Electronic Supplementary Material (ESI) for Dalton Transactions.

Nanoclay Based Hierarchical Interconnected Mesoporous CNT/PPy Electrode with Improved Specific Capacitance for High Performance Supercapacitor

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Supporting Information

1. SEM ANALYSIS:

The SEM micrographs suggest different structure and morphology of nanocomposite. PPy shows the existence of irregular stacked globular particle morphology which are tightly bound to each other shown in Fig. S1a. Nanocomposite CP shows tubular and interwoven structure indicating CNT are uniformly coated with PPy Fig. S1b. The SEM micrographs on loading nanoclay suggests effective interpenetration of nanoclay into CNT and vice versa. At lower magnification, both in-situ and ex-situ ternary composite illustrates the interwoven structure with porous nature with high degree of interlocking presented in Fig. S1c & Fig. S1d.

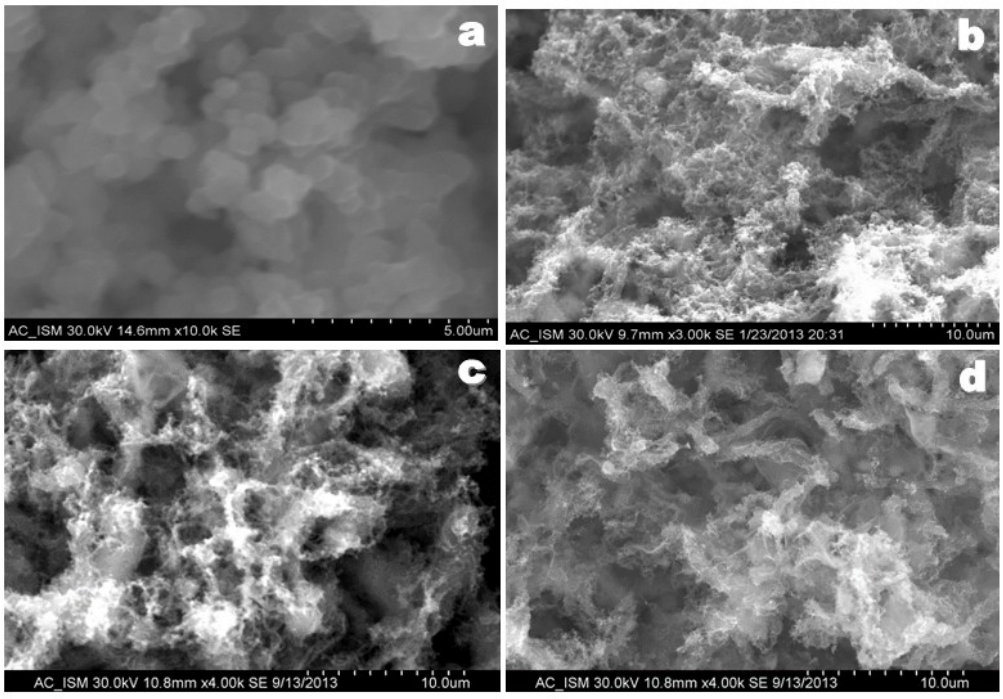

Figure S1: SEM images of (a) PPy (b) CP (c) CNP (d) CPN

2. Cyclic voltammetry Analysis at higher scan rates:

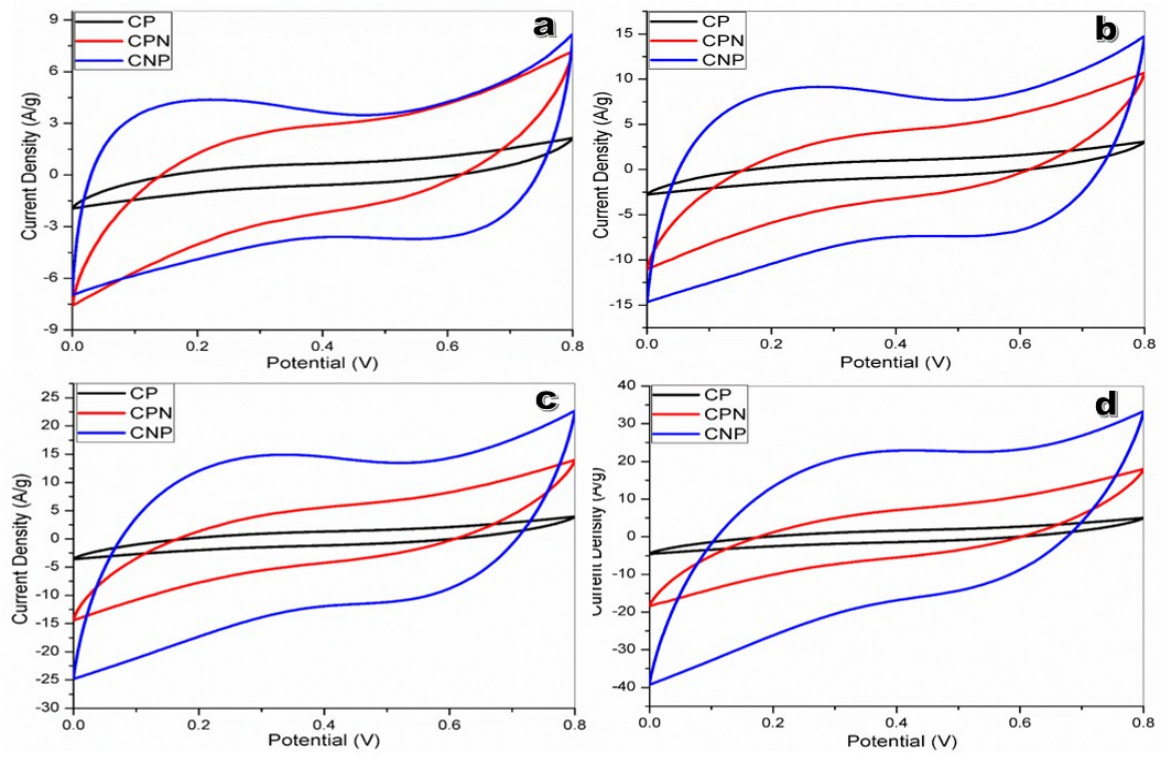

Figure S2: Cyclic voltammetry of different sample at (a) 20 (b) 50 (c) 100 (d) 200 mV/s

3. EXPERIMENTAL SECTION:

3.1. Electrode Preparation for electrochemical Analysis:

A supercapacitor testing cell was fabricated by coating working electrode (prepared by mixing sample with PVDF, carbon black in the mass ratio of 80:15:5 in dispersant N-methyl-pyrrolidone) over two symmetrical platinum foils. For exact weight measurement prepared electrodes were vacuum dried overnight around 80°C. Two symmetrical electrodes were separated by a thin filter paper soaked in 1M $TEABF_4$ (tetraethyl ammonium tetrafluro borate) in acetonitrile solution. Electrochemical performance of these electrodes were evaluated by cyclic voltammetry and galvanostatic charging discharging employing two electrode configuration in the following section.

3.2. Cyclic voltammetry study in organic electrolyte:

All electrochemical properties were measured for two electrode configuration within two potential window (0-0.8V) & (0-1.6V) and presented in figure S2 & S3.

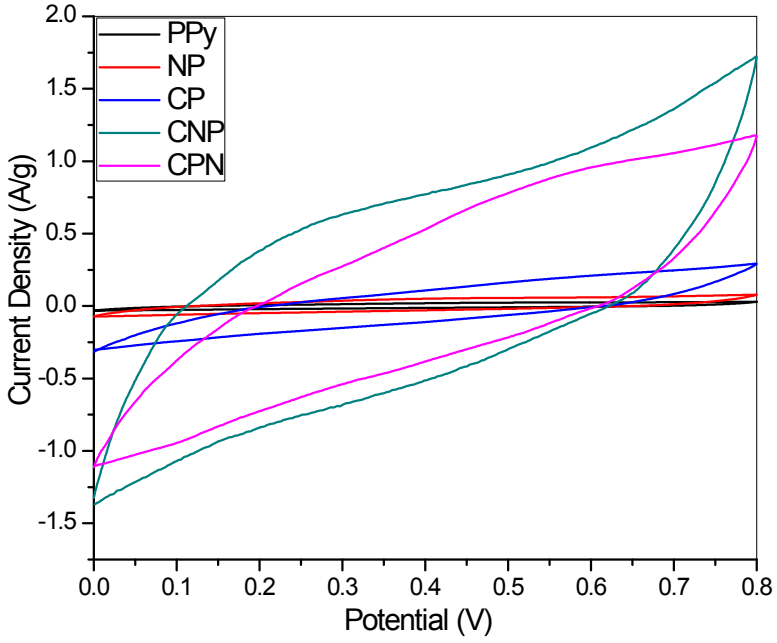

Figure S3 (a): Comparative CV plots of different sample at 10 mV/s in the potential window of 0-0.8V in organic electrolyte ($TEABF_4$)

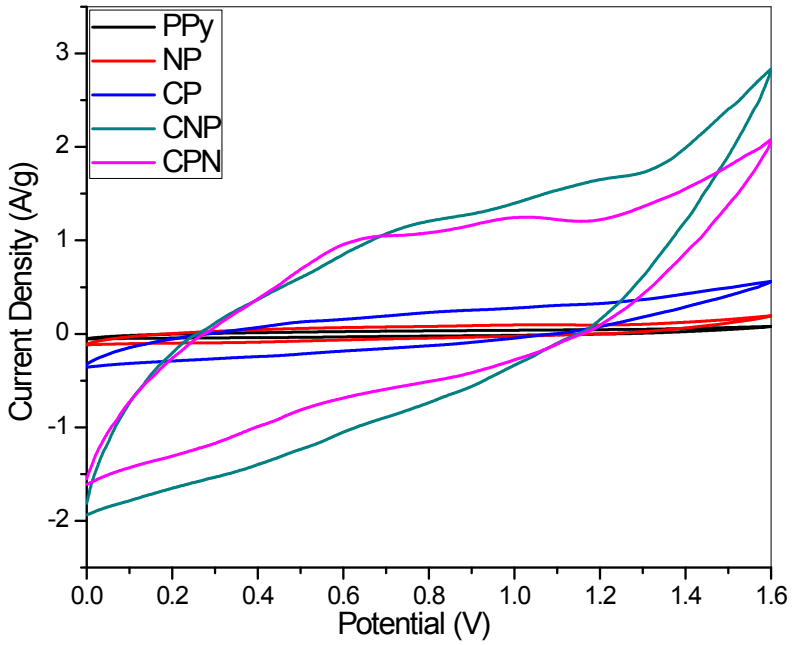

Figure S3 (b): Comparative CV plots of different sample at 10 mV/s in the potential window of (0-1.6V) in organic electrolyte ($TEABF_4$)

At scan rate 10 mV/s all comparative CV curves of different samples shows deviation from ideal rectangular behavior which demonstrate the formation of typical hybrid nanocomposite contributing both EDLCs and pseudocapacitance. It was revealed that in both potential window (0-0.8V & 0-1.6V) ternary nanocomposite (in-situ CNP & ex-situ CPN) exhibited maximum current density as compared to pure PPy and binary nanocomposite CP, NP. Fast diffusion kinetics of all samples were also notified with the increase in current density and cyclic enclosed area with respect to scan rate. Specific capactance (SC), energy density (ED) and power density were calculated using the following formulae:

$$SC = \left(4 \int_{V-}^{V+} I\,(V)dv\right)/m\Delta Vv \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Where, m= mass of the active sample, v= scan rate, ΔV= voltage window

$$ED = \tfrac{1}{2}\, CV^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

Where, C=specific capacitance in F/g, V= Potential window

$$PD = E/t \quad \text{.....(3)}$$

Where, E= Energy Density in Wh/Kg, t= time in second, Power density in W/Kg

Electrochemical calculation within potential window (0-0.8V) (as shown in figure S2 & S3 (a)) revealed that ternary in-situ CNP (422.5 F/g) and ex-situ CPN (295 F/g) possessed maximum specific capacitance as compared to other systems like pure PPy (10.34 F/g) and binary NP (24.6 F/g) & CP (68.25 F/g), respectively. Moreover, similar trend were observed in case of energy density and power density.

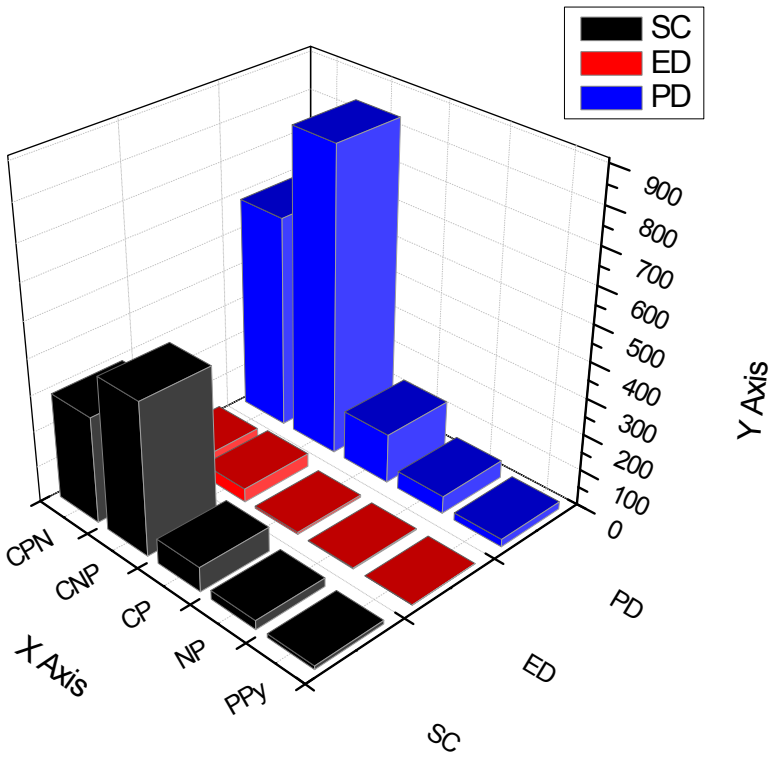

Figure S4 (a): Comparative bar plots of SC, ED & PD different sample at 10 mV/s in the potential window of (0-0.8V) in organic electrolyte ($TEABF_4$)

It should be mentioned that these capacitance performance are comparatively lower than capacitance values reported in 1M aq. KCl. It is due to the restricted ionic mobility in organic electrolyte caused due to larger ionic size during electrochemical analysis. To improve the

electrochemical performance, CV analysis was performed with extended potential from 0-1.6V (presented in figure S2 & S3 (b)).

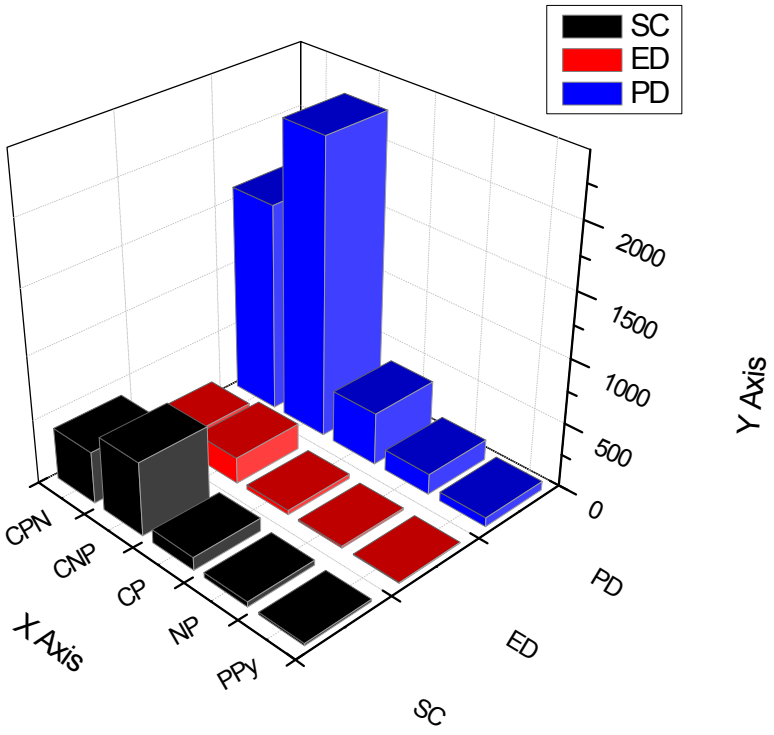

Figure S4 (b): Comparative bar plots of SC, ED & PD different sample at 10 mV/s in the potential window of (0-1.6V) in organic electrolyte ($TEABF_4$)

At scan rate 10 mV/s, similar potentio-dynamic response were evidenced for all sample where again ternary in-situ CNP and ex-situ CPN were found to be superior to related binary nanocomposite and pure PPy. In-situ CNP (572 F/g) and ex-situ CPN (404 F/g) exhibited maximum specific capacitance which is relatively higher than pure PPy (17.55 F/g) and binary nanocomposite NP (40 F/g) & CP (101.13 F/g), respectively. Among ternary nanocomposite, the higher specific capacitance value of in-situ CNP than ex-situ CPN could be ascribed to their enhanced specific surface area and dual electron hopping process for conduction which leads to increase their overall electrochemical performance. For the time being, in-situ CNP exhibited maximum energy density (203 Wh/Kg) at the power density (2283 W/Kg) at scan rate 10 mV/s. These improved observations were further confirmed from the cyclic stability analyzed by charging-discharging analysis.

3.3. Galvanostatic charging discharging analysis in organic electrolyte:

Galvanostatic charging discharging analysis was performed in the organic electrolyte ($TEABF_4$/Acetonitrile) in two electrode configuration within two potential window (0-0.8V) & (0-1.6V) and presented in figure S4 (a) & S4 (b), respectively. It was revealed that in both potential window charging discharging curves exhibits deviation from linearity which depicts electrochemical performance from both EDLCs and pseudocapacitance. It is also found that ternary nanocomposite posses larger dischare time as compared to binary nanocomposite. This demonstrates high capacitive performance of ternary nanocomposite than binary nanocomposite. These results are in good agreement with resutlts occurred from CV analysis. Specific capacitance (SC), energy density (ED) & power density (PD) were calculated at 5 A/g using the equation as follow:

$$SC = (i*\Delta t)/(m*\Delta V) \text{ ……..(4)}$$

Where, i/m = current density, Δt = discharge time, V= potential window

$$ED = CV^2/2 \text{ [42]…….. (5)}$$

Where, C= specific capacitance (F/g), V= potential

$$PD = E/\Delta t \text{ [42]……... (6)}$$

Where, E = energy density (Wh/Kg), Δt = discharge time, Power density W/Kg

Within potential window (0-0.8V) at 5 A/g, maximum specific capacitance was obtained for in-situ CNP (315 F/g) & ex-situ CPN (175 F/g) which is relatively higher as compared to other related system like CP (100 F/g). In-situ CNP (28 Wh/Kg) & ex-situ CPN (15.55 Wh/Kg) possess maximum energy density at the power density of (1976 W/Kg) & (2073.87 W/Kg), respectively. The comparative charging discharging plots are shown in figure S3 (a):

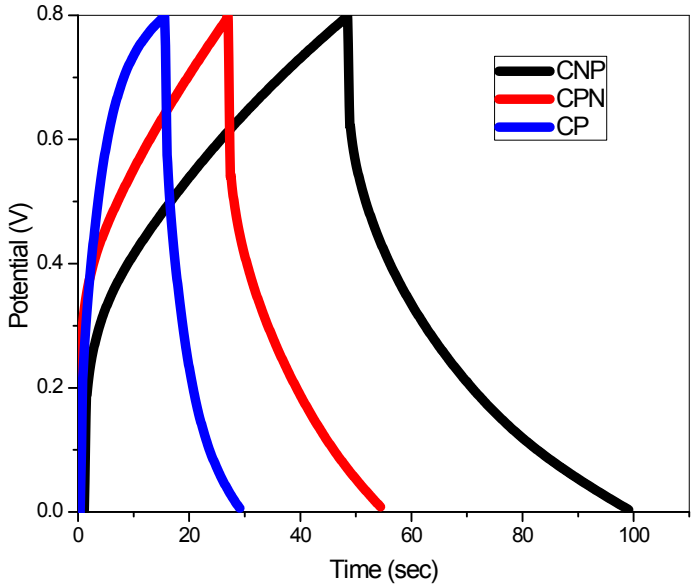

Figure S5 (a): Galvanostatic charging discharging plots of different sample in the potential window ranging from (0-0.8V) at 5 A/g

Similarly when electrochemical performance measured within potential window (0-1.6V) at same current density 5 A/g shows the similar trend, where specific capacitance were found to be superiro for in-situ CNP (510 F/g) & ex-situ CPN (230 F/g) significantly higher as compared to binary CP (125 F/g) in the same organic electrolyte ($TEABF_4$/Acetonitrile). In-situ CNP (181.33 Wh/Kg) & ex-situ CPN (81.77 Wh/Kg) exhibited maximum energy density at the power density of (4004.83 W/Kg) & (4088 W/Kg), respectively. In figure S3 (b), comparison of charging discharging plots are shown below

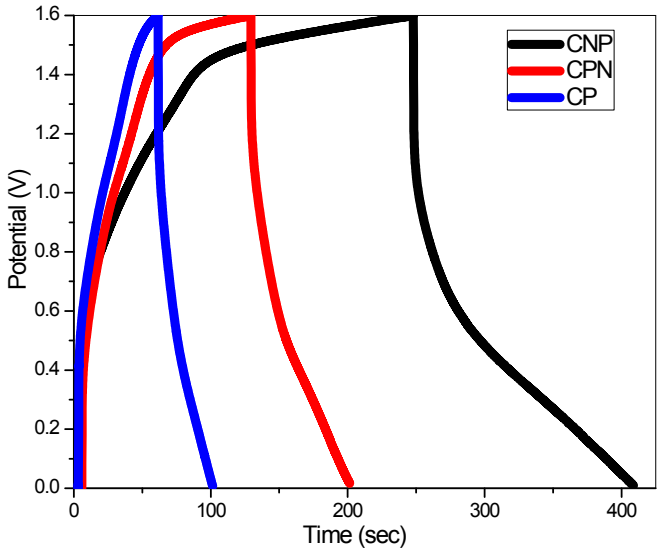

Figure S5 (b): Galvanostatic charging discharging plots of different sample within potential window ranging from (0-1.6V) at 5 A/g