Hierarchical carbon nanopetal/polypyrrole nanocomposite electrodes with brush-like architecture for supercapacitors

Jayesh Cherusseri\textsuperscript{a} and Kamal K. Kar\textsuperscript{a,b,*}

\textsuperscript{a}Advanced Nanoengineering Materials Laboratory, Materials Science Programme, Indian Institute of Technology, Kanpur, Uttar Pradesh-208016, India.
\textsuperscript{b}Advanced Nanoengineering Materials Laboratory Department of Mechanical Engineering, Indian Institute of Technology, Kanpur, Uttar Pradesh-208016, India.

*Corresponding Author. Tel: +91-512-2597687, E-mail: kamalkk@iitk.ac.in (Kamal K. Kar)

Electronic Supplementary Information

**Supplementary Methods:**

**Method S1.** Calculation of ionic conductivity of CNPCF-PPY nanocomposite electrodes.

**Method S2.** Calculation of the cell capacitance of CNPCF-PPY supercapacitor.

**Method S3.** Calculation of the areal capacitance of CNPCF-PPY supercapacitor.

**Method S4.** Calculation of the areal energy density of CNPCF-PPY supercapacitor.

**Method S5.** Calculation of the area specific capacitance of CNPCF-PPY supercapacitor.

**Method S6.** Calculation of the area specific energy density of CNPCF-PPY supercapacitor.

**Method S7.** Calculation of the volumetric capacitance of CNPCF-PPY supercapacitor.

**Method S8.** Calculation of the volumetric energy density of CNPCF-PPY supercapacitor.

**Method S9.** Calculation of the volume specific capacitance of CNPCF-PPY supercapacitor.

**Method S10.** Calculation of the volume specific energy density of CNPCF-PPY supercapacitor.

**Method S11.** Calculation of the gravimetric capacitance of CNPCF-PPY supercapacitor.

**Method S12.** Calculation of the gravimetric energy density of CNPCF-PPY supercapacitor.

**Supplementary Figures:**

**Fig. S1.** (a,b) SEM images of CNPs synthesized on CF at different magnifications.

**Fig. S2.** (a,b) TEM images of the tip portion of a CNP at different magnifications.

**Fig. S3.** (a) \textsuperscript{14}N adsorption isotherms and (b) BJH pore-size distribution curve of CNPs.

**Fig. S4.** TEM images of CNPCF-PPY-10 (a), CNPCF-PPY-20 (b), CNPCF-PPY-30 (c), CNPCF-PPY-40 (d), CNPCF-PPY-50 (e), CNPCF-PPY-60 (f) and CNPCF-PPY-120 (g) nanocomposites [inset shows their corresponding selected area electron diffraction (SAED) pattern].

**Fig. S5.** FTIR spectra of CNPCF and CNPCF-PPY nanocomposites.

**Fig. S6.** XPS high-resolution spectra of CNPCF-PPY nanocomposites. XPS de-convolution C 1s spectra (a-g) and N 1s spectra (h-n): CNPCF-PPY-10 (a,h), CNPCF-PPY-20 (b,i), CNPCF-PPY-30 (c,j), CNPCF-PPY-40 (d,k), CNPCF-PPY-50 (e,l), CNPCF-PPY-60 (f,m) and CNPCF-PPY-120 (g,n) nanocomposites.

**Fig. S7.** Nyquist plot near the high frequency region of CNPCF-PPY-40, CNPCF-PPY-50, CNPCF-PPY-60 and CNPCF-PPY-120 SCs.

**Fig. S8.** (a-c) \textsuperscript{14}N adsorption isotherms and (d-f) BJH pore-size distribution curve of CNPCF-PPY-40 (a,d), CNPCF-PPY-50 (b,e) and CNPCF-PPY-60 (c,f) nanocomposite.

**Fig. S9.** Plot of areal capacitance of CNPCF and CNPCF-PPY SC cells.
**Fig. S10.** Plot of areal energy density of CNPCF and CNPCF-PPY SC cells.  
**Fig. S11.** Plot of volumetric capacitance of CNPCF and CNPCF-PPY SC cells.  
**Fig. S12.** Plot of volumetric energy density of CNPCF and CNPCF-PPY SC cells.  
**Fig. S13.** EPMA secondary electron image of CNPCF-PPY-50 nanocomposite electrode after completing 5000 charge/discharge cycles.  
**Fig. S14.** EPMA 2D elemental mapping of CNPCF-PPY-50 nanocomposite electrode after completing 5000 charge/discharge cycles.  
**Fig. S15.** XPS C 1s (a) and N 1s (b) de-convolution spectra of CNPCF-PPY-50 nanocomposite electrode after completing 5000 charge/discharge cycles.

**Supplementary Methods:**

**Method S1. Calculation of ionic conductivity of CNPCF-PPY nanocomposite electrodes.**  
The ionic conductivity of the supercapacitor electrodes is calculated by using the equation

$$\sigma = \frac{T}{R_b \times A}$$

Where $\sigma$ is the ionic conductivity in S cm$^{-1}$, $T$ is the total thickness of the supercapacitor cell (in cm), $R_b$ is the bulk electrolyte resistance (in $\Omega$), and $A$ is the geometrical area of electrodes (in cm$^2$).

**Method S2. Calculation of the cell capacitance of CNPCF-PPY supercapacitor.**  
The cell capacitance of the supercapacitor is calculated by using equation

$$C_{cell} = \frac{I_{dis} \times t_{dis}}{\Delta E}$$

Where, $C_{cell}$ is the cell capacitance of the supercapacitor, $I$ is the charging current, $t_{dis}$ is the discharging time, and $\Delta E$ is the operating potential window.

**Method S3. Calculation of the areal capacitance of CNPCF-PPY supercapacitor.**  
The areal capacitance of the supercapacitor is calculated by using the equation

$$C_{cell,A} = \frac{C_{cell}}{A_{cell}}$$

Where, $C_{cell,A}$ is the areal capacitance of the supercapacitor, and $A_{cell}$ is the total geometric area of two supercapacitor electrodes (i.e., two times the area of single electrode).

**Method S4. Calculation of the areal energy density of CNPCF-PPY supercapacitor.**  
The areal energy density ($E_{cell,A}$) of the supercapacitor is calculated by using the equation

$$E_{cell,A} = \frac{C_{cell,A} \times (\Delta E)^2}{2 \times 3600}$$

**Method S5. Calculation of the area specific capacitance of CNPCF-PPY supercapacitor.**  
The area specific capacitance of the supercapacitor is calculated by using the equation

$$C_{cell,sp,A} = \frac{C_{cell}}{A_{ele}}$$

Where, $C_{cell,sp,A}$ is the area specific capacitance of the supercapacitor and $A_{ele}$ is the geometric area of the supercapacitor electrode.
Method S6. Calculation of the area specific energy density of CNPCF-PPY supercapacitor.
The area specific energy density ($E_{\text{cell,sp,A}}$) of the supercapacitor is calculated by using the equation

$$E_{\text{cell,sp,A}} = \frac{C_{\text{cell,sp,A}} \times (\Delta E)^2}{2 \times 3600}$$

Method S7. Calculation of the volumetric capacitance of CNPCF-PPY supercapacitor.
The volumetric capacitance of the supercapacitor is calculated by using the equation

$$C_{\text{cell,V}} = \frac{C_{\text{cell}}}{V_{\text{cell}}}$$

Where, $C_{\text{cell,V}}$ is the volumetric capacitance of the supercapacitor and $V_{\text{cell}}$ is the total volume of the supercapacitor.

Method S8. Calculation of the volumetric energy density of CNPCF-PPY supercapacitor.
The volumetric energy density ($E_{\text{cell,V}}$) of the supercapacitor is calculated by using the equation

$$E_{\text{cell,V}} = \frac{C_{\text{cell,V}} \times (\Delta E)^2}{2 \times 3600}$$

Method S9. Calculation of the volume specific capacitance of CNPCF-PPY supercapacitor.
The volume specific capacitance of the supercapacitor is calculated by using the equation

$$C_{\text{cell,sp,V}} = \frac{C_{\text{cell}}}{V_{\text{ele}}}$$

Where, $C_{\text{cell,sp,V}}$ is the volume specific capacitance of the supercapacitor and $V_{\text{ele}}$ is the total volume of the supercapacitor electrodes.

Method S10. Calculation of the volume specific energy density of CNPCF-PPY supercapacitor.
The volume specific energy density ($E_{\text{cell,sp,V}}$) of the supercapacitor is calculated by using the equation

$$E_{\text{cell,sp,V}} = \frac{C_{\text{cell,sp,V}} \times (\Delta E)^2}{2 \times 3600}$$

Method S11. Calculation of the gravimetric capacitance of CNPCF-PPY supercapacitor.
The gravimetric capacitance ($C_{\text{m}}$) of the supercapacitor is calculated by using the equation

$$C_{\text{m}} = \frac{I \times t_{\text{dis}}}{m \times (\Delta E)} = \frac{C_{\text{cell}}}{m}$$

Where, ‘m’ is the total mass of electro-active materials (both CNP and PPY) in the two electrodes of the supercapacitor (excluding the mass of CF, separator, and electrolyte) and other variables are discussed above.
Method S12. Calculation of the gravimetric energy density of CNPCF-PPY supercapacitor.

The gravimetric energy density \( (E_m) \) of the supercapacitor is calculated by using the equation

\[
E_m = \frac{C_m X (\Delta E)^2}{2 X 3600}
\]

**Supplementary Figures:**

**Fig. S1.** (a,b) SEM images of CNPs synthesized on CF at different magnifications.

**Fig. S2.** (a,b) TEM images of the tip portion of a CNP at different magnifications.
Fig. S3. (a) N\textsubscript{2} sorption isotherms and (b) BJH pore-size distribution curve of CNPs.

Fig. S4. TEM images of CNPCF-PPY-10 (a), CNPCF-PPY-20 (b), CNPCF-PPY-30 (c), CNPCF-PPY-40 (d), CNPCF-PPY-50 (e), CNPCF-PPY-60 (f) and CNPCF-PPY-120 (g) nanocomposites [inset shows their corresponding selected area electron diffraction (SAED) pattern].
Fig. S5. FTIR spectra of CNPCF and CNPCF-PPY nanocomposites.
Fig. S6. XPS high-resolution spectra of CNPCF-PPY nanocomposites. XPS de-convolution C 1s spectra (a-g) and N 1s spectra (h-n): CNPCF-PPY-10 (a,h), CNPCF-PPY-20 (b,i), CNPCF-PPY-30 (c,j), CNPCF-PPY-40 (d,k), CNPCF-PPY-50 (e,l), CNPCF-PPY-60 (f,m) and CNPCF-PPY-120 (g,n) nanocomposites.
Fig. S7. Nyquist plot near the high frequency region of CNPCF-PPY-40, CNPCF-PPY-50, CNPCF-PPY-60 and CNPCF-PPY-120 SCs.

Fig. S8. (a-c) N$_2$ sorption isotherms and (d-f) BJH pore-size distribution curve of CNPCF-PPY-40 (a,d), CNPCF-PPY-50 (b,e) and CNPCF-PPY-60 (c,f) nanocomposite.
Fig. S9. Plot of areal capacitance of CNPCF and CNPCF-PPY SC cells.

Fig. S10. Plot of areal energy density of CNPCF and CNPCF-PPY SC cells.

Fig. S11. Plot of volumetric capacitance of CNPCF and CNPCF-PPY SC cells.
**Fig. S12.** Plot of volumetric energy density of CNPCF and CNPCF-PPY SC cells.

**Fig. S13.** EPMA secondary electron image of CNPCF-PPY-50 nanocomposite electrode after completing 5000 charge/discharge cycles.
**Fig. S14.** EPMA 2D elemental mapping of CNPCF-PPY-50 nanocomposite electrode after completing 5000 charge/discharge cycles.

**Fig. S.15.** XPS C 1s (a) and N 1s (b) de-convolution spectra of CNPCF-PPY-50 nanocomposite electrode after completing 5000 charge/discharge cycles.