## **Supporting Information**

## Carbon Nanofiber-RuO<sub>2</sub>-Poly(benzimidazole) Ternary Hybrids for Improved Supercapacitor Performance

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## Results



Figure S1: HR-TEM images of (a) Pristine carbon nanofiber support [CNF] clearly indicating the open tips (b) high magnification images of the CNFs depicting the active terminal graphene edges and the deactivated outer wall due to the deposition of a pyrolitic carbon layer.

Figure S1(a) and (b) are the HRTEM images of carbon nanofibers (CNF) at different magnifications. The low magnification image given in Figure S1 (a) clearly indicates that the length these CNFs is in few micrometers. The open tips of the CNFs are also clear from the image. The duplex structure of the system with the edges of the slanting graphene planes in the inner cavity and the smooth outer wall formed due to the stacking on the parallel graphene planes is clarly evident from the Figure 1(b). The inner and outer diamters of the CNFs are ca.  $50 \pm 10$  and  $100\pm 10$  nm respectively.



Figure S2: XP spectra of (a) C 1s and Ru 3d core levels (b) O 1s level and (c) Ru 3p levels of F-20RuO<sub>2</sub> after deconvolution; the circles represent the experimental data, the solid line represents the fitting data for the overall signal and the dotted lines are the deconvoluted individual peaks for different species present in the sample.

Figure S2 (a), (b) and (c) respectively show the deconvoluted C1s, O1s and Ru 3p levels of this material. The C 1s spectrum of F-20RuO<sub>2</sub> after deconvolution gives 5 peaks. The first three peaks observed at the binding energy 284.5, 286.1 and 288.2 eV corresponds to graphitic carbon and carbon bonded to -OH and -COOH groups respectively. The additional two peaks at 281.6 and 284 eV respectively, corresponding to the  $3d_{1/2}$  and  $3d_{3/2}$  levels of Ru. Form the peak position, it is evident that Ru is in the form of RuO<sub>2</sub> in all the catalysts and no metallic Ru is detected. Oxygen part of the XPS after deconvolution gives two peaks, one corresponding to the functional groups present in the pre-treated CNF and the second one corresponding to the oxygen in the RuO<sub>2</sub>. As the more intense Ru 3d levels overlap with the with the intense C1s peak, the presence of RuO<sub>2</sub> is further confirmed using the 3p levels also. The deconvoluted XP spectra of Ru 3p levels given in Figure S2 (c) also show one doublet at 462.8 and 485.4 eV. This binding energy value is in excellent agreement with that reported for hydrous RuO<sub>2</sub> and it gives an unambiguous evidence for the formation of RuO<sub>2</sub> in this material.



Figure S3: HRTEM image showing the empty outer wall and the selective decoration of  $RuO_2$  nanoparticles in the inner cavity of carbon nanofiber.



Figure S4. TEM image of RP-1 which clearly indicate the formation of a thin layer of PBI-BuI on the outer wall of CNF. The insets show a clear picture of the skin layer of PBI-BuI formed on the RuO<sub>2</sub> nanoparticles.



Figure S5: HRTEM images of (a) & (b) pristine CNF and (c) & (d) CNF after PBI-BuI incorporation.

The uniform wrapping of the polymer (PBI-BuI) formed on the CNFs is evident on a comparison of the TEM images of pristine and polymer incorporated CNF given Figure S4 (a) and (c) respectively. From the high magnification images of the same given in Figure S4 (b) and S4(d), it can be concluded that the thickness of the polymer coating formed is ca. 10 nm. Apart from this, the incorporation of PBI-BuI in the inner cavity is also elear from the high magnification images where the air bubbles formed direct toward the discontinuous filling of the PBI-BuI in the inner cavity of the CNFs.



Figure S6: Comparison of the CV response obtained in 0.5 M H<sub>2</sub>SO<sub>4</sub> at different scan rates (5-300 mV/s) for (a) F-20RuO<sub>2</sub>, (b) RP-0.25, (c) RP-0.5 and (d) RP-1 electrodes.



Figure S7: Cyclic voltammograms of CNF in 0.5 M H<sub>2</sub>SO<sub>4</sub> at the scan rates of 5, 25, 50, 100 and 150 mV/s.

The specific capacitance calculated for CNF from the CV given in Figure S8 is 4 F/g only.



Figure 8. Comparison of the cyclic voltammograms of CNF, CP-0.25, CP-0.5 and CP-1 electrodes at the scan rate of 50 mV/s in 0.5M aqueous  $H_2SO_4$ .