (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 FeCl₃ and dopant of HCl; (c) PPy/BC nanocomposites were formed after filtration and lyophilization.

![Proposed mechanism](attachment:mechanism.png)

**Figure S1.** Schematic illustration of the process of preparation of PPy/BC in DMF/H₂O 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


